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**The Photochemical Nucleophile-Olefin Combination,  
Aromatic Substitution (Photo-NOCAS) Reaction.  
The Scope of the Reaction with Respect to the  
Aromatic Electron Acceptor.**

by

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**Submitted in partial fulfilment of the requirements  
for the degree of Doctor of Philosophy**

at

**Dalhousie University  
Halifax, Nova Scotia  
August, 1991**

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This thesis is dedicated to my mother

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## Abstract

The photochemical nucleophile-olefin combination, aromatic substitution (photo-NOCAS) reaction is a potentially useful synthetic procedure. Readily available starting materials (a nucleophile, an olefin, and an aromatic molecule) are combined to make a more complex bifunctional product in one simple step; two new bonds are made during the process. The utility of this procedure for the synthesis of *para*-cyanophenyl  $\beta$ -alkyl ethers has been amply demonstrated, and a mechanism has been proposed which is consistent with all of the observations. The reaction has been shown to be fairly general with respect to the olefin: both acyclic and cyclic olefins react regio- and stereoselectively, to give primarily the *anti*-Markovnikov products. Until now no study has been undertaken to examine the role and diversity of the electron accepting aromatics.

Previous work has emphasised 1,4- and 1,2-dicyanobenzene as the electron accepting aromatic reactant. While the *para*- or *ortho*-cyano group incorporated in the product is a useful functionality for further synthetic modification, for many applications it will be desirable to have some other functional group. Consideration of the mechanism leads to the suggestion that the reaction may incorporate other electron withdrawing substituted aromatic molecules. A series of *para*-substituted benzonitriles (*para* = CO<sub>2</sub>CH<sub>3</sub> (**22**), -SO<sub>2</sub>CH<sub>3</sub> (**58**), -F (**59**), -CF<sub>3</sub> (**60**), -N(CH<sub>3</sub>)<sub>3</sub>I (**61**), -COH (**68**), and -COPh (**69**)) was examined and the results will be discussed.

When an acetonitrile-methanol solution of methyl 4-cyanobenzene (**22**) and 2,3-dimethyl-2-butene (**2**) is irradiated in the presence of added co-donor biphenyl (**12**), three 1:1:1 (methanol : olefin : aromatic) adducts are formed. However, when the irradiation is repeated in the absence of **12**, only one 1:1 (olefin : aromatic) adduct, a cyclic imine (**23**), is obtained (83%). No such imine formation has been observed using 1,4-dicyanobenzene (**1**) as an electron acceptor, and there are few examples of this type of photochemical reaction. The singlet lifetime of (**22**) has been estimated in this study ( $\tau_s < 2$  ns). The apparent reactivity from the singlet excited state of **22** has been explained in terms of an excited charge transfer complex. Ultraviolet absorption studies confirm the existence of a ground state association between the acceptor and olefin **2**.

The reactivity of all the acceptors (except **69**) involves photochemically induced electron transfer (PET). Observations can be rationalised in terms of the electrochemical behaviour, and calculated (*ab initio* and semi-empirical) spin and charge densities of the intermediate radical-anions. The mechanism, originally proposed for reactions involving **1**, has been extended to explain the observations from this study.

## List of Abbreviations

anal.	analysis
CRIP	contact radical-ion pair
CT	charge transfer
CV	cyclic voltammetry
d	doublet (spectral)
$\delta$	scale (nmr) dimensionless
DCFC	dry column flash chromatography
DEPT	distortionless enhanced polarisation transfer
$\epsilon$	molar absorptivity
$E_{1/2}^{\text{ox}}$	oxidation potential
$E_{1/2}^{\text{red}}$	reduction potential
ESR	electron spin resonance
ET	electron transfer
eV	electronvolt
F	Faraday constant
G	Gibbs free energy
GC-MS	gas chromatography-mass spectrometry
GC-FID	gas chromatography-flame ionisation detector
HOMO	highest occupied molecular orbital
ISC	inter-system crossing
<i>ipso</i>	position of substitution
$K_a$	association constant
$\lambda$	reorganisational energy
LUMO	lowest unoccupied molecular orbital
<i>m/z</i>	mass-to-charge ratio

MPLC	medium pressure liquid chromatography
n	nano ( $10^{-9}$ )
PET	photochemically induced electron transfer
Ph	phenyl
Photo-NOCAS	photochemical-Nucleophile olefin combination, aromatic substitution
q	quartet
s	singlet
SET	singlet electron transfer
SIM	selective ion monitoring (GC-MS)
SSRIP	solvent separated radical-ion pair
STO-3G	Slater-type orbital, three Gaussian functions
SCE	saturated calomel electrode
t	triplet
<i>tert</i>	tertiary
uv	ultraviolet
V	volt
VT	variable temperature

All other abbreviations are standard



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# **Chapter 1**

## **General Introduction**

### **1.1 Electron transfer**

The process of photochemically-induced electron transfer (PET) was postulated as early as 1923 as a key step in plant photosynthesis (1). It was also speculated by Weiss in 1936 that electron transfer was responsible in some circumstances for observed fluorescence quenching of excited states (2). For a long time the PET process remained largely a mechanistic curiosity. However, the past twenty years has seen a growth in our understanding of this seemingly simplistic process, and the incorporation of the concept of electron transfer and the chemistry of radical-ions into organic synthesis (3). Several good reviews covering this topic have appeared (4). A few examples, demonstrating the potential synthetic utility, will be shown below. While several methods exist to produce radical-ions, e.g., use of metal salts (5), treatment with sulphuric acid (6), radiolysis (7), and electrochemical methods (8), this work will concentrate on the photochemically-induced technique. As an introduction to the synthetic utility, it would be instructive to examine the PET process in some detail.

### **1.2 Electron transfer (ET) process in organic chemistry**

The process of electron transfer in chemistry is certainly not confined to the bastion of organic photochemists. Inorganic chemists have recognised for some time its importance in the redox chemistry of metal complexes (9,10). This has been widely studied and is arguably now becoming better understood. While this present study confines itself largely to transfer involving the excited state, the process of single electron transfer (SET) in organic

chemistry is believed to accompany many ground state reactions. Woodward first postulated that electron transfer was a possible pathway in the Diels-Alder reaction mechanism (11), where transfer could occur from the diene to the dienophile. The idea was largely ignored until 1981, when evidence was found to corroborate his idea (12). It has been noted that reactions using neutral and electron-rich dienophiles leads to inefficient reactions, and has in some ways limited the scope of this reaction. However, the addition of catalytic amounts of radical-cation salts (eg. tris(4-bromophenyl)aminium hexachlorostibate), has a significant effect on the efficiency of some of these reactions, where the radical-cation of the dienophile is believed to play an important role in the pericyclic addition.

The Grignard reaction (13) and the electrophilic nitration of aromatic compounds (14) are two additional examples where a large ever-growing body of knowledge points to a process involving ground state electron transfer. More recently electron transfer is thought to play a significant role in the reaction of alkyl cuprates (eg.  $\text{Bu}_2\text{CuLiLiI}$ ) with alkyl iodides (15), where the majority of products is thought to be derived from the alkyl radicals. There is growing evidence to suggest that reactions involving the hydroxide ion (e.g. the Cannizzaro reaction (16,17)) involve an electron transfer step to form the  $\text{HO}\cdot$  radical (18). The recent study of hydroxide ion in the aromatic nucleophilic substitution of dinitrochlorobenzenes is believed to occur via a single electron transfer (SET) step leading to an  $\text{HO}^\bullet/\text{Ar}^-$  charge transfer complex (19). These ground state electron transfers will be discussed in more detail in Chapter 2.

### 1.3 Photochemically-Induced electron transfer (PET)

#### 1.3.1 Absorption of light

Why does this electron transfer occur following absorption of light, and since not all bimolecular photochemical reactions proceed with electron transfer, is it possible to predict

when it will happen?

Absorption of light by a molecule promotes an electron from the highest occupied molecular orbital (HOMO) to a higher lying unoccupied orbital. Rapid relaxation in solution leads to the electron going into the lowest unoccupied molecular orbital (LUMO), to give the first excited singlet state ( $S_1$ ), assuming a ground state singlet ( $S_0$ ). Since the movement of the electron is rapid in comparison to molecular relaxation ( $10^{-16}$  vs.  $10^{-13}$ , Franck-Condon principle) or vibration relaxation, the molecular geometry will remain fixed. In simplistic terms, the first excited state of the molecule can be regarded as an electronic isomer of the ground state. This electronic excitation occurs much faster than any chemical reaction. It is this increase in electronic energy that gives the excited molecule properties not easily accessible in the ground state.

Since an electron is now in a higher energy orbital after excitation, the energy required to remove it to infinity, the ionisation potential (IP), is reduced by the energy gap between the  $S_0$  and  $S_1$  states (singlet energy  $E_{0,0}$ ). The amount of energy released when the excited molecule gains an electron (electron affinity EA) is now increased by  $E_{0,0}$ , since the added electron goes into a lower lying half-filled orbital, Figure.1.1. The molecule in an excited state now becomes both a better electron acceptor (oxidant) and a better electron donor (reductant).

After excitation has taken place, the excited state can undergo several deactivating processes, Figure. 1.2. Fluorescence (F) or internal conversion (IC) will return the excited molecule to the ground state. Intersystem crossing (ISC) gives the lower energy triplet state, which can decay to the ground state by ISC or phosphorescence (P). Three other processes exist to quench the excited state, energy transfer, chemical reaction, and electron transfer (ET). In a solution containing a mixture of chromophores, the excited state can undergo energy transfer if a second molecule has a lower excited singlet state energy. If the excited state is sufficiently long-lived there is also the possibility of chemical reaction.

Electron transfer will occur if a suitable donor or acceptor is present, *i.e.*, the process is thermodynamically feasible. It is this last process of electron transfer which has been exploited in this work, and shall be explained below.

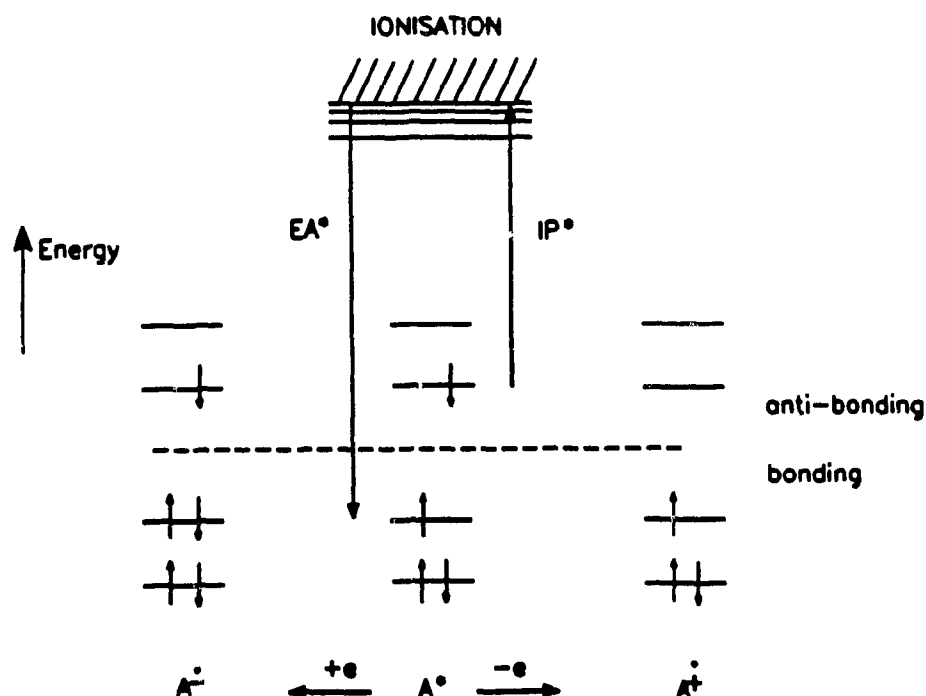


Figure. 1.1 Molecular orbital levels involved in oxidation or reduction of the excited state.

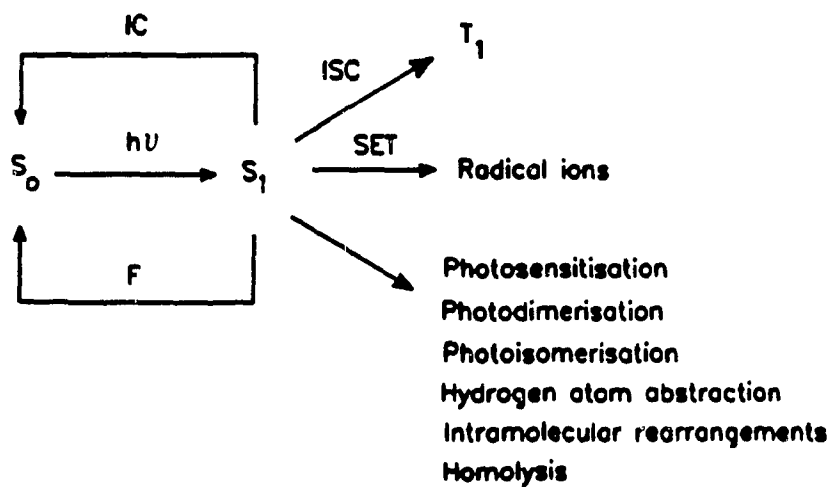


Figure. 1.2 The fate of the singlet excited state.

### 1.3.2 Energetics of the electron transfer process (20)

The energy required to remove an electron from a molecule in its ground state to infinity is the ionisation potential (IP). The energy released when an electron combines with a molecule in the ground state is the electron affinity (EA). When the EA is greater than the IP electron transfer becomes possible in the ground state, *i.e.*,  $\Delta E < 0$ , equation [1.1].

$$\Delta E = IP - EA \quad \text{equation [1.1]}$$

However, after absorption of a photon the IP of the absorbing molecule decreases, so the excited state now has a lower ionisation potential  $IP^*$ . Conversely, the electron affinity of the excited molecule  $EA^*$  increases, Figure 1.1, equations [1.2] and [1.3].

$$IP^*(\text{excited state}) = IP - E_{o,o} \quad \text{equation [1.2]}$$

$$EA^*(\text{excited state}) = EA + E_{o,o} \quad \text{equation [1.3]}$$

The change in energy accompanying an electron transfer from the excited molecule (acting as a donor) is given by equation [1.4], while the energy difference when it is an electron acceptor is given by equation [1.5].

$$\Delta E = IP^* - EA = IP - EA - E_{o,o} \quad \text{equation [1.4]}$$

$$\Delta E = IP - EA^* = IP - EA - E_{o,o} \quad \text{equation [1.5]}$$

Essentially it doesn't matter whether the electron acceptor or donor is excited to enable electron transfer to occur. Energy transfer ensures that the molecule with the lowest singlet energy ( $E_{o,o}$ ) will be the excited species. Figure 1.3 shows schematically that either the donor or the acceptor can be excited for electron transfer to occur, providing the process is still thermodynamically feasible.

Equations [1.2]-[1.5] form the basis of the Rehm-Weller equation [1.6] which is an empirically derived formula to allow one to predict the feasibility of electron transfer occurring, rather than energy transfer (21).

$$\Delta G_{ET} \approx \Delta G_{SSRIP} = E_{1/2}^{ox} (D^{+•}/D) - E_{1/2}^{red} (A/A-•) - \Delta G^* + W_{product} - W_{reactant}$$

SSRIP = solvent separated radical-ion pair

equation [1.6]

$\Delta G^*$  is the free-energy of the excited state after molecular relaxation and is approximated to  $E_{o,o'}$ .  $W_{product}$  and  $W_{reactant}$  are the work terms for electrostatic interaction in the reactant and product states. In polar solvents, the columbic attraction term is small since the interaction between the resultant radical-ions is reduced by the shielding effect of the solvent molecules. Ions can therefore become separated or at least solvent separated. This term is generally unimportant in polar systems, but must be considered in non-polar systems. IP and EA are linearly related to the oxidation and reduction potentials respectively. The gas phase electron affinity can be related to the  $E_{1/2}^{red}$  by equation [1.7] (22), where  $\Delta G_A^{\circ}(A)$  is the free-energy for the reaction  $e^{-} + A = A-•$ . The value of  $\Delta G_{solv}^{\circ}$  was found to be constant for a series of electron acceptors, it can therefore be included in the constant. Thus  $E_{1/2}^{red}$  can be reduced to the form shown in equation [1.8] (23). A similar relationship is found between the IP and  $E_{1/2}^{ox}$ .

$$E_{1/2}^{red} (A) = -\Delta G_A^{\circ}(A) - \delta \Delta G_{solv}^{\circ}(A-•) + \text{constant} \quad \text{equation [1.7]}$$

$$E_{1/2}^{red} (A) = EA(A) - \text{constant} \quad \text{equation [1.8]}$$

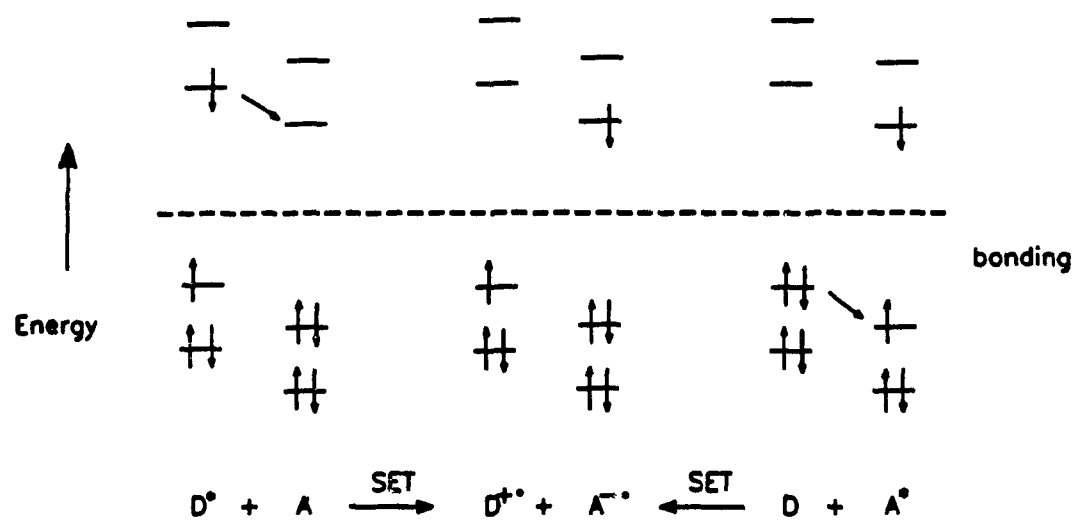


Figure. 1.3 Molecular orbital representation of the PET process



The form of the Rehm-Weller equation generally used, and employed throughout this thesis, is that shown below, equation [1.9].

$$\Delta G_{ET} = 23.06[E_{1/2}^{ox}(\text{donor}) - E_{1/2}^{red}(\text{acceptor}) - e/\epsilon\alpha] - \Delta E_{o,o}$$

equation [1.9]

$e$  charge of an electron

$\epsilon$  dielectric constant

$\alpha$  encounter distance between donor and acceptor

$e^2/\epsilon\alpha$  free-enthalpy gained by bringing the radical-ion pair to an encounter distance  $\alpha$  in a medium of dielectric constant  $\epsilon$ .

23.06 units  $\text{kcal mol}^{-1} \text{V}^{-1}$

$E_{1/2}^{ox}$ ,  $E_{1/2}^{red}$  given in Volts (V)

The SET process will be feasible if it is calculated by the Rehm-Weller equation to be exothermic ( $\Delta G_{ET} < 0$ ), and can be expected to proceed at the diffusion controlled rate, if  $\Delta G_{ET} < -4 \text{ kcal mol}^{-1}$  ( $-16.7 \text{ kJ mol}^{-1}$ ). Electron transfer can lead to the formation of a contact radical-ion pair (CRIP), solvent separated radical-ion pair (SSRIP), or freely solvated radical-ions. If the process is found to be endothermic ( $\Delta G_{ET} > 0$ ), the reaction at best will proceed via a polar exciplex, and can lead to cycloaddition products (24). Once ET has occurred, there are several options for the radical-ions. Back electron transfer will give the donor-acceptor pair, or diffusion outside the solvent cage will ultimately result in reaction of the free radical-ions.

### 1.3.3 Competitive back electron transfer.

A consequence of the back electron process is manifest in the reduction of the efficiency of the reactions. The challenge remains from a synthetic point of view to limit this

energy wasting step. From a theoretical viewpoint, there exist two methods to minimise this process, both of which are grounded in quantum mechanics (25). (i) Electron tunnelling allows electron transfer to occur at distances greater than the van der Waal's contact distance (3.5 Å), and allows escape of products before collapse of the radical-ion pair to give back electron transfer. Values for the distance over which electron transfer can occur, have been measured in the 10's of Å in rigid organic glasses between biphenyl radical-anion and arenes (26). (ii) If the radical-ion pair can be produced in their triplet state, the lifetime of the pair will be much longer, since reversion to the singlet state is a spin-forbidden process. However, there is a limitation to this last approach. Triplet sensitisation affords the lower energy pair, and generally reduces the thermodynamic feasibility of PET.

Unless a fast secondary reaction pathway is possible, the fate of the geminate radical-ion pair is in question. There are however, some practical methods to reduce the back electron transfer process (27). The probability of back electron transfer occurring can be reduced by addition of magnesium salts (28). This special salt effect extends the lifetime of the radical-ion pair. It has been postulated that the magnesium cation forms a complex with the radical-anion, thereby slowing down the deactivating back electron transfer step.

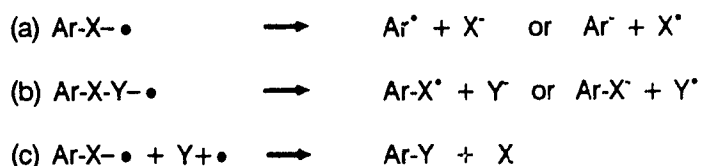
One of the major factors governing the efficiency of back electron transfer is the exothermicity of the forward electron transfer process (29). Where the electron transfer is least exothermic, *i.e.*, the radical-ion pair stores the most energy, the back electron transfer is slowest, and the quantum yields for formation of the free ions increase. Where the reaction is most exothermic, control is governed by the Marcus inverted region effect. Consequently, the exothermicity of the initial electron transfer should be relatively small for efficient PET to occur. This control is one of the major reasons that the use of a co-donor, *e.g.*, biphenyl, with a relatively high oxidation potential, has a dramatic effect on reaction efficiencies (30,31).

One of the simpler approaches to reduce this energy wasting process is modification

of the electrostatic nature of donor-acceptor pair in the ground state. In the case of a neutral acceptor and donor, electron transfer produces the geminate radical-ion pair, which is held together by strong attractive electrostatic interactions. This of course can be advantageous in some circumstances where cyclisation can occur from the radical-pair within the tightly held exciplex. However, the quantum yield for radical-ion escape is reduced. If one starts with either the acceptor or donor in a charged ground state, there is no overall change in the net charge after PET has occurred. Therefore, the electrostatic attraction remains unchanged. Many examples of this methodology have been reported, involving electron-donating carbanions (32), and electron-accepting carbocations (33). This approach increases the possibility of separation of the donor acceptor pair, and therefore, increases the efficiency of chemical reaction. One other method employed to increase the efficiency of PET is the use of an anisotropic medium, *e.g.*, micelles (34). This allows efficient separation of the radical-ion pair before back electron transfer can occur.

#### 1.4 Reactions of radical-anions.

The work described in this thesis concerns the photochemistry of a series of electron accepting benzonitriles. For this reason, the present discussion will be limited to the reactions of aromatic radical-anions. Ions of this nature undergo three important types of reactions; (i) fragmentation of a bond  $\alpha$  to the aromatic ring, (ii) fragmentation of a bond  $\beta$  to the aromatic ring, and (iii) addition and substitution at the aromatic ring, Scheme 1.1.



Scheme 1.1

#### 1.4.1 Fragmentation of a bond $\alpha$ to the aromatic ring

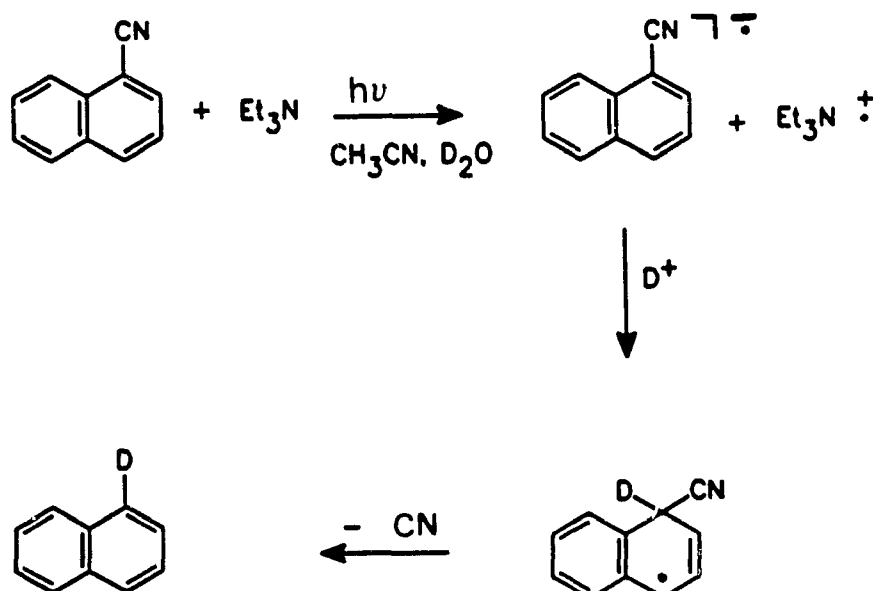
A common example of the first of these processes, in which the aryl radical is formed, is the photochemical dehalogenation of aryl halides in the presence of an electron donor (D), reaction [1.1]. Formation of aryl radical is generally followed by hydrogen atom abstraction.



The same type of reaction is observed for aliphatic halides, where initial homolysis of the alkyl halide bond is followed by electron transfer between the radical pair. The intermediate alkyl cation can then undergo electrophilic reactions. This is found to be a useful method for generating carbocations at sterically strained centres (35). In certain cases the aromatic dehalogenation can involve proton addition to the radical-anion followed by hydrogen halide elimination. Cleavage now occurs from the intermediate radical  $\text{ArHX}^\bullet$ , reaction [1.2].



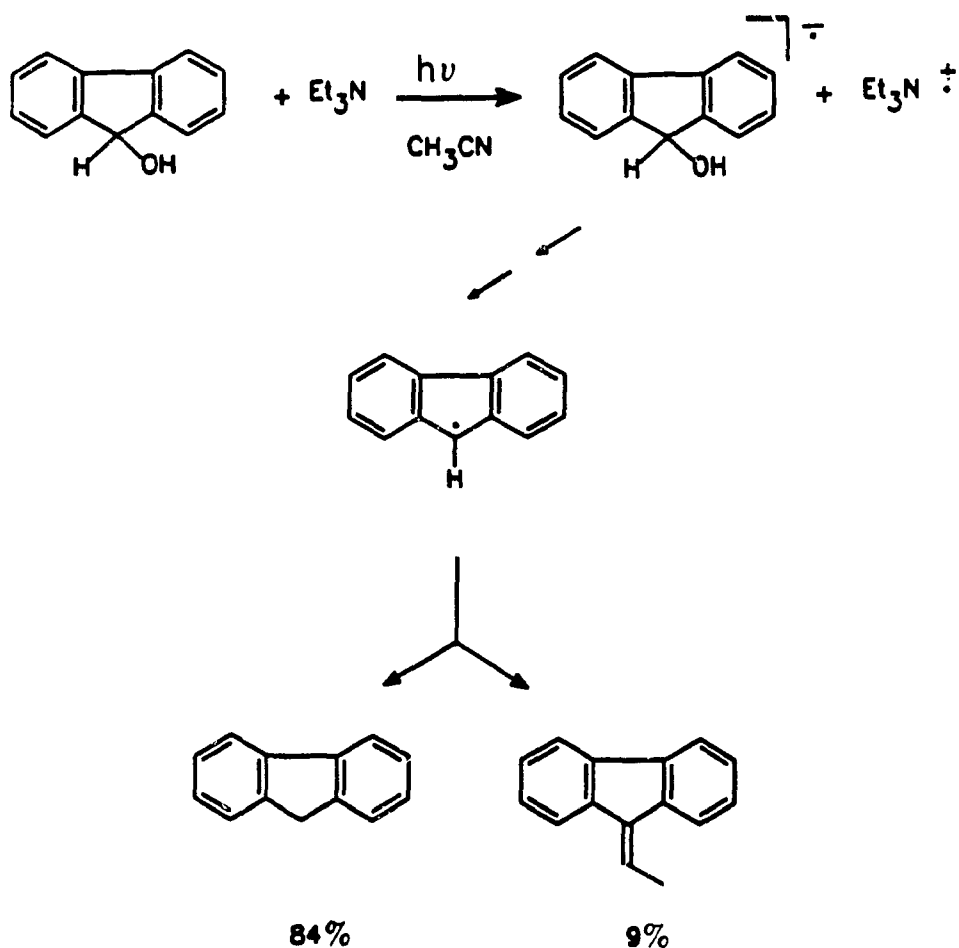
This process has been exploited in amine and sulphide enhanced photoinduced degradation of chloro- and cyano-aromatic hydrocarbons (36). Addition of  $^2\text{H}^+$  in the reaction mixture led to deuterium incorporation at the *ipso* ring position, reaction [1.3].



[1.3]

#### 1.4.2 Fragmentation of a bond $\beta$ to the aromatic ring

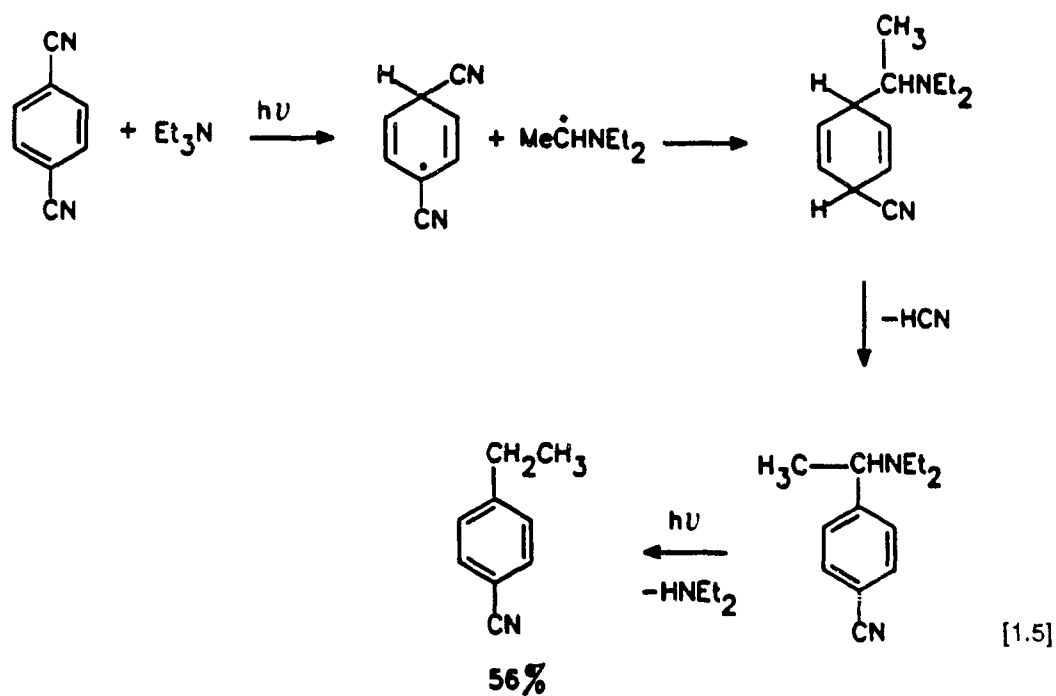
Fragmentation of the bond  $\beta$  to the aromatic system can also follow electron transfer, and has as its driving force the stabilisation of the resulting benzylic anion or radical by resonance. This type of cleavage is more commonly observed for radical-cations (37). There are however, examples which demonstrate this cleavage of radical-anion (38). 9-Fluorene (or the acetate) readily undergo photoinduced electron transfer with triethylamine to form a radical-ion pair. Fluorenyl radical is formed following proton transfer from the amine radical-cation to the radical-ion. A second ground state electron transfer, followed by protonation, leads to formation of fluorene in high yield. A second competing pathway involves the coupling of the fluorenyl radical with  $\text{MeCHNEt}_2^{\cdot+}$ . Loss of diethylamine gives a small amount of an olefin product, reaction [1.4].



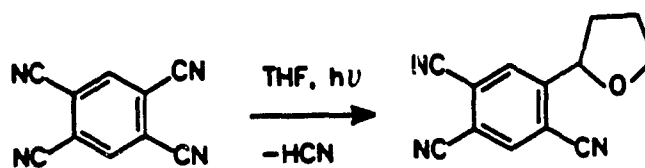
[1.4]

#### 1.4.3 Addition and substitution at the aromatic ring.

The third class of reaction is pertinent to the work presented in this thesis. Bryce-Smith observed the 1,4-photoaddition of aliphatic amines to benzene (39). His work has been extended to include the light induced ethylation of *ortho*- and *para*-dicyanobenzenes carried out in the presence of triethylamine (40), reaction [1.5]. Initial electron transfer is followed by a proton transfer step. Protonation of the radical-anion of dicyanobenzene forms the aromatic radical, which undergoes radical coupling with  $\text{MeCHNEt}_2^{\cdot+}$ . Loss of HCN, followed by secondary photolysis to remove triethylamine, gives the *ortho*- and *para*-alkylated benzonitriles in good yields.

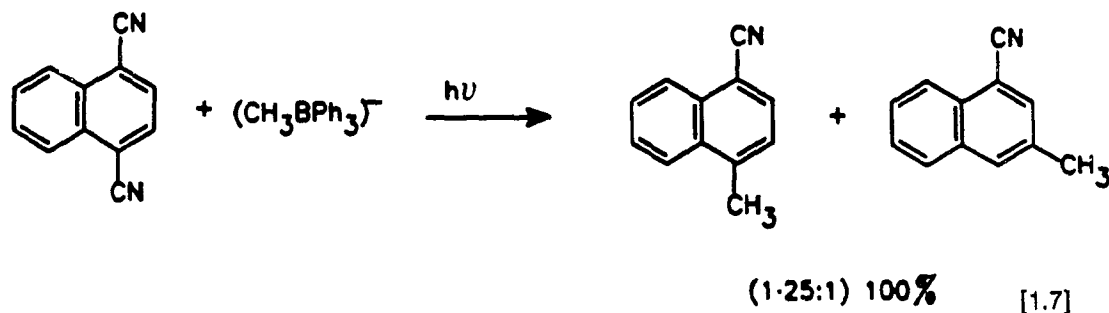


Photosubstitution of 1,2,4,5-tetracyanobenzene by a series of electron donating ethers was shown to give 1:1 (olefin : aromatic) adducts with substitution of the cyano group (41), reaction [1.6]. This reaction also occurs with aliphatic nitriles by a similar electron transfer process.



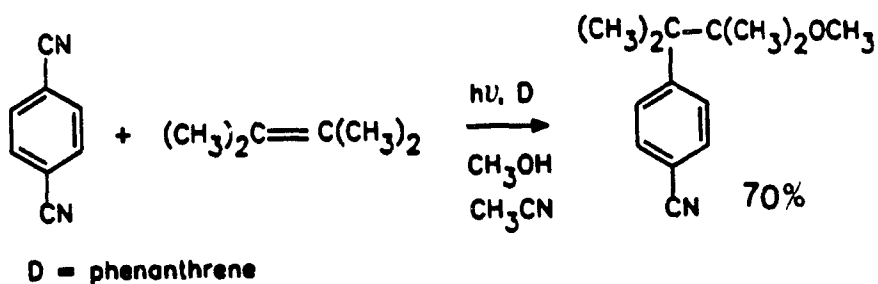
[1.6]

Photochemical alkylation is not restricted to the cyanobenzenes. A similar substitution is found with dicyanonaphthalene (42). Alkylation occurs under photooxidative conditions in the presence of alkyltriphenylborate salts. Products are formed in essentially quantitative yields by a radical process, initiated by a PET step, reaction [1.7].



Work in this lab has shown that photosubstitution of 1,2- and 1,4-dicyanobenzene occurs with 2,3-dimethyl-2-butene in acetonitrile to give two 1:1 (olefin : aromatic) adducts in the presence of a photosensitiser (phenanthrene), reaction [1.8] (43). The reactions follow initial radical-ion formation by an electron transfer process. Subsequent deprotonation of the resultant radical-cation of the olefin, and attack by the alkyl radical at the *ipso* aromatic position leads to adduct formation. Further studies have shown that the reaction can occur in the presence of added nucleophiles with incorporation to yield 1:1:1 (nucleophile : olefin : aromatic) adducts (44). This reaction forms the basis of the current research and will be expanded upon later. While much more work is still needed to fully understand the PET process, the synthetic potential is becoming apparent. The simplicity of the process, coupled with the complexity of the products that are generally formed, makes a synthetic scheme centred around a PET step appealing.





[1.8]

One such reaction, the photo-NOCAS reaction, has been developed in this lab. A considerable effort has been expended in order to understand the fundamental chemistry involved. The primary goal of this work has been to define the synthetic utility and scope of the reaction with regards to the aromatic electron acceptor. A series of electron acceptors has been screened and their photochemistry will be discussed.

## Chapter 2

### The Photo-NOCAS Reaction

#### 2.1 The photo-NOCAS reaction.

##### 2.1.1 Historical background.

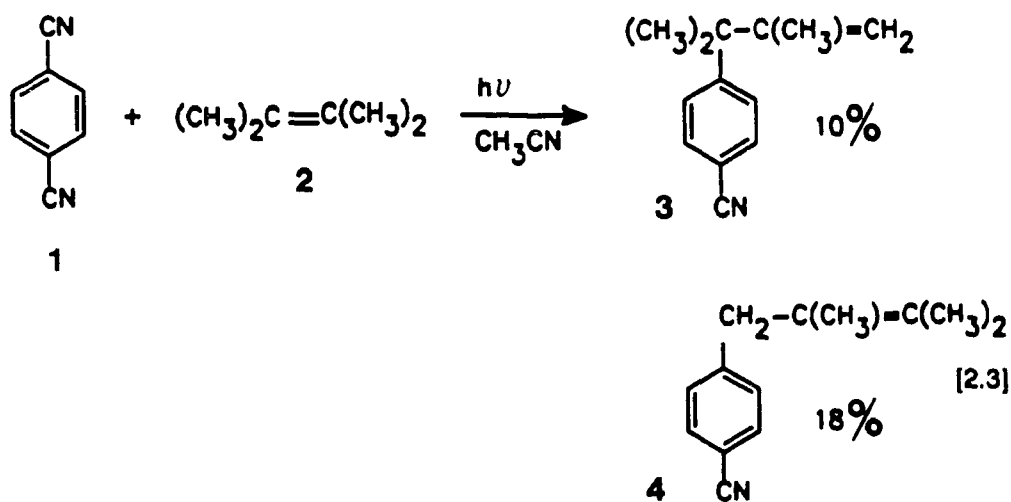
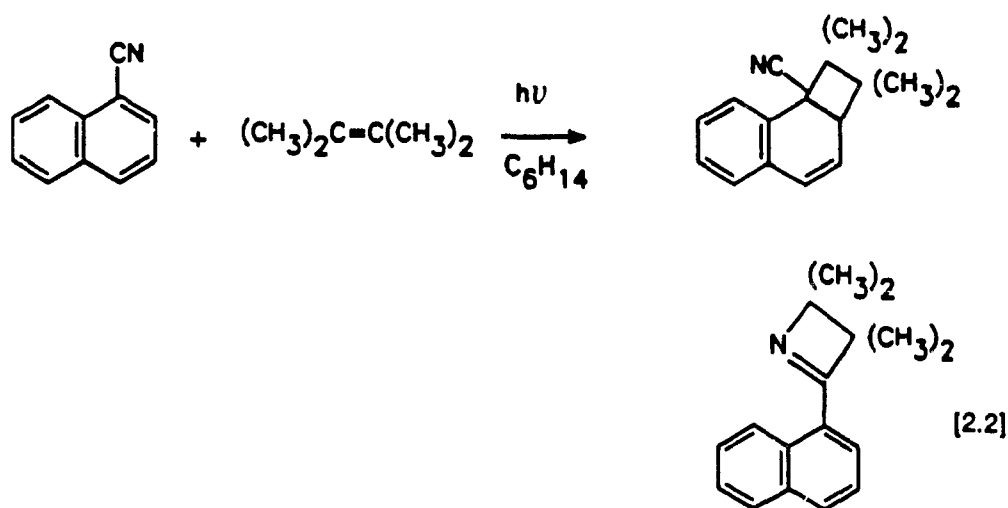
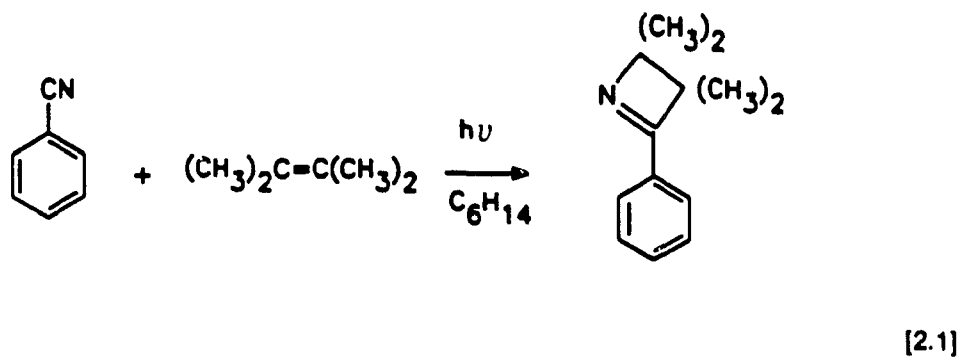
When benzonitrile and 1-cyanonaphthalene were irradiated separately with 2,3-dimethyl-2-butene in a non-polar solvent, hexane, 1:1 (olefin : aromatic) cycloadducts were formed as the major products, reactions [2.1] and [2.2] (45,46). The observed products were believed to form through the intermediate exciplex.

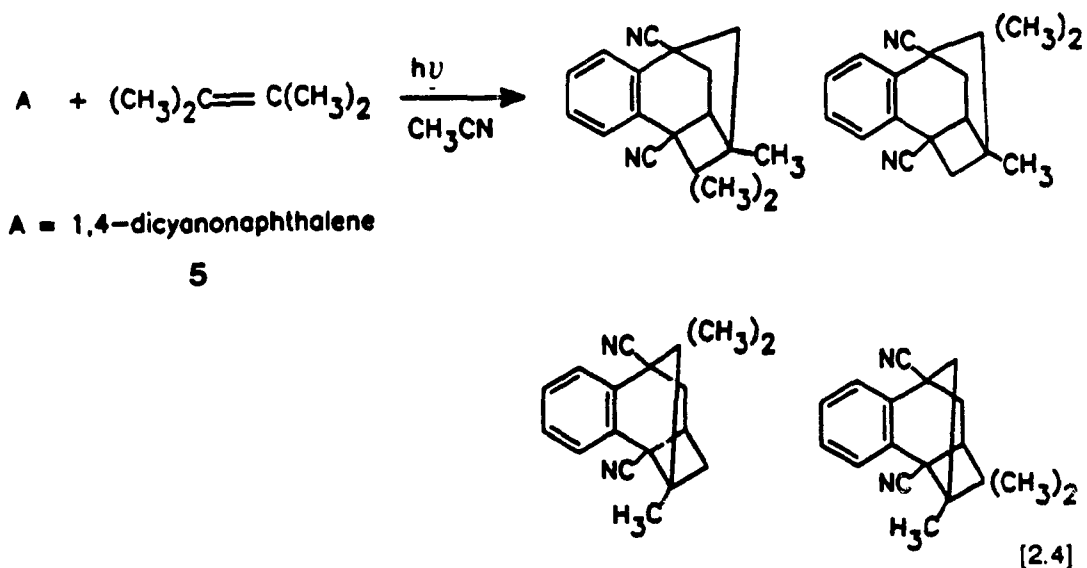
In their study of the photosensitised (electron transfer) cross cyclisation of olefins using 1,4-dicyanobenzene (1) and 2,3-dimethyl-2-butene (2) in a more polar solvent, acetonitrile, Arnold and Maroulis (47) noticed the photosensitiser 1 was partially consumed in the reaction. They observed the formation of 1:1 (olefin : aromatic) photosubstitution products (3) and (4), reaction [2.3].

This discovery, coupled with the contrasting chemistry observed in non-polar solvents, prompted an investigation into the mechanism of the substitution process. One of the secondary goals of their research was to establish the synthetic potential of this substitution with respect to olefins and aromatic nitriles (48). The authors also found that 1,4-dicyanonaphthalene (5) behaved similarly yielding the cycloaddition products, which were formed via intramolecular cyclisation following the initial photosubstitution, reaction [2.4].

The above reactions, [2.3] and [2.4], were thought to occur via an initial photoinduced electron transfer (PET) process. It was further proposed that after electron transfer, the reactions could follow two pathways (Scheme 2.1). Pathway (a) involves the coupling of the radical ions, followed by an intramolecular proton transfer step to form the zwitterionic intermediate (6). Rearomatisation, by loss of HCN, gives only one of the observed products (3). The second pathway (b), involves proton transfer within the radical

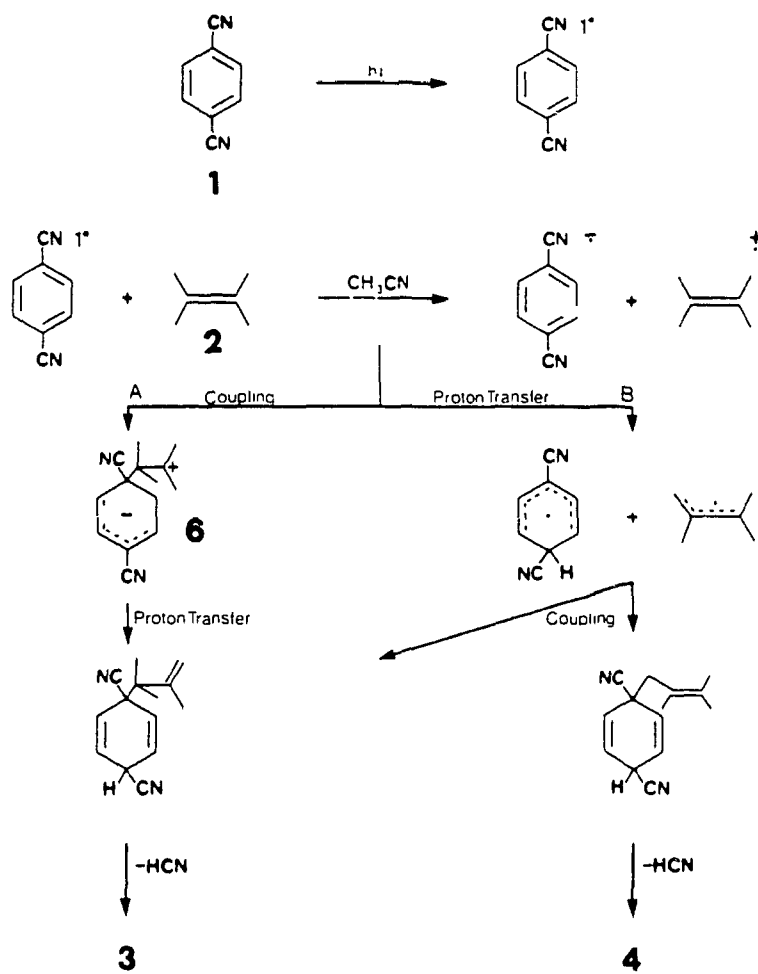
ion pair. Radical coupling can then occur at either end of the ambident radical, at the tertiary or terminal carbon centres, to give the 1:1 adducts 3 and 4.





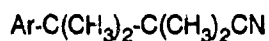
The synthetic limitations became apparent. The yields were relatively low, and in the case of 5, secondary photolysis led to a complex mixture of isomers. This, coupled with the fact that little was known at the time about the addition of radicals to radical ions of aromatic nitriles, confounded the issue.

The degree to which proton transfer occurred, if at all, was still uncertain, and the reaction remained mechanistically unclear. The authors did point out however, that the use of molecular orbital calculations (MNDO) could be employed to predict the regioselectivity of radical addition to the radical anion at the centres of high spin density, and the site of protonation of the radical ion at the centres of high charge density.



Scheme 2.1

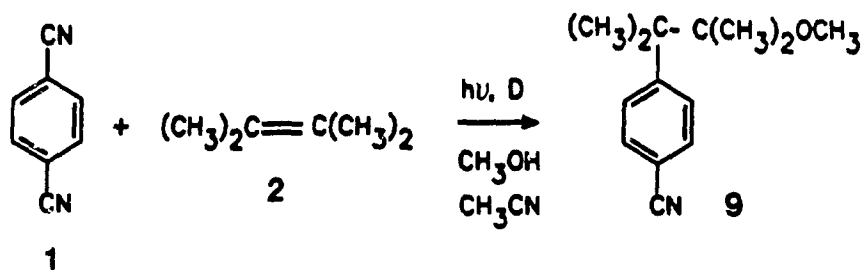
Reaction [2.3] was further studied in the presence of a photosensitiser, phenanthrene (**7**) (43).<sup>1</sup> The yield of the 1:1 adducts **3** and **4** was found to more than double (combined 65%) in comparison to the direct irradiation, while the product ratio remained essentially constant (2:1). A key finding in this study with **1** as the electron acceptor, was the isolation of a trace amount of an adduct containing cyanide ion (**8**).



Ar = 4-(cyanophenyl)-

8

It became apparent that the displaced cyanide ion was taking part in the reaction. When this reaction was repeated in the presence of a nucleophilic solvent system, acetonitrile-methanol (3:1), the reaction proceeded to give a single 1:1:1 (methanol : olefin : aromatic) adduct (9) as the major product in high yield (70%), reaction [2.5].

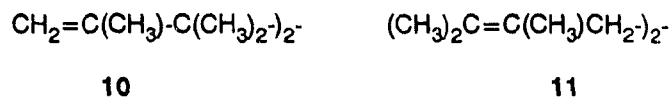


[2.5]

It had originally been assumed that proton transfer played a key role in the reaction mechanism of the photosubstitution to form **3** and **4**, Scheme 2.1. Indeed, the radical cation

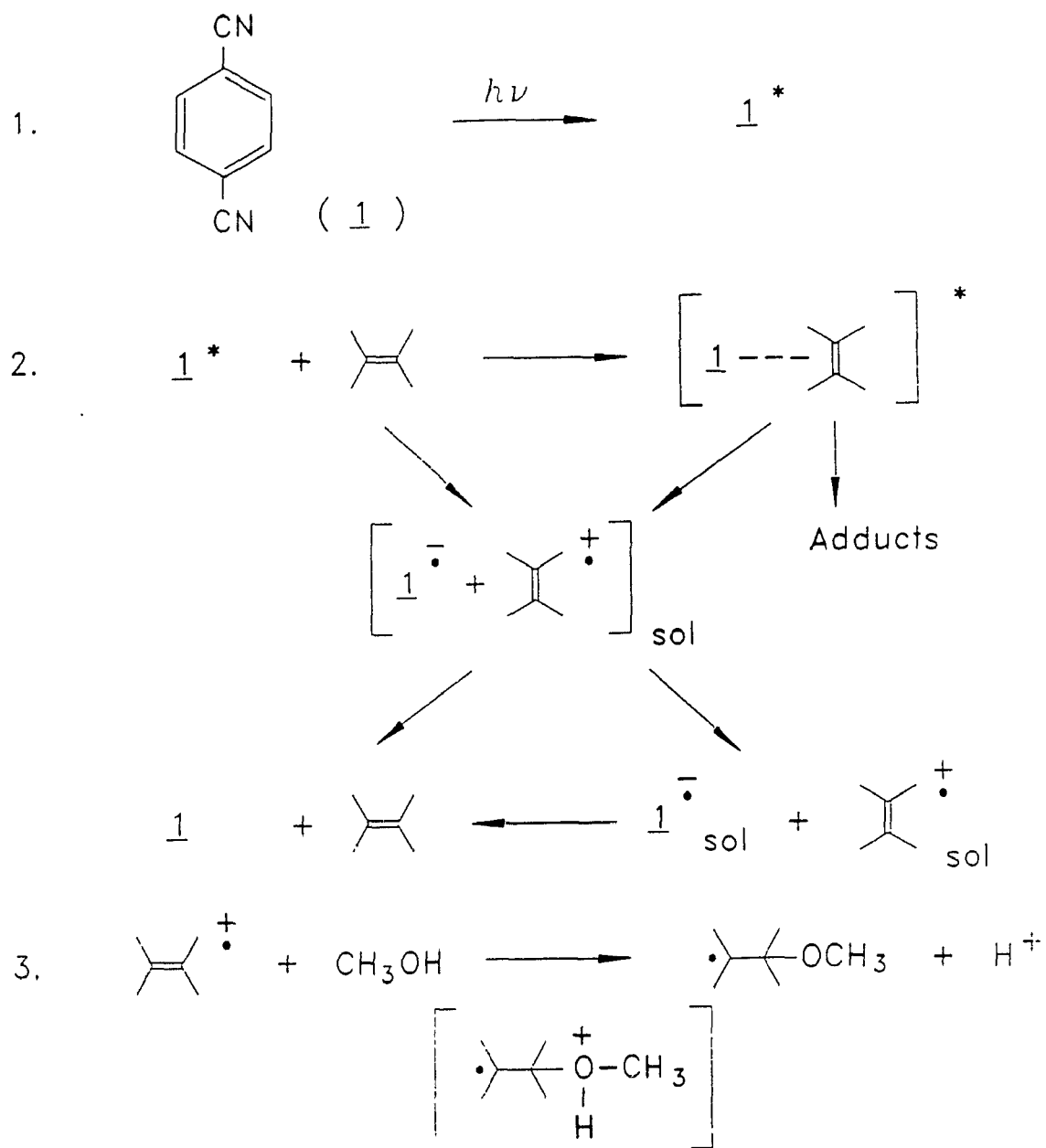
<sup>1</sup>A distinction is made between a photosensitiser and a co-donor. While both are effective as electron donors, only the photosensitiser absorbs light.

of 2,3-dimethyl-2-butene (**2**) has since been found to be strongly acidic ( $pK_a = -4$ , in acetonitrile) (**49**). Coupling products **10** and **11**, resulting from deprotonation of the radical cation of the olefin, were also found in these reactions.



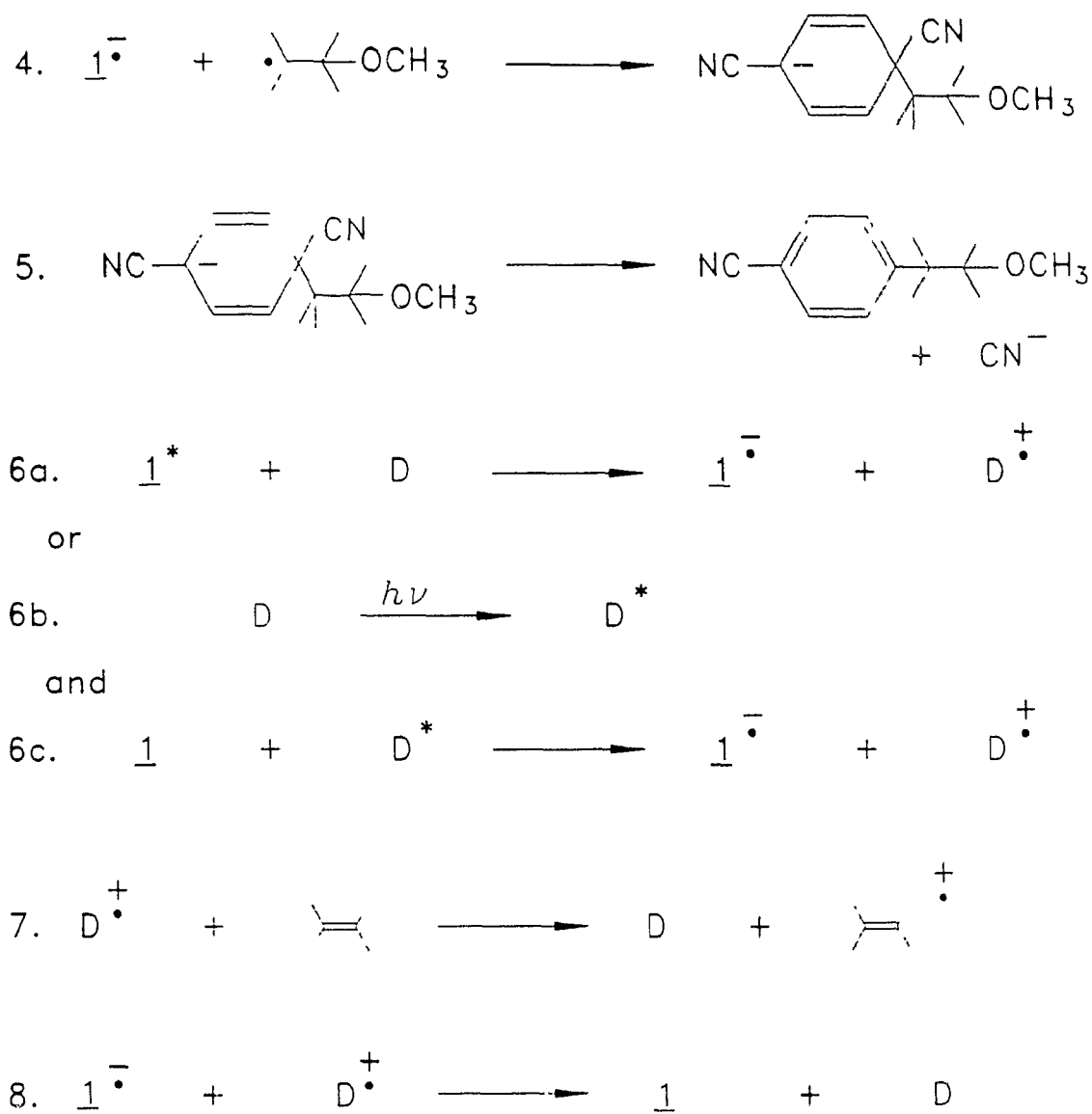
When reaction [2.3] was carried out using perdeutero-2,3-dimethyl-2-butene, no deuterium was incorporated into the final products, thereby excluding the role of the proton transfer pathway. The revised mechanism for the reaction is shown in Scheme 2.2. This now includes the possibility of nucleophile incorporation and the use of hole-transfer co-donor, biphenyl (**12**) and photosensitiser **7** (**30**).

Further work by Snow and Arnold (**30**) on this reaction, using **1** as the electron acceptor, has shown the synthetic generality of the reaction with regard to the olefin. The reaction was given the acronym 'Photo-NOCAS' (**Photochemical Nucleophile-Olefin-Combination, Aromatic Substitution**). This study encompassed a variety of cyclic alkyl-substituted olefins, and examined the effect of added co-donor on the reaction efficiencies and product yields. To date, quantum yields have not been measured for the reaction, but are assumed to be of the order  $\Phi < 0.01$ . The reactions gave synthetically useful yields, some of which are summarised in Table 2.1.



Scheme 2.2/cont.





D = biphenyl (4) or phenanthrene

Scheme 2.2

Table 2.1<sup>a</sup> Yields of Photo-NOCAS reactions with olefins and 1,4-dicyanobenzene (1), and calculated free energies  $\Delta G_{ET}$  for electron transfer, as a function of olefin oxidation potential.

Olefin	$E_{1/2}^{ox}$	no. of Photo-NOCAS (% of major product) <sup>d</sup>	Total yield/% <sup>b</sup>	$\Delta G_{ET}$ <sup>c</sup>
1,2-dimethyl-2-butene (2)	1.62	1(70) <sup>e</sup> -	70	-23.4
2-methylnorbornene	1.82	5(34) <sup>e</sup> 5(30) <sup>f</sup>	62(54)	-18.7
1-methylcyclohexene (19)	1.93	4(62) <sup>e</sup> 4(50) <sup>f</sup>	77(66)	-16.2
norbornene	2.19	3(56) <sup>e</sup> 3(51) <sup>f</sup>	88(100)	-10.2
cyclohexene	2.31	2(55) <sup>e</sup> 2(46) <sup>f</sup>	64(55)	-7.5

<sup>a</sup>Values taken from reference (30).

<sup>b</sup>Combined yields with added co-donor, biphenyl (12); yields in paranthesis are for direct irradiation.

<sup>c</sup>Based on the Rehm-Weller equation;  $E_{o,o}(1) = 97.6 \text{ kcal mol}^{-1}$  (50); values in  $\text{kcal mol}^{-1}$ .

<sup>d</sup>Yields are based upon the aromatic molecule; the olefin is generally present in excess. Side products include: 1:1 (olefin : aromatic) adducts formally resulting from substitution of the allylic radical, formed upon deprotonation of the olefin radical cation, for cyanide; dimers of the olefin resulting from coupling of the allylic radicals; and ethers resulting from the addition of methanol to the olefin.

<sup>e</sup>Added biphenyl (12).

<sup>f</sup>Direct irradiation

### 2.1.2 Mechanistic discussion

Fluorescence lifetime measurements and Stern-Volmer studies pointed to a diffusion controlled quenching of the singlet excited state of **1** by the olefins (43). Calculations using the Rehm-Weller equation predicted that these donor/acceptor systems should also undergo a diffusion controlled electron transfer, Table 2.1. To confirm that a PET process was involved and the reaction proceeded via the formation of freely solvated radical ions, the irradiations were carried out in non-polar solvents and gave no photo-NOCAS products.

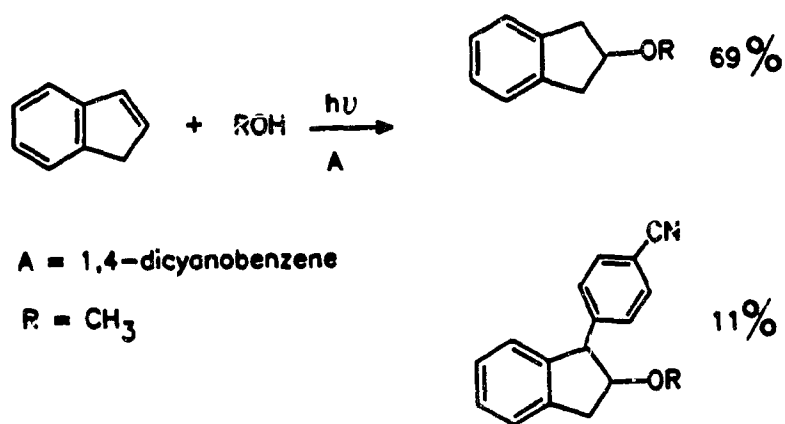
There are some aspects of the proposed mechanism that require further elaboration. Step 3, Scheme 2.2, shows the addition of the methanol nucleophile to the olefin radical cation; a distonic radical cation is formed. This can then undergo deprotonation to yield the  $\beta$ -alkoxy-alkyl radical (**13**). The 1:1 (nucleophile : olefin) radical now undergoes addition to the radical anion of the acceptor, which leads to the photo-NOCAS products.

Nucleophilic addition to olefins has been described before (4d). The addition of methanol to 1,1-diphenylethylene (**14**) is found to proceed in an *anti*-Markovnikov fashion (51).<sup>2</sup> Methanol adds to form the more stable benzylic radical. This is then readily reduced by the acceptor radical anion to form an anion which can be protonated by the solvent, finally giving the *anti*-Markovnikov product (**15**). Photocyanation of conjugated phenyl alkenes occurs by a similar photosensitisation (SET) process involving **1**<sup>\*</sup>, giving both *cis*- and *trans*- products with *anti*-Markovnikov regiochemistry (52). This type of nucleophilic addition of olefins to radical cations can also proceed by via an intramolecular PET process (53).

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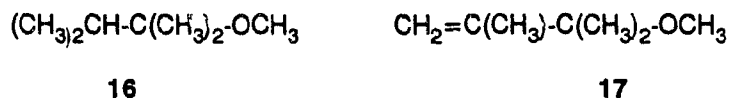
<sup>2</sup>The designation of regiochemistry as *anti*-Markovnikov is in keeping with the original designation. The methanol (anion) is attached at the less substituted ethenoid carbon atom. The designation *cis*- or *trans*- refers to the relative orientation of the aryl and methoxy groups.

1-Indene has been reported to add nucleophiles, water and alcohols, by a PET process (54). In this instance, the intermediate alkoxy indenyl radical is reduced to give the 1:1 adduct ether as the major product (69%); this radical also adds to give the photo-NOCAS 1:1:1 adduct in 11% yield, reaction [2.6].



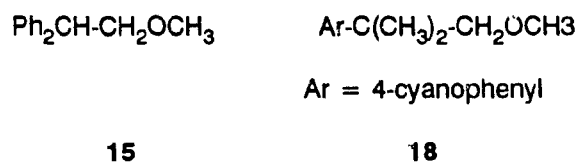
[2.6]

Evidence that a radical is formed after the addition of methanol to  $2^{+\bullet}$ , following deprotonation, has been shown by Lewis (55). Generation of  $2^{+\bullet}$  in the presence of methanol leads to a 1:1 mixture of ethers **16** and **17**, by disproportionation of the radical.

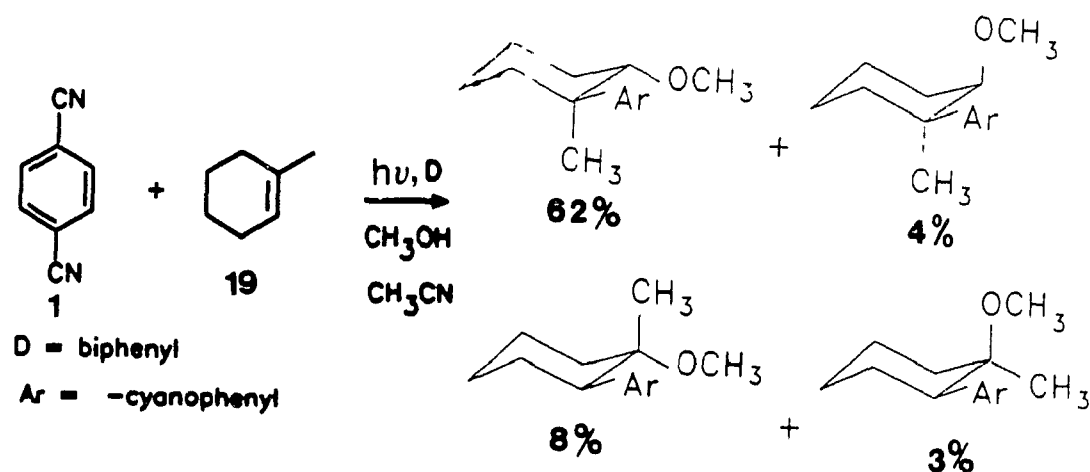


Generally, this addition of nucleophile can be envisaged to occur by two different pathways. The first involves the direct attack of the methanol to give the distonic radical cation. The second involves the formation of an ion-dipole  $\pi$ - complex. Regardless of the addition process, the results indicate that the addition, which is followed by proton loss,

favours the formation of the more hindered (stable) radical. Two examples show this selectivity. Addition across 1,1-diphenylethylene gave exclusively the diphenylmethyl-substituted radical, giving ether (15) (50). Addition of 2-methylpropene to 1 in the presence of methanol gives predominantly product (18) of the two possible 1:1:1 (nucleophile : olefin : aromatic) adduct, 26:1, (30).



This preference for the formation of the more hindered radical is also reflected in the product distribution generally observed in the photo-NOCAS reaction, and exemplified by the irradiation of 1 with 1-methylcyclohexene (19), reaction [2.7].



Addition in this case favoured formation of the *anti*-Markovnikov products over the Markovnikov products (6:1). The actual mode of addition is still somewhat uncertain. There are two pathways which could be followed. Methanol could add to  $2^{+\bullet}$  at the geminate radical ion pair stage, or addition could occur after the free radical ions have formed. Separation of the radical ions is known to occur with a unimolecular rate constant ca.  $5 \times 10^8 \text{ s}^{-1}$ , while the addition of methanol to olefins radical cations has been measured at  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in the case of diphenylethylene (56). However, some methanol additions have been measured with lower bimolecular rate constants,  $10^7 \text{ M s}^{-1}$  for 1,1-anisylethylene radical cation, and  $9.6 \times 10^6 \text{ M s}^{-1}$  1,1-dimethylindene radical cation (57). It is therefore possible that addition of methanol can occur in the geminate or solvent separated radical ion pair (SSRIP) stage, before the ions become freely solvated.

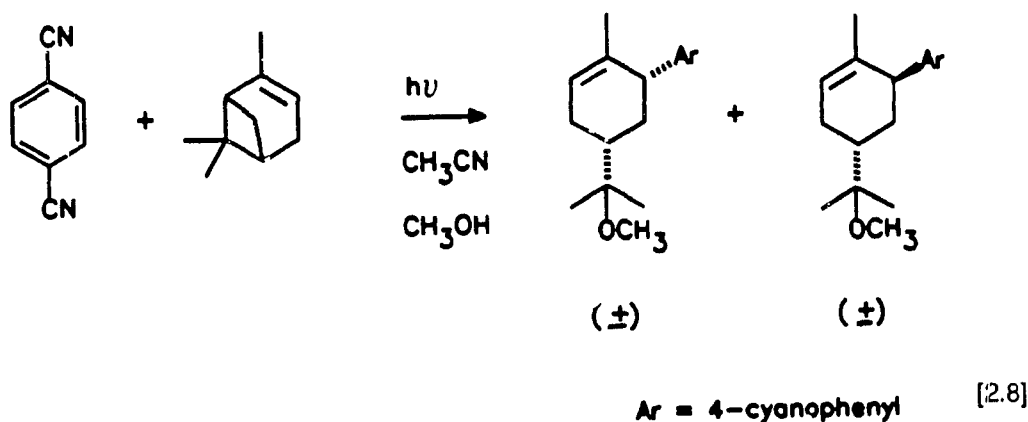
In the biphenyl (12) assisted reaction where the radical cation of the olefin is formed away from the radical ion of the aromatic nitrile, it would appear improbable that reaction could occur since the methanol alkyl radical and the radical anion of the acceptor are formed apart and will be in low concentration. The probability of encounter would then be extremely small. The high yields in these cases however, may result from a build up in concentration of the radical anion, which increases the probability of encounter. This would then constitute an example of a reaction controlled by the internal suppression of fast modes (58).

The rules regarding the regioselectivity of methanol adding to the olefin radical cation are still not well defined. There is no question that in the co-sensitised (phenanthrene) photo-NOCAS reactions and irradiations in the presence of added co-donor (biphenyl), radical-cations are formed, since methoxy- and cyano-substituted products have been isolated. Pac has also noticed, during photosensitised (phenanthrene) irradiations, incorporation of cyanide ion into the sensitizer to give 9-cyanophenanthrene and 9-cyano-9,10-dihydrophenanthrene (59). The use of a co-donor also has an effect on the product

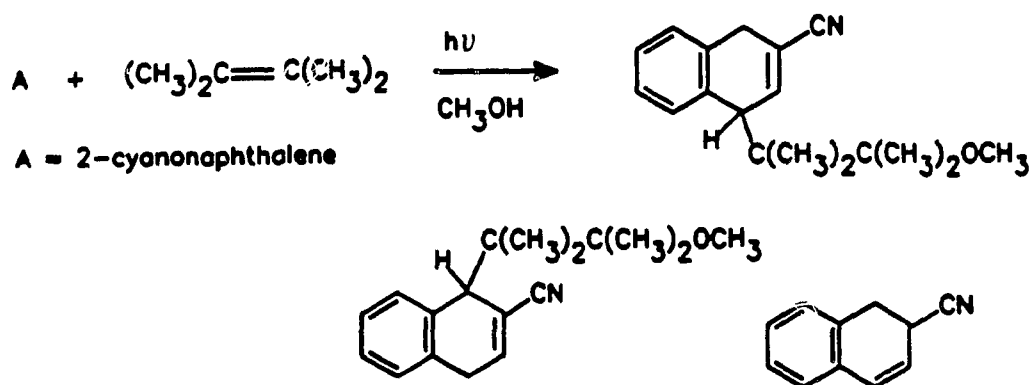
ratios (Markovnikov : *anti*-Markovnikov). This has been explained in terms of the radical ions reacting at the geminate radical-ion pair stage, in contrast to the reaction involving the solvated olefin radical cation or radical cation olefin complex, free from the influence of the radical anion. The factors that influences this control are not well understood.

### 2.1.3 Related photochemical adduct formation.

The photo-NOCAS reaction has been extended to include reactions with  $\alpha$ - and  $\beta$ -pinene with **1** (44). Addition occurs following the irreversible cleavage of the 4-membered ring of the radical cation, to the distonic radical cation. This cleavage is found to be regioselective, and gives the allylic radical-tertiary cation (**20**). The cleavage of the radical cations is selective to give the carbocation of the fragment radical with the lower oxidation potential (60), reaction [2.8].

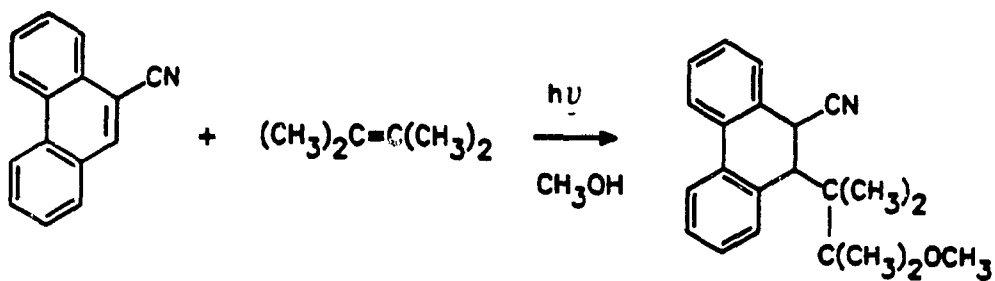


McCullough has also observed 1:1:1 (nucleophile : olefin : aromatic) adduct formation in the reaction of 2-cyanonaphthalene with **2** in methanol (46a). This example is closely related to the present work, but the process is an overall addition at the aromatic centre, not a substitution. This reaction results in the formation of the dihydro products, reaction [2.9].



[2.9]

Pac also carried out this same reaction using cyanophenanthrene. He observed 20-30% of the 1:1:1 (nucleophile : olefin : aromatic) adduct, again with no rearomatisation, reaction [2.10] (59).

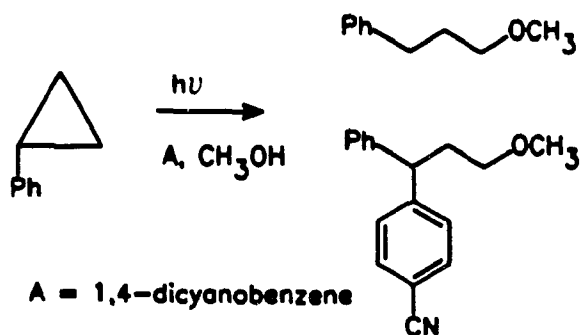


[2.10]

An interesting variation of the 1:1:1 (nucleophile : olefin : aromatic) adduct formation, is the nucleophilic assisted (61)  $\sigma$  bond cleavage ring opening of radical cation of arylcyclopropanes (62). Instead of the olefin, a cyclopropane ring has been used. Irradiation of **1** and 1-methylphenylcyclopropane gives addition of methanol to the open ring, as well as a 1:1:1 adduct (**21**) (17%), reaction [2.11]. This type of 1:1:1 adduct formation

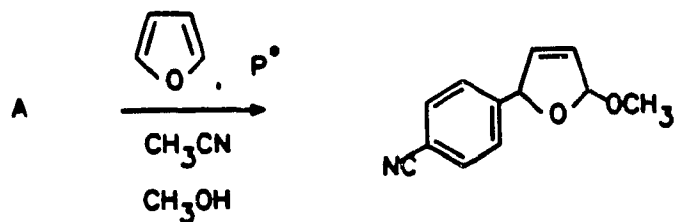


with cyclopropanes occurs with a variety of nucleophiles, water, alcohols, and cyanide (63).



[2.11]

The 'redox photosensitised' (electron transfer) reaction of **1** with furans gives 1:1:1 adducts in high yields, reactions [2.12] (64). The reaction however, is best described as a 1:1:1 (nucleophile : aromatic : aromatic) combination, due to the aromatic character of the furan ring.



**A = 1,4-dicyanobenzene**

**P = phenanthrene**

[2.12]

## 2.2 Extension of the photo-NOCAS reaction to other aromatic electron acceptors

### 2.2.1 The primary goal of this research

The photochemical nucleophile-olefin combination, aromatic substitution (photo-NOCAS) reaction is a potentially useful synthetic procedure. Readily available starting materials (a nucleophile, an olefin, and an aromatic molecule) are combined to make a more complex bifunctional product in one simple step; two new bonds are made during the process. The utility of this procedure for the synthesis of *para*-cyanophenyl  $\beta$ -alkyl ethers has been amply demonstrated (30,43,44) and a mechanism has been proposed which is consistent with all of the observations (Scheme 2.2). Reaction occurs when an acetonitrile-methanol solution of 1,4-dicyanobenzene (1) and the alkene is irradiated through Pyrex; however, the efficiency and yield of photo-NOCAS product may be significantly increased when a co-donor, *e.g.*, biphenyl (12), is added to the reaction mixture.

In order to demonstrate the synthetic utility of any organic reaction, it is essential to define its scope and limitations, *i.e.*, show where it works and fails. To this end, a research programme has been initiated to examine all aspects of the reaction; nucleophiles, alkenes and to a lesser extent, solvents. Nucleophiles that have been incorporated include methanol, water, and cyanide ion. The reaction has been shown to be fairly general with respect to the olefin: both acyclic and cyclic olefins react regio- and stereoselectively, to give primarily the *anti*-Markovnikov products. Until now no study has been undertaken to examine the role and diversity of the electron accepting aromatics. This work was initiated with this goal in mind. A series of *para*-substituted benzonitriles was examined and the results will be discussed below. Previous work has emphasised 1,4- and 1,2-dicyanobenzene as the electron accepting aromatic reactant (30,43,44). While the *para*- or *ortho*-cyano group incorporated in the product is a useful functionality for further synthetic modification, for many applications it will be desirable to have some other functional group. Consideration of the mechanism leads to the suggestion that the reaction may incorporate

other electron withdrawing substituted aromatic molecules.

### 2.2.2 Methyl 4-cyanobenzoate as an alternative electron acceptor in the Photo-NOCAS reaction.

The main objective of this study was to determine the reactivity of such an alternative, methyl 4-cyanobenzoate (**22**), under these conditions. While there are some obvious similarities between 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**), there are also important differences (Table 2.2). Comparison of the behaviour of the two under these reaction conditions has led to a better understanding of the mechanism.

### 2.2.3 Results

Irradiation of an acetonitrile-methanol (3:1) solution of methyl 4-cyanobenzoate (**22**) and 2,3-dimethyl-2-butene (**2**) gave the cyclic imine (**23**) as the only significant volatile product (83% yield based upon **22**), reaction [2.13]. There is no evidence (capillary column gas chromatography with mass selective detection, GC-MS) for formation of the photo-NOCAS product. Imine (**23**) is readily hydrolysed to ketone (**24**) under mild conditions by treatment with aqueous acidic methanol (reaction [2.14]). Reactions [2.13] and [2.14] were repeated using *tert*-butyl 4-cyanobenzoate (**22a**) instead of the methyl ester. The resulting *tert*-butyl ester imine (**23a**) and *tert*-butyl ester ketone (**24a**) were fully characterised; **24a** was converted to **24** upon transesterification.

When an acetonitrile-methanol solution of methyl 4-cyanobenzoate (**22**) and 1-methylcyclohexene (**19**) is irradiated, the analogous imine (**25**) is obtained (30%, reaction [2.15]). Analysis (GC-MS) of the crude photolysate indicates that **25** is the only isomer formed in appreciable amounts, less than 1% of any regio- or stereoisomer is detected, and there are no photo-NOCAS products.

**Table 2.2** Comparison of some photophysical properties of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**).

	$\lambda_{\max}^a$	$E_{0,0}^S$ <sup>b</sup>	$\tau_s^c$	$E_{1/2}^{\text{red d}}$	$E_{0,0}^T$ <sup>e</sup>
<b>1</b>	286 (3.15)	97.6 <sup>f</sup> (408.4)	9.73 <sup>f</sup>	-1.66 <sup>i</sup>	70.9 <sup>j</sup> (296.6)
<b>22</b>	285 (3.13)	95.3 <sup>f</sup> (398.7)	<2.0 <sup>h</sup>	-1.76 <sup>f</sup>	72.0 <sup>g</sup> (301.2)

<sup>a</sup>Long wavelength (<sup>1</sup>L<sub>b</sub>) absorption maximum, nm (log  $\epsilon$ ), in acetonitrile-methanol (3:1).

<sup>b</sup>Excited singlet state energy in kcal mol<sup>-1</sup> (kJ mol<sup>-1</sup>).

<sup>c</sup>Singlet excited state lifetime (ns).

<sup>d</sup>Reduction potential (V, vs. sce) in acetonitrile (0.1 TEAP).

<sup>e</sup>Triplet energy in kcal mol<sup>-1</sup> (kJ mol<sup>-1</sup>) taken from the 0,0 band of the phosphorescence emission spectrum (EtOH:MeOH, 4:1, at 77 K).

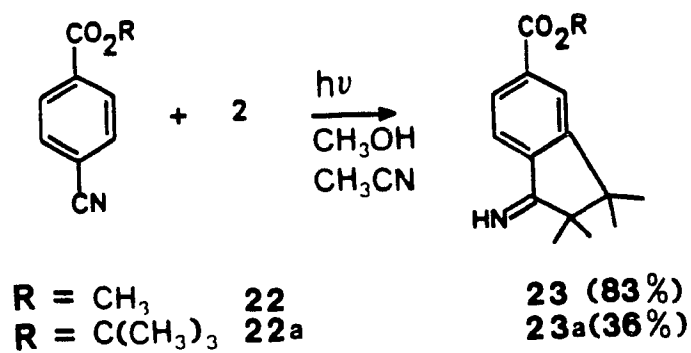
<sup>f</sup>Reference (50).

<sup>g</sup>Reference (65).

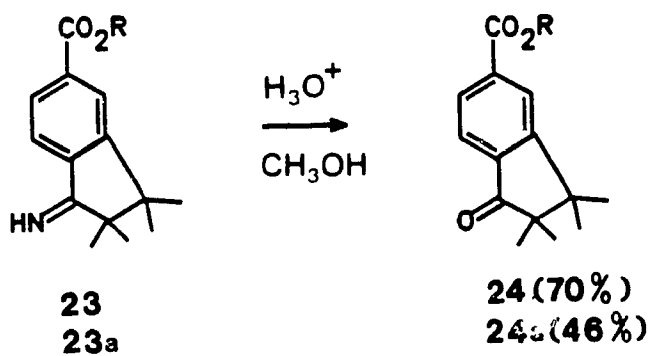
<sup>h</sup>Too short to measure by nano-second single-photon counting.

<sup>i</sup>Reference (30).

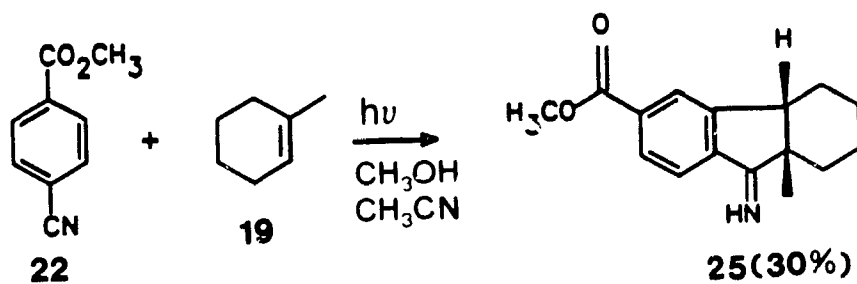
<sup>j</sup>Reference (66).



[2.13]

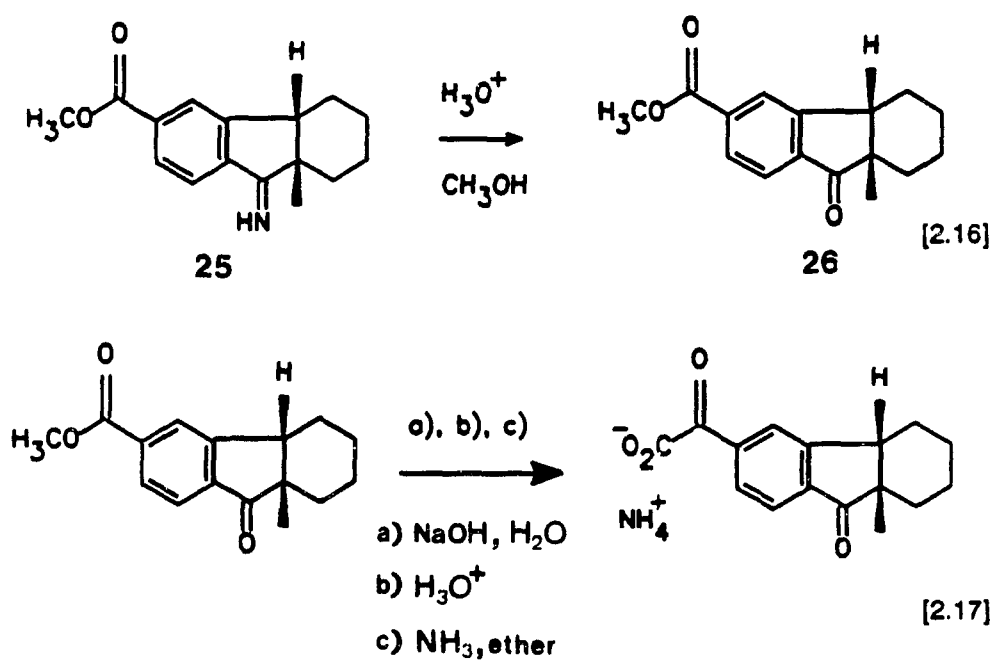


[2.14]



[2.15]

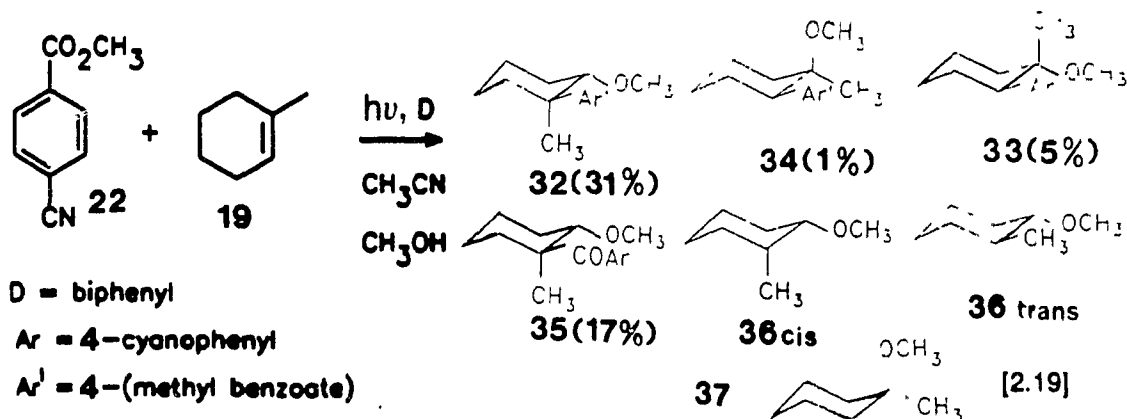
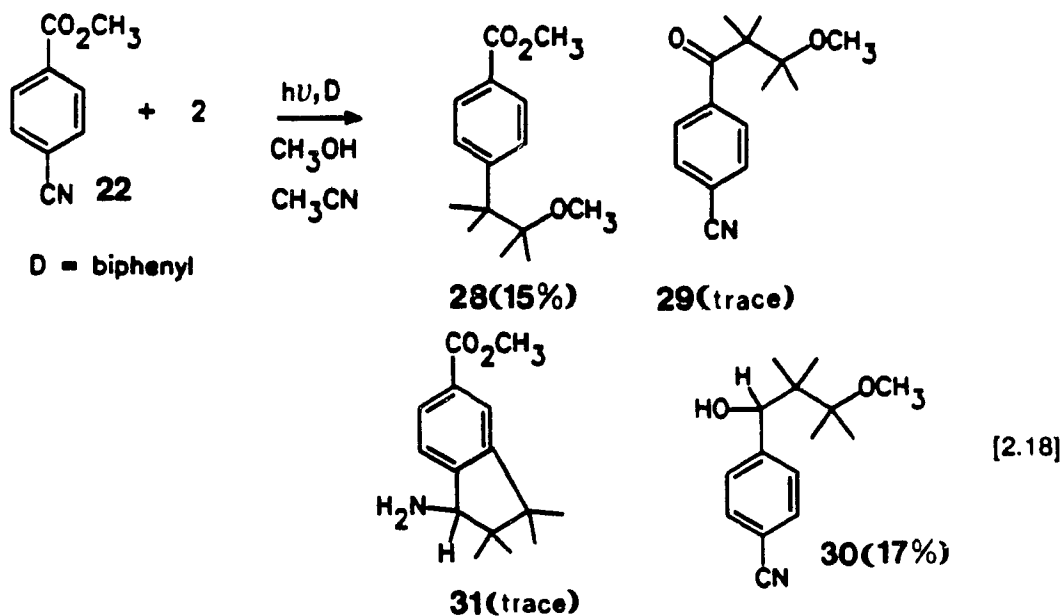
Imine (25) gives ketone (26) under mild hydrolysis conditions (reaction [2.16]). More rigorous hydrolysis of ketone 26 gives the keto acid, isolated as a crystalline ammonium salt 27 (reaction [2.17]).



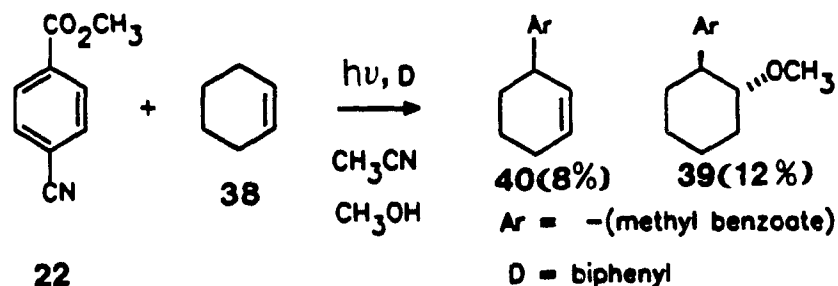
The addition of biphenyl (**12**) to these reaction mixtures has a profound effect. Irradiation of an acetonitrile-methanol solution of methyl 4-cyanobenzoate (**22**), 2,3-dimethyl-2-butene (**2**), and biphenyl (**12**) gives the photo-NOCAS product (**28**) (15%) along with the alcohol (**30**) (17%, reaction [2.18]). When this irradiation is carried out to low conversion, ketone (**29**) is obtained in low yield. This ketone is not detected in the photolysate when the irradiation is carried out to high conversion. Trace amounts of the imine (**23**) and the amine (**31**) are also formed under these conditions.

Photo-NOCAS products are also obtained upon irradiation of acetonitrile-methanol solutions of methyl 4-cyanobenzoate (**22**) and 1-methylcyclohexene (**19**) when biphenyl (**12**) is added (reaction [2.19]). Three isomeric esters (**32-34**) (combined yield, 37%) were characterised. The major product (**32**) has the *trans* configuration of the *anti*-Markovnikov

regiochemistry. Also isolated from the reaction mixture is the 4-cyanophenyl ketone (**35**) with the *trans* anti-Markovnikov configuration. Substantial amounts of the ethers, 2-methoxy-1-methylcyclohexane (**36** *cis* and *trans*) and 1-methoxy-1-methylcyclohexane (**37**) are also formed.



Cyclohexene (**38**) is also incorporated into a photo-NOCAS product; irradiation of an acetonitrile-methanol solution of **22**, **12** and **38** gives the *trans* 1:1:1 adduct (**39**, 8%, reaction [2.20]). The major product is the 1:1 (olefin : aromatic) adduct, 3-(methyl 4-benzoate)cyclohexene (**40**).



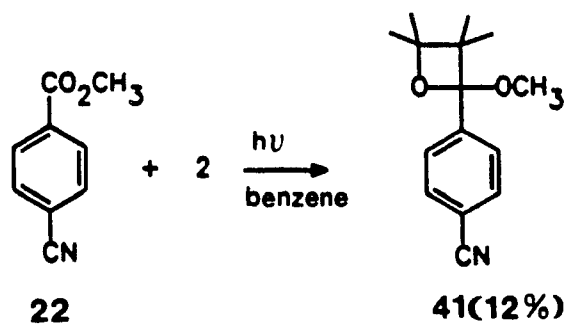
[2.20]

All of the photochemical reactions described so far were carried out using acetonitrile-methanol (3:1) as solvent; irradiations were also performed in benzene solution in order to assess the importance of solvent polarity. Irradiation of a benzene solution of methyl 4-cyanobenzoate (**22**) and 2,3-dimethyl-2-butene (**2**) gives the oxetane (**41**) (12%) along with a trace of the imine (**23**) (reaction [2.21]). Similar irradiation of the *tert*-butyl ester (**22a**) gives only the imine (**23a**); there is no evidence for formation of the oxetane in this case. Acid catalysed cleavage of the oxetane (**41**) gives the ketones (**42**) and (**43**) (reaction [2.22]).

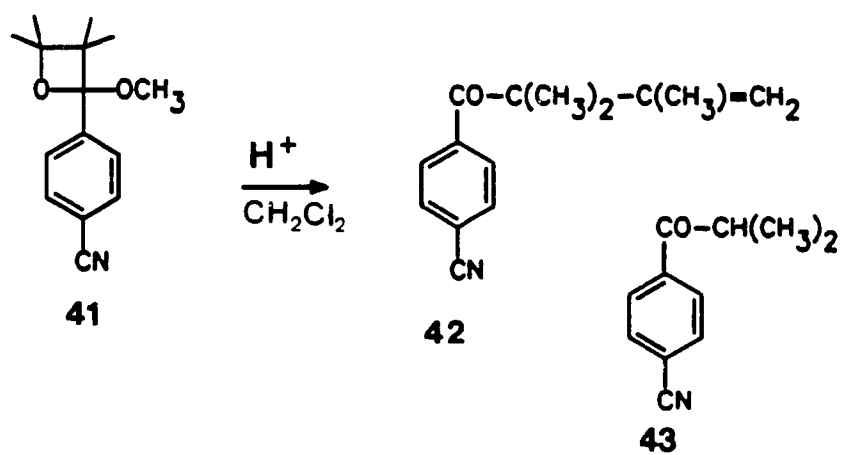
When a benzene solution of **22** and 2-methylpropene (**44**) is irradiated, the expected oxetane analogous to **41** is not detected. The only volatile product formed is oxetane (**45**) (reaction [2.23]).

The reactions of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**) with methyl and *tert*-butyl Grignard and lithium reagents were studied in order to gain a better understanding of the mechanism. The products obtained with the Grignard reagent are shown in reactions [2.24] - [2.27]; these results are summarised in Table 2.3.

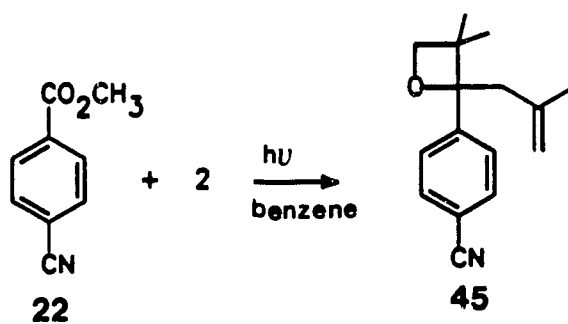




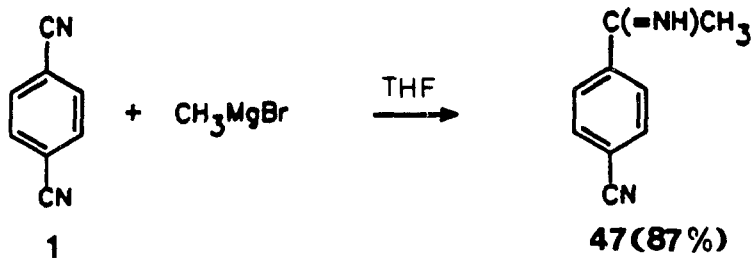
[2.21]



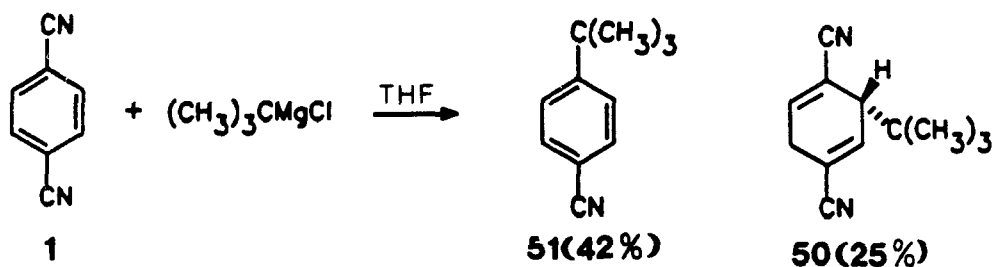
[2.22]



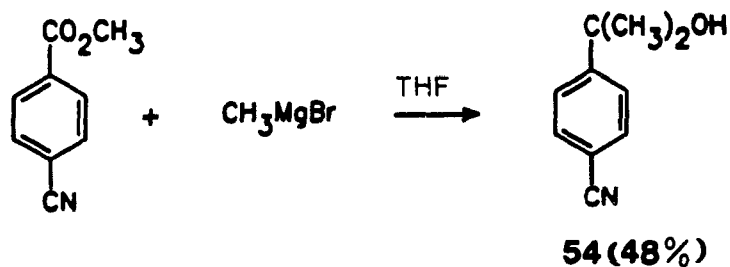
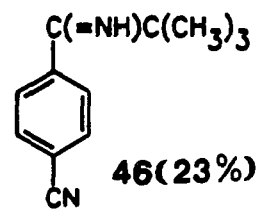
[2.23]



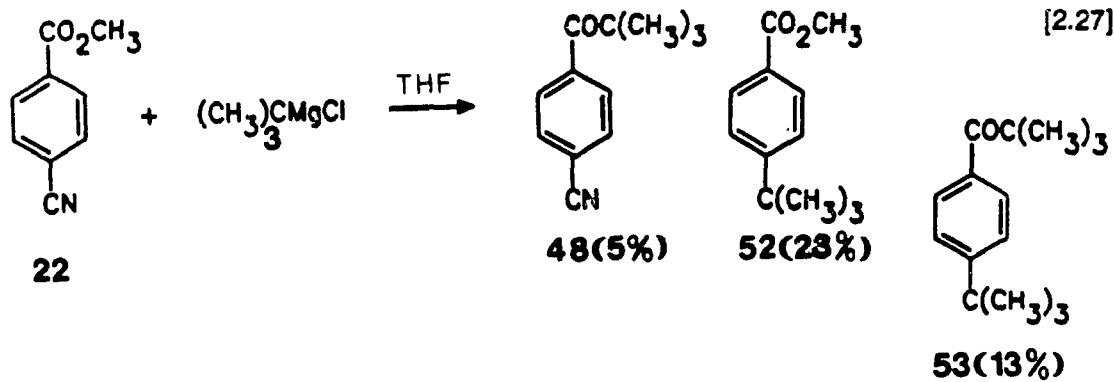
[2.24]



[2.25]



[2.26]



[2.27]

**Table 2.3** Results of reactions of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**) with alkyl lithium and alkyl Grignard reagents in THF.

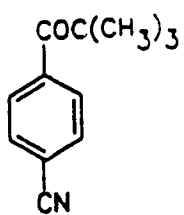
	Product yields <sup>a,b</sup>						
	48	49	50	51	52	53	54
<b>Reagents</b>							
<b>1</b> + <i>tert</i> -BuMgCl	23	-	25	42	-	-	-
<b>1</b> + <i>tert</i> -BuLi	-	-	23	77	-	-	-
<b>1</b> + CH <sub>3</sub> MgBr	-	87	-	-	-	-	-
<b>1</b> + CH <sub>3</sub> Li	-	58	-	-	-	-	-
<b>22</b> + <i>tert</i> -BuMgCl	5	-	-	-	23	13	-
<b>22</b> + <i>tert</i> -BuLi	20	-	-	-	13	12	-
<b>22</b> + <i>tert</i> -BuLi <sup>c</sup>	-	-	-	-	100	-	-
<b>22</b> + CH <sub>3</sub> MgBr	-	-	-	-	-	-	97
<b>22</b> + CH <sub>3</sub> Li	-	44	-	-	-	-	25

<sup>a</sup>Yields obtained by GC-FID; % based on consumed **1** and **22**; conversion > 50%.

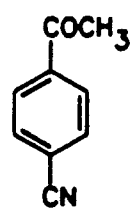
<sup>b</sup>Details of reaction conditions given in experimental section.

<sup>c</sup>Reaction stopped after 1% conversion of **22**.

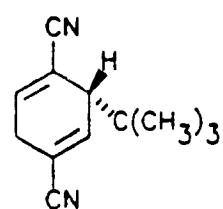
Table 2.3/cont.



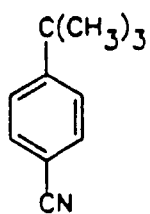
48



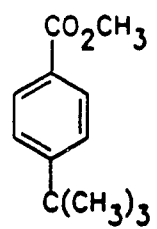
49



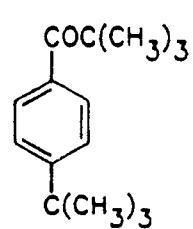
50



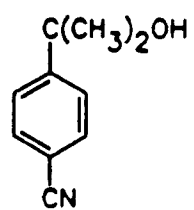
51



52

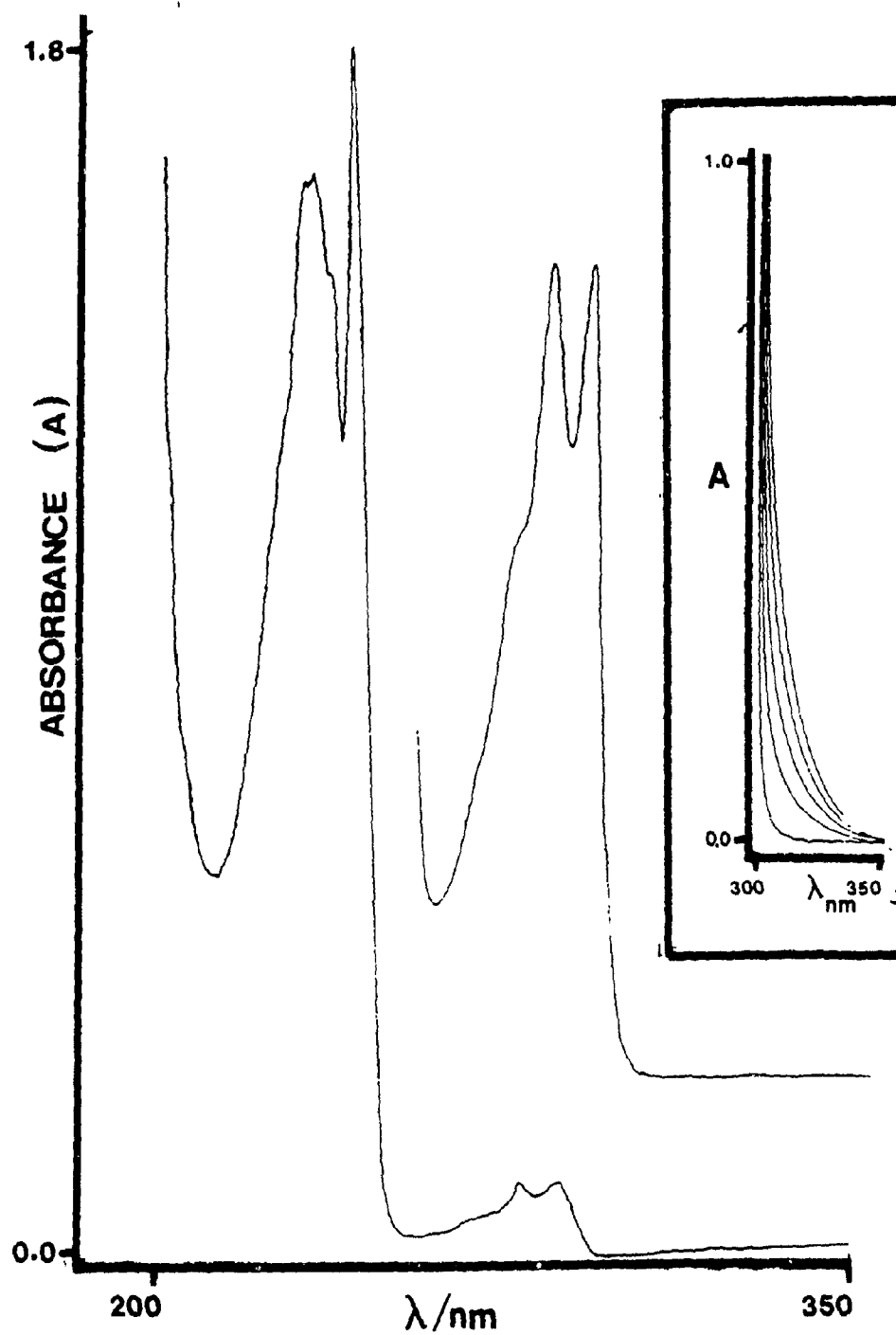


53

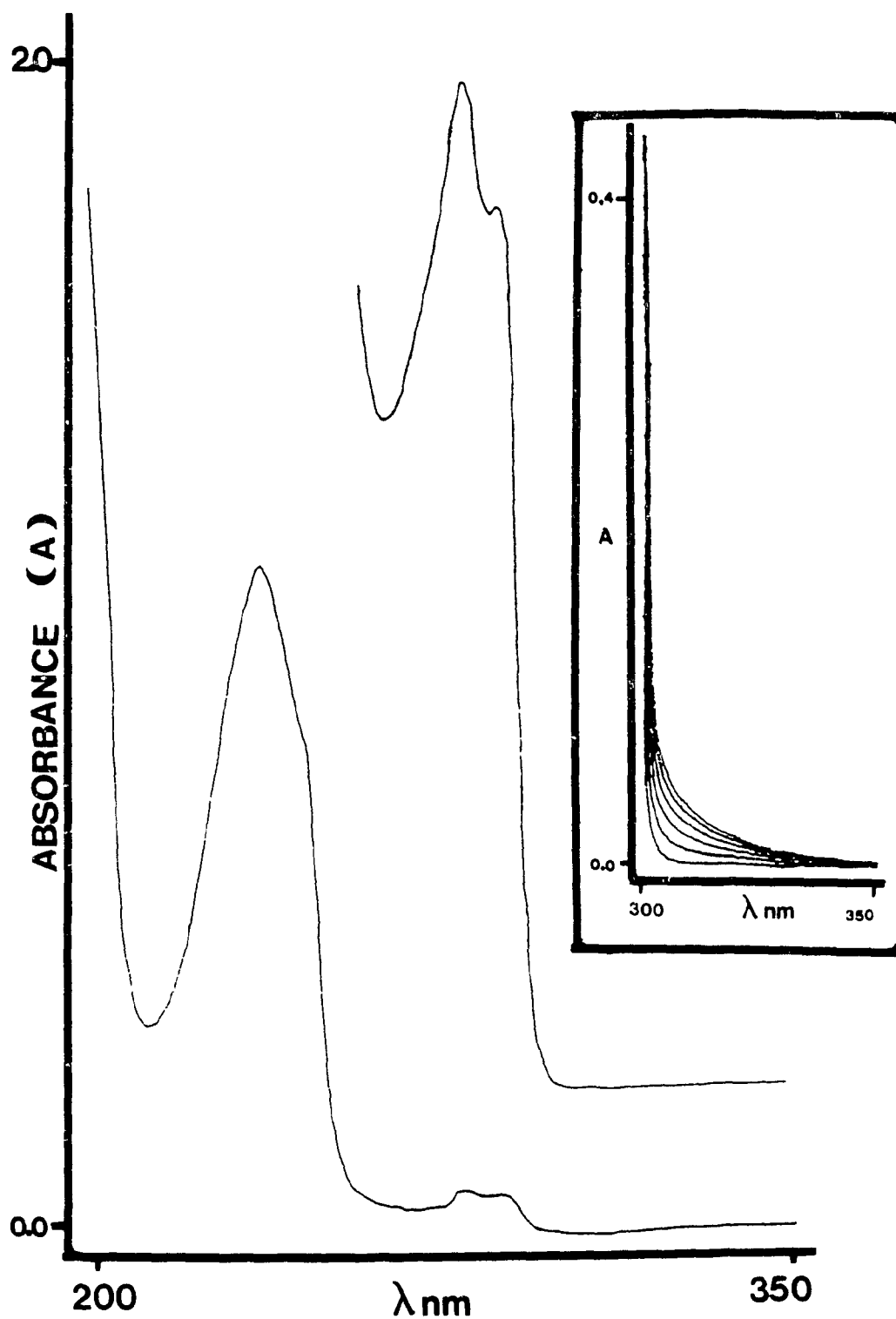


54

Ultraviolet absorption spectra of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**) are shown in Figure 2.1 and 2.2. The long wavelength ultraviolet absorption of solutions of **1** and **22**, and varying concentrations of 2,3-dimethyl-2-butene (**2**) and 1-methylcyclohexene (**19**) are indicative of ground state charge-transfer complex formation, (see insets) Figures. 2.1 and 2.2. These are also shown in Figure 2.3 and Table 2.4. Benesi-Hildebrand plots of  $[A]_0/A$  against  $1/[D]_0$  for a series of acetonitrile-methanol (3:1) solutions of **22** with varying concentrations of **2** and **19** are shown in Figures 2.4 and 2.5, and Table 2.5. The association constants ( $K_a$ ) for the charge-transfer complex involving **22** are  $0.36 \pm 0.02$  for **2**, and  $0.4 \pm 0.2$  for **19**. Similar results observed for **1** and **22a**, Figures 2.6 and 2.7, Table 2.6, are described later. Details of the technique are given in the experimental section.



**Figure 2.1** Ultraviolet absorption spectrum of 1,4 dicyanobenzene (1) in acetonitrile-methanol (3:1); inset shows absorption of charge-transfer complex as a function of increasing 2,3-dimethyl-2-butene (2) concentration.



**Figure 2.2** Ultraviolet absorption spectrum of methyl 4-cyanobenzoate (**22**) in acetonitrile-methanol (3:1); inset shows absorption of charge-transfer complex as a function of increasing 2,3-dimethyl-2-butene (**2**) concentration.

**Table 2.4** Absorbance of charge-transfer complexes as a function of olefin concentration.

[Alkene]/Mol L <sup>-1</sup>	Absorbance/A			
	22 + 2	22 + 19	1 + 2	22a + 2
0.00	0.00	0.00	0.02	0.07
0.05	0.12	0.02	0.18	0.19
0.10	0.22	0.04	0.32	0.28
0.15	0.32	0.06	0.46	0.38
0.20	0.42	0.08	0.59	0.43



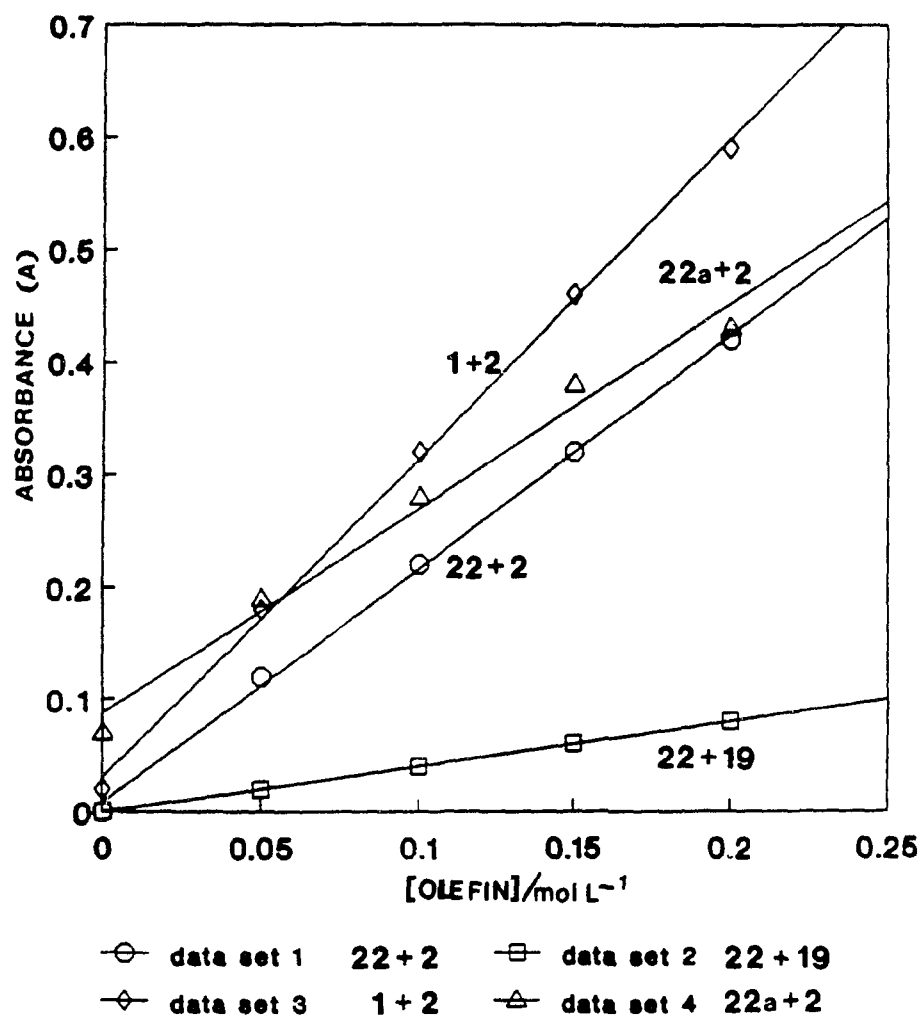
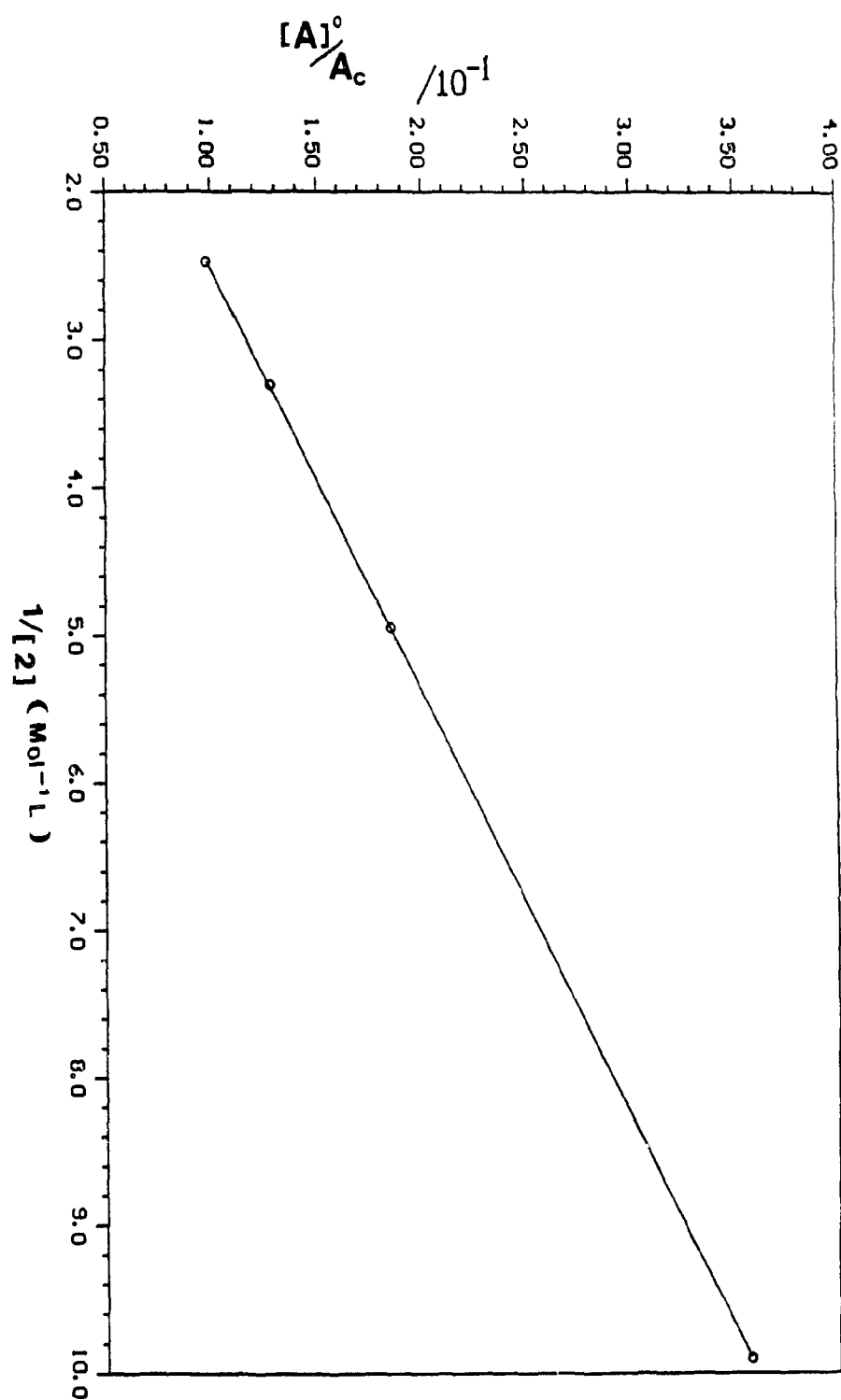


Figure 2.3 Absorption of charge-transfer (CT) complex as a function of olefin concentration.

**Table 2.5** Benesi-Hildebrand analysis of uv data for methyl 4-cyanobenzoate (**22**) with olefins **2** and **19**.

Sample	[alkene]	(22 + 2)			(22 + 19)		
		$A_c$	$[A]_o/A_c$	$1/[D]_o$	$A_c$	$[A]_o/A_c$	$1/[D]_o$
1	0.101	0.028	0.357	9.901	0.006	1.667	9.901
2	0.202	0.054	0.185	4.950	0.012	0.833	4.950
3	0.303	0.078	0.128	3.300	0.016	0.303	3.300
4	0.404	0.102	0.098	2.475	0.022	0.454	2.475
		$r^2 = 1.000$			$r^2 = 0.998$		
		$K_a = 0.36 \pm 0.02$			$K_a = 0.4 \pm 0.2$		
		$\epsilon_{310nm} = 80 \pm 4$			$\epsilon_{310nm} = 22 \pm 11$		

$l = 1 \text{ cm}$ ,  $[A]_o = 0.01 \text{ M}$



**Figure 2.4** Absorption of CT complex (22 and 2) as a function of olefin concentration (Benesi-Hildebrand).

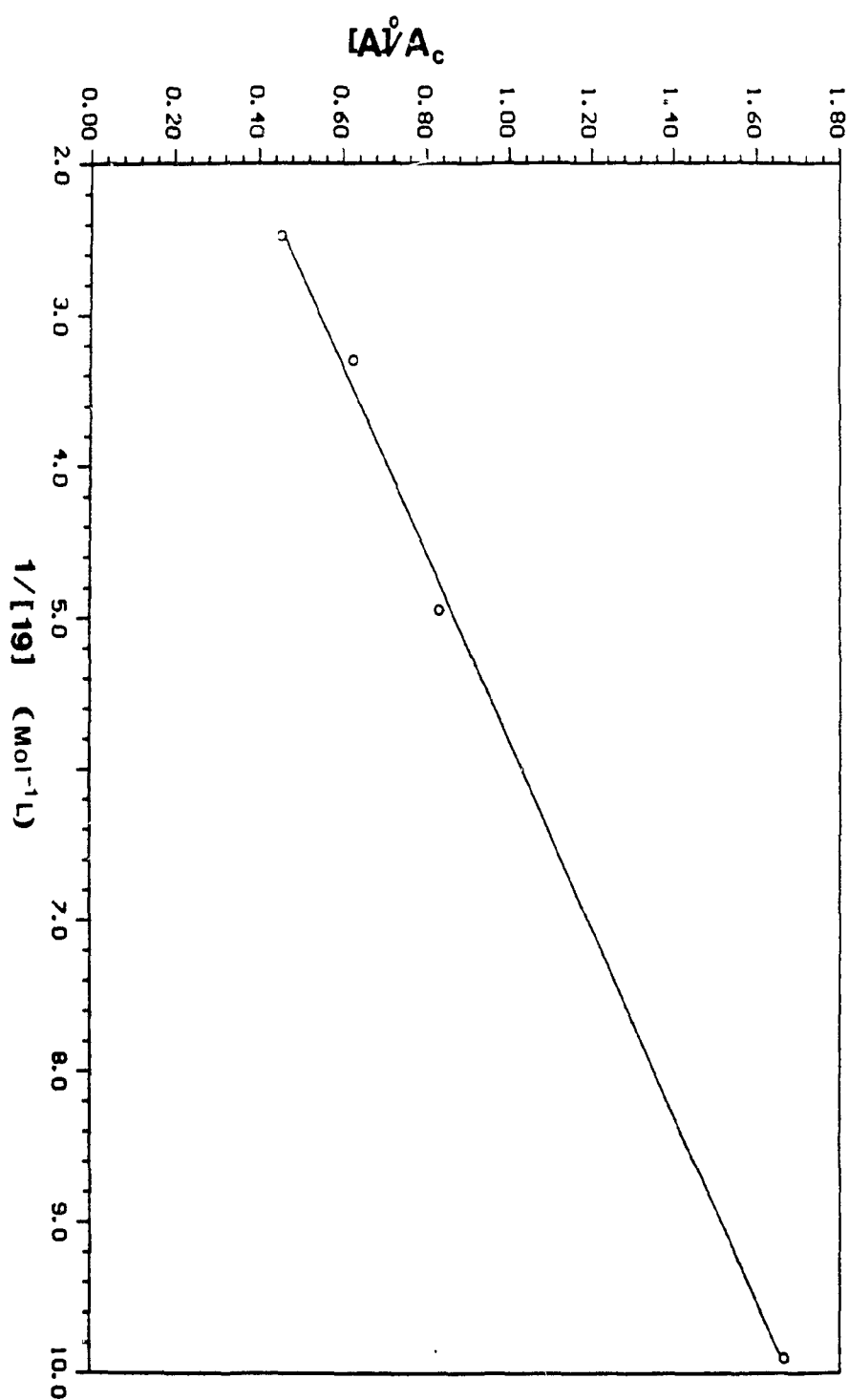
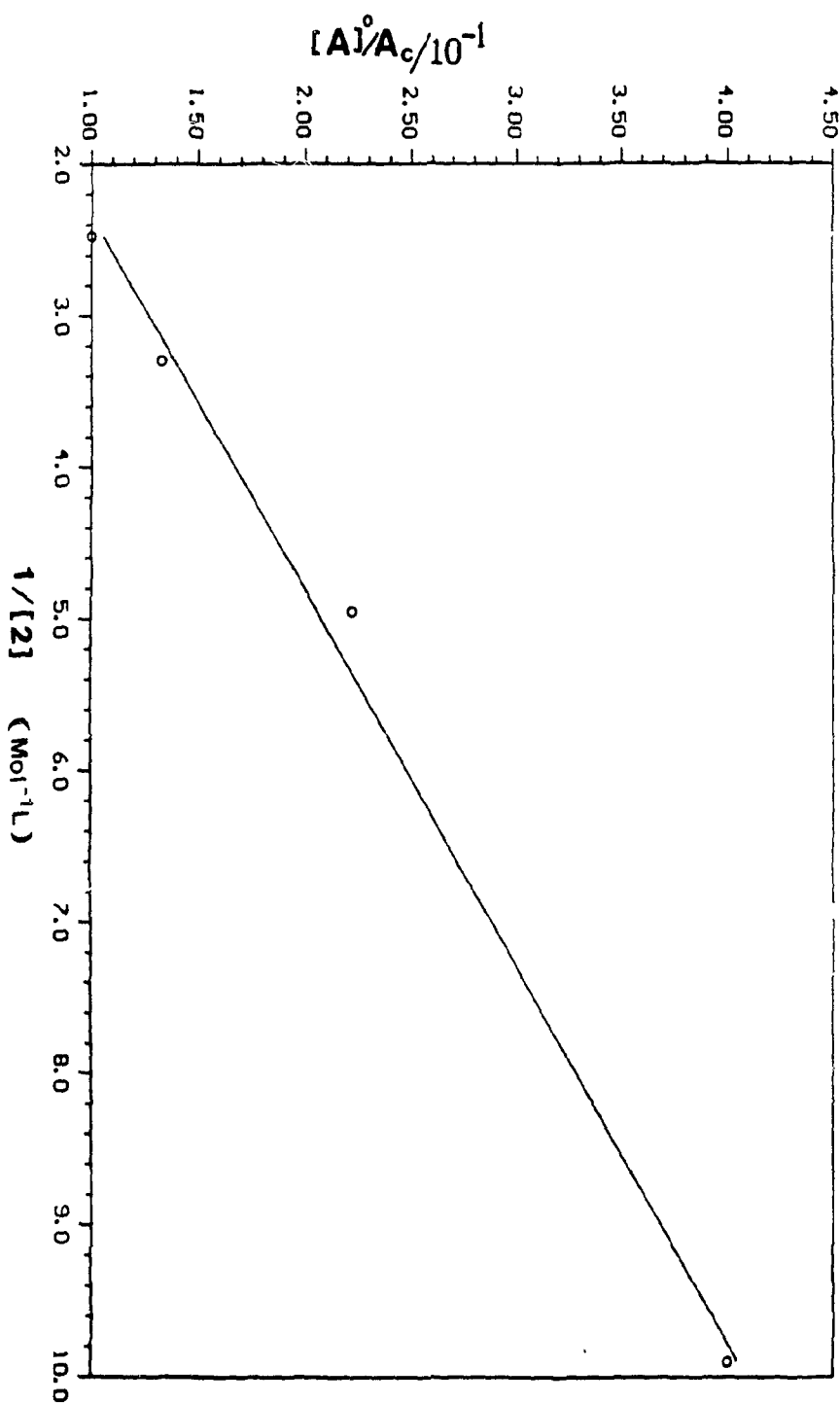


Figure 2.5 Absorption of CT complex (22 and 19) as a function of olefin concentration (Benesi-Hildebrand).

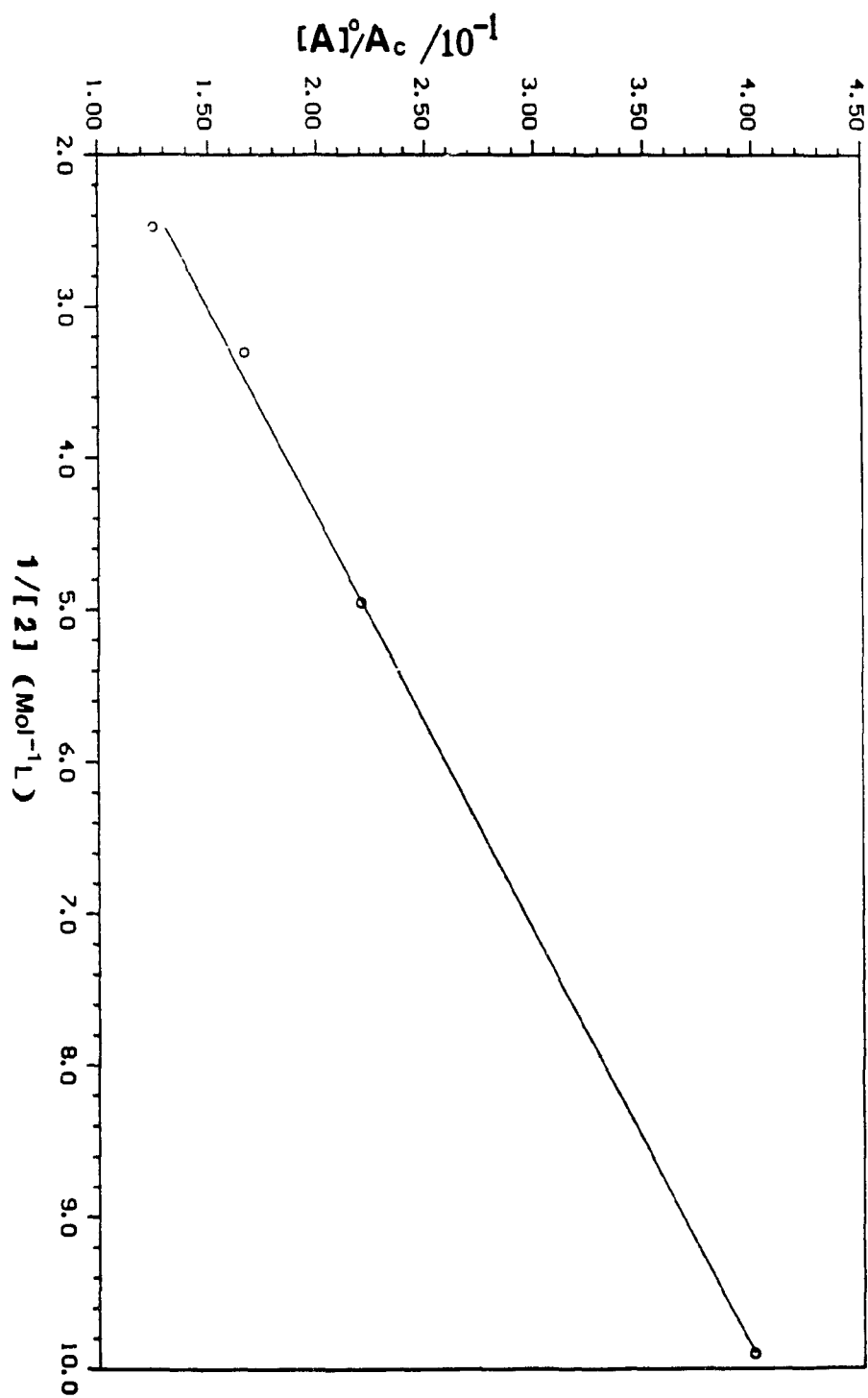
**Table 2.6** Results of the Benesi-Hildebrand analysis of uv data.

Sample	[alkene]	(1 + 2)			(22a + 2)		
		$A_c$	$[A]_o/A_c$	$1/[D]_o$	$A_c$	$[A]_o/A_c$	$1/[D]_o$
1	0.101	0.025	0.400	9.901	0.025	0.400	9.901
2	0.202	0.045	0.222	4.950	0.045	0.220	4.950
3	0.303	0.075	0.133	3.300	0.060	0.167	3.300
4	0.404	0.100	0.100	2.475	0.080	0.125	2.475
$r^2 = 0.993$				$r^2 = 0.994$			
$K_a = 0.15 \pm 0.01$				$K_a = 1.27 \pm 0.23$			
$\epsilon_{310nm} = 165 \pm 10$				$\epsilon_{310nm} = 23 \pm 6$			

$\ell = 1 \text{ cm}, [A]_o = 0.01 \text{ M}$



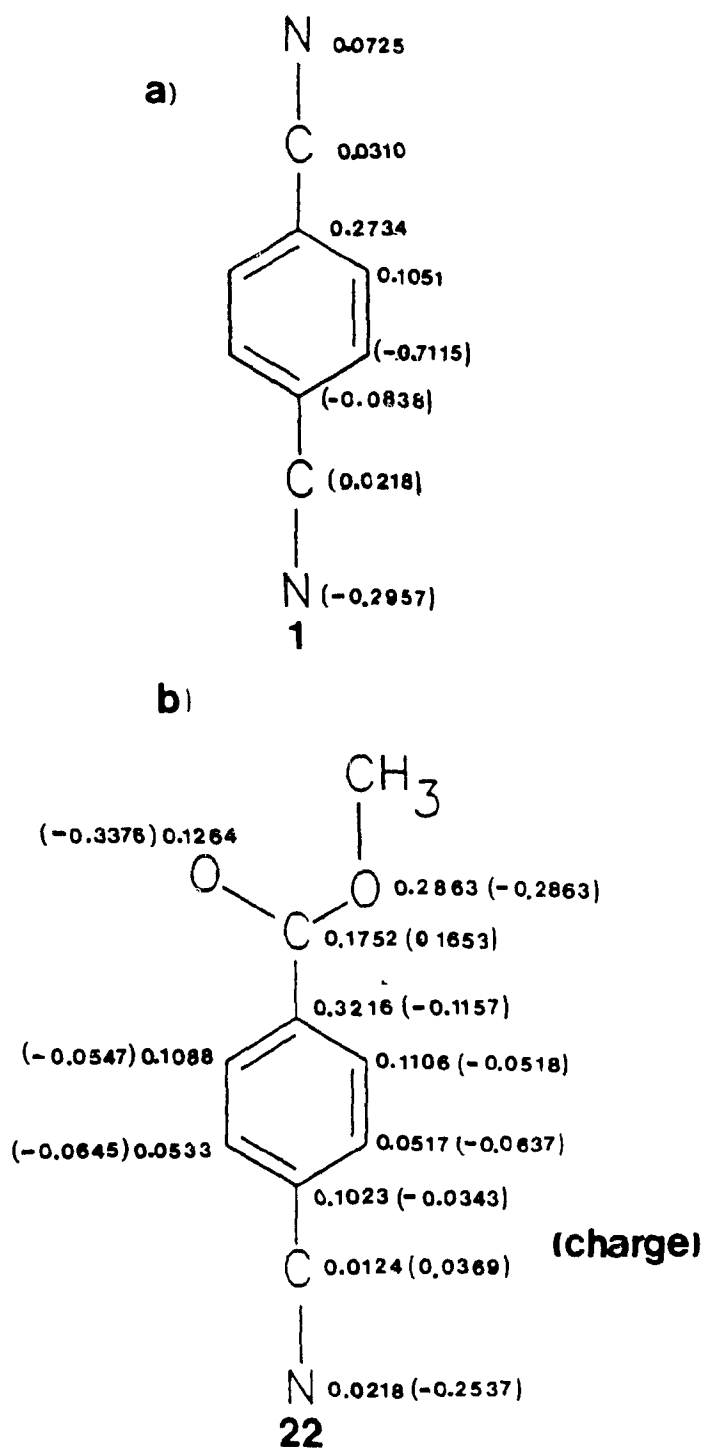
**Figure 2.6** Absorption of CT complex (1 and 2) as a function of olefin concentration (Benesi-Hildebrand)



**Figure 2.7** Absorption of CT complex (22a and 2) as a function of olefin concentration (Benesi-Hildebrand)

Spin and charge distribution on the radical anions of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**) were calculated. The *ab initio* molecular orbital calculations were carried out with the Gaussian 90 series of programmes (67). The six carbons of the aromatic ring and the atoms directly attached were constrained to a plane; the remaining structural features were fully optimised at the UHF/STO-3G level. In the case of ester **22**, the methyl group was not allowed to rotate. The spin density was taken as the square of the coefficient at the atomic  $p_z$ -orbital in the singly occupied molecular orbital (SOMO) and the charge distribution was calculated by Mulliken population analysis (68). The limitations of this method have been discussed (69). These data are summarised in Figure 2.8.





**Figure 2.8** Spin and charge densities calculated (STO-3G) for the radical anions of (a) 1,4-dicyanobenzene (1) and (b) methyl 4-cyanobenzoate (22).

#### 2.2.4 Structural determination

The imine (**23**) (reaction [2.13]) was labile towards hydrolysis, but could be isolated and characterised. A broad band was observed in the infrared spectrum at  $3400\text{ cm}^{-1}$  attributed to the N-H stretching frequency. There was a strong absorption band at  $1645\text{ cm}^{-1}$  due to the carboxyl carbonyl, but no absorption in the region of the nitrile stretching frequency. An exchangeable ( $\text{D}_2\text{O}$ ) proton was observed at 8.6 ppm in the  $^1\text{H}$  nmr spectrum. Signals due to three hydrogens were clearly resolved in the aromatic region of the  $^1\text{H}$  nmr spectrum, with three corresponding doublets in the aromatic region of the coupled  $^{13}\text{C}$  nmr spectrum. The two pairs of equivalent methyl groups were evident in the  $^1\text{H}$  nmr spectrum as sharp singlets at 1.19 and 1.10 ppm.

After hydrolysis (reaction [2.14]), the spectra of the ketone (**24**) were similar to those of the imine (**23**), with some important differences. The band due to the N-H stretching frequency observed in the infrared, and the signal attributed to the exchangeable proton in the  $^1\text{H}$  nmr spectra of the imine were no longer present. Two sharp singlets at 1.26 and 1.10 ppm in the  $^1\text{H}$  nmr were attributed to the two pairs of equivalent methyl groups. The singlet resonance observed at 188.23 ppm in the  $^{13}\text{C}$  nmr spectrum of **23**, attributed to the carbon of the imine group, was shifted to 210.59 ppm, indicative of a ketone carbonyl carbon. The mass spectrum of **24** also showed the expected one mass unit increase in the molecular ion and in the base peak (loss of  $\text{CH}_3^\bullet$ ).

Structures assigned to the *tert*-butyl ester imine (**23a**) and ketone (**24a**), similar to those of the analogous methyl ester, were consistent with the observed spectra. The assignment of the regio- and stereochemistry of structure **25** and **26** (reaction [2.15] and [2.16]), from the  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra, was not as straightforward and was ultimately achieved by an X-ray analysis of a single crystal of the ammonium salt of the carboxylic acid derivative (**27**). Trisubstitution of the aromatic ring in **26** was apparent from the three distinct signals due to aromatic hydrogens (8.13, 8.04 and 7.80 ppm) in the  $^1\text{H}$  nmr

spectrum, and three doublets in the aromatic region of the  $^{13}\text{C}$  nmr spectrum (128.60, 124.25 and 125.59 ppm). An apparent triplet ( $J = 5.24$  Hz) due to a single hydrogen was observed at low field (3.08 ppm). Acid and base catalysed deuterium exchange experiments were carried out to determine if this hydrogen was exchangeable and therefore adjacent to the carbonyl at the junction between the 5- and 6-membered rings. An attempt was also made to alkylate the enolate anion. These reactions were carried out using conditions found to be effective for the exchange and alkylation at the carbon next to the carbonyl of 1-indanone. However, there was no evidence ( $^1\text{H}$  nmr and GC-MS, with selective ion monitoring) for deuterium exchange or alkylation of **26**. These results provided the first indication that the low-field signal (3.08 ppm) was due to a benzylic hydrogen (not a hydrogen next to a carbonyl group) and thus established the regiochemistry of the cycloaddition.

The  $^1\text{H}$  nmr of the ester (**26**) was recorded in benzene- $d_6$  and chloroform- $d$ ; the change in chemical shift for the signals due to the methyl and the benzylic hydrogens were compared. Benzene is known to interact with electron deficient sites on the solute molecule (70). The orientation of the solute-solvent complex is governed by local dipolar interactions, and the benzene will be remote from the negative end of the solute molecule. This distortion causes a change in the total screening constant ( $\sigma$ ) which has a contribution from the solute-solvent interaction. The "carbonyl plane rule" has been proposed as a method for assigning the position of a hydrogen (or a group of hydrogens) relative to a plane drawn through the carbonyl carbon perpendicular to the C-O bond (71). Hydrogens which lie on the oxygen side of this plane will have a negative difference in chemical shift ( $\Delta = \delta_{\text{CDCl}_3} - \delta_{\text{C}_6\text{D}_6}$ ), while those on the other side the plane will be shifted positively. Hydrogens in the reference plane will be relatively unaffected. In the case of **26** a much larger difference in chemical shifts was observed for the single hydrogen (+0.55 ppm) than for the methyl group (+0.19 pm). This suggests that the methyl group is nearer the reference plane,

therefore,  $\alpha$ - to the carbonyl group. Again, this is indicative of the regiochemistry of the ring-juncture; however, the stereochemistry of the ring juncture was still uncertain.

Therefore, **26** (an oil) was converted into a crystalline derivative for X-ray analysis.

The ester (**26**) was hydrolysed under basic conditions to the acid. The acid was readily converted to the crystalline ammonium salt (**27**) (reaction [2.17]) which was used for the X-ray analysis. The results clearly show that the methyl group is  $\alpha$ - to the carbonyl group, and the 5- and 6-membered rings are fused in a *cis*- juncture (Figure 2.9, Appendix 1).

Identification of the products from reaction [2.20]: the peak characteristic of the nitrile stretching frequency was not observed in the infrared spectrum of photo-NOCAS product (**28**). The  $^1\text{H}$  nmr spectrum of **28** is indicative of the symmetric structure: an  $A_2X_2$  pattern in the aromatic region confirms the 1,4- ring substitution. Two low-field peaks assigned to the methyl groups on oxygen as well as two peaks due to six equivalent hydrogens of the two pairs of methyl groups, are observed.

Ketone (**29**) was easily identified. The  $^1\text{H}$  nmr spectrum showed the methyl groups as two signals indicative of the symmetric structure. The carbonyl group was detected in the infrared spectrum (the carbonyl stretching frequency at  $1680\text{ cm}^{-1}$ ) and in the  $^{13}\text{C}$  nmr spectrum (a singlet due to the carbonyl carbon at  $210.65\text{ ppm}$ ). The nitrile stretching frequency ( $2240\text{ cm}^{-1}$ ) in the infrared spectrum and the symmetric pattern in the aromatic region of the  $^1\text{H}$  nmr spectrum confirm the *para*-cyano substitution on the aromatic ring.

For compound **30**, the presence of the hydroxyl group was indicated by a broad, exchangeable ( $\text{D}_2\text{O}$ ), low-field ( $5.72\text{ ppm}$ ), absorption due to the hydroxyl proton in the  $^1\text{H}$  nmr spectrum, and a peak due to the O-H stretching frequency observed at  $3450\text{ cm}^{-1}$  in the infrared spectrum. The presence of a chiral centre renders the geminal methyl groups heterotopic, four distinct singlets are observed in the  $^1\text{H}$  nmr spectrum. The signal due to the benzylic hydrogen geminal to a hydroxyl group occurs as a singlet at  $4.98\text{ ppm}$

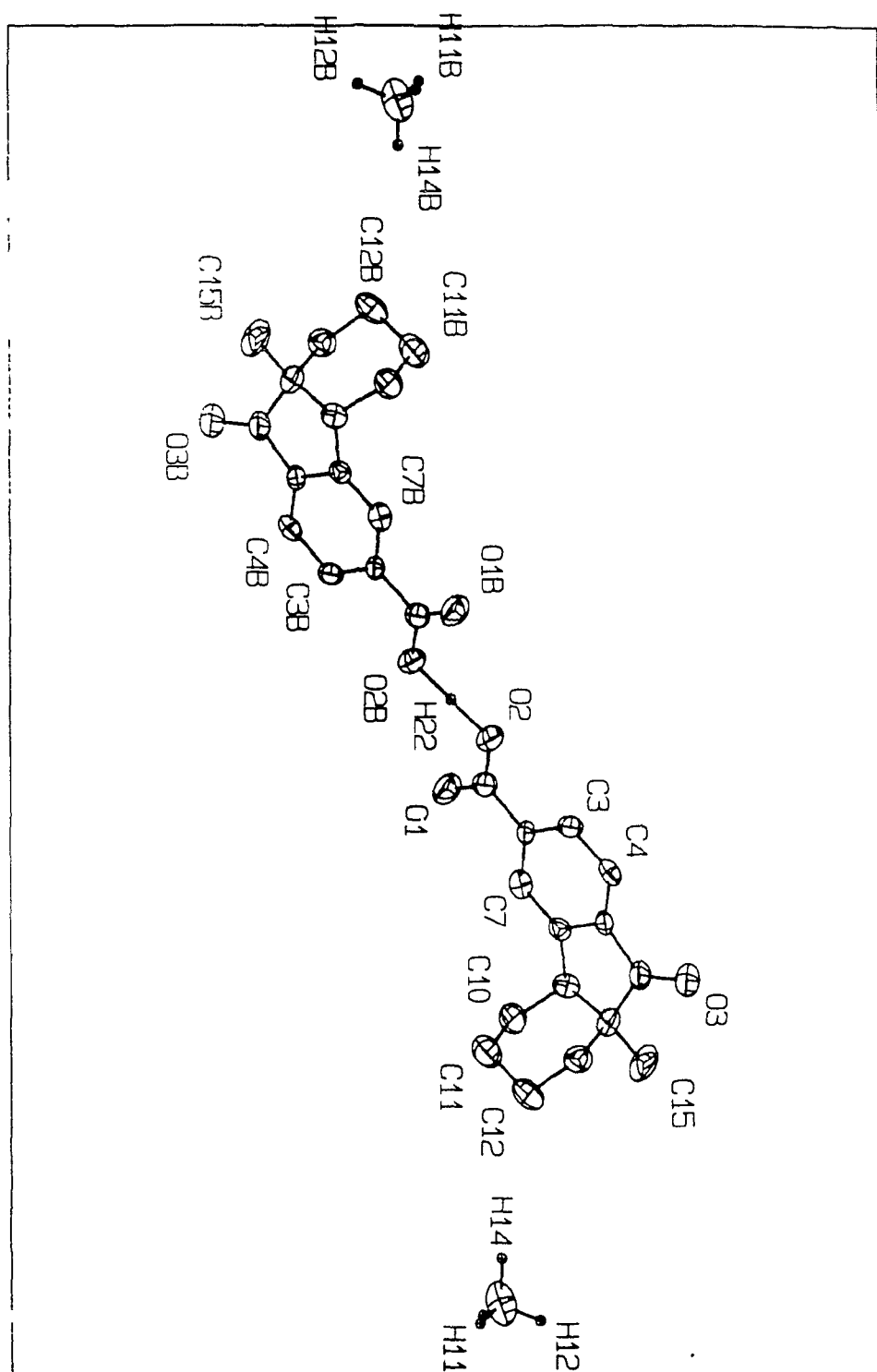


Figure 2.9 X-ray crystal structure (CHEMGRAF) of ammonium salt 27.

(compare with the signal due to the benzylic hydrogen of benzyl alcohol which occurs at 4.58 ppm). The nitrile stretching frequency ( $2260\text{ cm}^{-1}$ ) is observed in the infrared spectrum and an AA'XX' pattern in the aromatic region of the  $^1\text{H}$  nmr spectrum confirms the 1,4-disubstitution.

The four methyl groups in the spectrum of the product assigned to the amine (**31**) appear as distinct singlets in the  $^1\text{H}$  nmr spectrum, indicative of a chiral molecule. The benzylic hydrogen shows up as a singlet at low-field (4.10 ppm). The primary amine function is indicated by a broad exchangeable ( $\text{D}_2\text{O}$ ) singlet equivalent to two hydrogens at 1.46 ppm in the  $^1\text{H}$  nmr spectrum, attributed to the protons on nitrogen, and by a broad band centred at  $3400\text{ cm}^{-1}$  in the infrared spectrum due to the N-H stretching frequency. The mass spectrum gives a molecular ion with an odd mass ( $m/z = 247$ ) and a major fragment (72%) resulting from loss of one mass unit indicative of a molecular ion of an amine which loses the  $\alpha$ -hydrogen ( $\text{CH-NH}_2$ ) to give the nitrogen stabilised cation. The aromatic region of the  $^1\text{H}$  nmr spectrum is consistent with a tri-substituted aromatic ring, three distinct resonances with the expected couplings.

The structure proof of the photo-NOCAS products from methyl 4-cyanobenzoate (**22**) and 1-methylcyclohexene (**19**) (reaction [2.19]) was aided by comparison of spectra with those from the analogous cyano- compounds (**30**). The distinction between the Markovnikov and *anti*-Markovnikov adducts was made on the basis of the chemical shift due to the single proton multiplet at low-field, geminal to either the phenyl ring or the methoxy group. On this basis, adduct (**32**) (low-field dd at 3.48 ppm, hydrogen *alpha* to oxygen) and the ketone (**35**) (dd at 3.58 ppm) were assigned the *anti*-Markovnikov structure, while **33** (higher field dd at 2.86 ppm, therefore a benzylic hydrogen) and **34** (dd at 2.47 ppm) are Markovnikov adducts. Additional evidence for these assignments comes from the  $^{13}\text{C}$  nmr spectrum where the signals due to carbon adjacent to the ether oxygen also appear at lower field than benzylic carbons. Low-field doublets at 84.12 ( $J = 139.3\text{ Hz}$ ) and 81.92 ( $J = 143.1$

Hz) ppm are consistent with the assigned structures, **32** and **35** respectively. The signal due to the carbon of the methoxy group in these spectra is observed as a quartet of doublets, showing the long-range coupling ( $^3J_{C-H} = 4.3$  Hz for **32** and 4.2 Hz for **35**) to the hydrogen geminal to the methoxy group. The signals due to the carbon of the methoxy group in **33** and **34** were simply quartets, with no evidence of long-range coupling.

Having established the regiochemistry of these products (**32-35**), the stereochemistry was determined on the basis of vicinal proton-proton and proton-carbon coupling; axial-axial coupling is relatively large. The  $^1H$  nmr spectrum of isomer **32** shows a large vicinal coupling in the signal due to the proton geminal to the methoxy group ( $^3J_{H-H} = 9.6$  and 3.6 Hz) indicative of axial-axial and axial-equatorial coupling. The methoxy group is therefore in the equatorial position. The same large coupling is observed in the signal due to the proton geminal to the methoxy group in the spectrum of the ketone (**35**) ( $^3J_{H-H} = 10.1$  and 3.9 Hz); in this case also, the methoxy group is assigned to the equatorial position. For isomer (**32**) and the ketone (**35**), the relative position of the methyl and aryl groups was determined by examining the long-range coupling between the methyl carbon and the vicinal hydrogens, in the coupled  $^{13}C$  nmr spectra. One of the central lines of the quartet due to the carbon of the methyl group was expanded, and a measure of the width at half-height gave an indication of the magnitude of the coupling. This long-range hydrogen-carbon coupling can be related to the vicinal proton-proton coupling by the empirical relationship shown in equation [2.1] (72).

$$^3J_{C-H} = 1.2 \times ^3J_{H-H} - 3.5 \text{ Hz} \quad \text{equation [2.1]}$$

The central lines of the quartet due to the methyl group in the  $^{13}C$  nmr spectrum of isomer (**32**) are broad (13.5 Hz). Similar broad lines (14.4 Hz) are observed in the spectrum of the ketone (**35**). The methyl groups in **32** and **35** are therefore in the axial position.

Signals in the  $^1\text{H}$  nmr spectrum due to the benzylic hydrogens of isomers (**33**) and (**34**) are broad; large coupling constants (**33**, 11.7 and 4.0 Hz; **34**, 12.8 and 3.3 Hz) indicate that these protons are in the axial position. The signal of the C-methyl group at 16.94 ppm in the coupled  $^{13}\text{C}$  nmr spectrum of isomer (**33**) appeared as a doublet of quartets with  $^3J_{\text{C-H}}$  coupling 12.9 Hz indicative of an axial methyl group. The structure of isomer (**34**), with an axial benzylic hydrogen was therefore assigned with an equatorial methyl group and an axial methoxy group.

The ethers (**36** *cis* and *trans* and **37**) are known compounds, positively identified by direct comparison (GC/MS, retention times and mass spectra) with authentic samples prepared by the reported procedure.

The structure of the photo-NOCAS product (**39**), formed in reaction [2.20], was determined in much the same manner as that for **32**. In the  $^1\text{H}$  nmr spectrum of **39**, the signal for the hydrogen adjacent to the methoxy group shows up at low-field (3.27 ppm) as an apparent triplet of doublets ( $J = 10.2$  and  $4.2$  Hz). This corresponds to two (coincidentally equivalent) large axial-axial and one smaller axial-equatorial couplings. The methoxy group is therefore in the equatorial position, adjacent to the equatorial aryl group. The substitution product (**40**) is clearly a 1:1 (olefin:aromatic) adduct. Only one signal (3.90 ppm) for a methoxy group was observed in the  $^1\text{H}$  nmr spectrum, and this is associated with the carboxyl group, hence, there was no incorporation of methanol. Two olefinic hydrogens were evident from signals in the vinyl region (5.69 and 5.92 ppm). The high-field signal is clearly coupled to two other hydrogens, one large geminal coupling (9.9 Hz) to the other vinyl hydrogen and one smaller coupling (2.0 Hz) to the benzylic proton. Hence, the aryl group is attached at the allylic position of the olefin.

The strong absorption in the infrared spectra, at  $1020\text{ cm}^{-1}$  for **41** and  $955\text{ cm}^{-1}$  for **45**, is characteristic of the C-O stretching frequency of the oxetanes formed in reactions [2.21] and [2.23] (73). The  $^1\text{H}$  nmr spectra of these oxetanes are particularly interesting.



There is clear evidence, from the multiplicity of peaks in the aromatic region, that there is a significant barrier for rotation of the 4-cyanophenyl group. In the spectrum of **41**, at  $-70^{\circ}\text{C}$ , the signals assigned to  $\text{H}_5$  and  $\text{H}_6$  are coincidentally equivalent (7.79 ppm) while  $\text{H}_2$  and  $\text{H}_3$  appear as an AB quartet (7.34 ppm,  $J = 8.2$  Hz and 7.73 ppm,  $J = 8.1$  Hz). As the temperature is increased,  $\text{H}_3$  and  $\text{H}_5$  coalesce at  $-20^{\circ}\text{C}$  and  $\text{H}_2$  and  $\text{H}_6$  coalesce at  $+10^{\circ}\text{C}$ , Figure 2.10. Analysis of this data indicates that the barrier for rotation of the 4-cyanophenyl group is  $54.4 \pm 0.9$  kJ mol $^{-1}$  ( $13.0 \pm 0.2$  kcal mol $^{-1}$ ) (74). The results for **45** are similar: at  $-70^{\circ}\text{C}$ , the signals due to  $\text{H}_5$  and  $\text{H}_6$  overlap at 7.71 ppm and  $\text{H}_2$  and  $\text{H}_3$  appear as an AB quartet (6.97 ppm,  $J = 8.3$  Hz and 7.60 ppm,  $J = 8.3$  Hz). The signals due to  $\text{H}_3$  and  $\text{H}_5$  coalesce at  $-20^{\circ}\text{C}$  while the signals due to  $\text{H}_2$  and  $\text{H}_6$  coalesce at  $+10^{\circ}\text{C}$ . The barrier to rotation of the 4-cyanophenyl group in **45** is  $53.18 \pm 0.97$  kJ mol $^{-1}$  ( $12.7 \pm 0.2$  kcal mol $^{-1}$ ), Figure 2.11.

The products from reactions [2.24] - [2.27] were easily established by analysis of  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra. The imines (**46**) and (**47**) were hydrolysed to the ketones (**48**) and (**49**) which were fully characterised. The structure of the product which results from addition of the *tert*-butyl Grignard reagent to the ring of (**1**), (**50**), reaction [2.26]) was evident from the  $^1\text{H}$  nmr spectrum; signals due to the vinyl hydrogens on C-2 and C-5 (3.03 ppm and 2.95 ppm) are not coupled to each other.

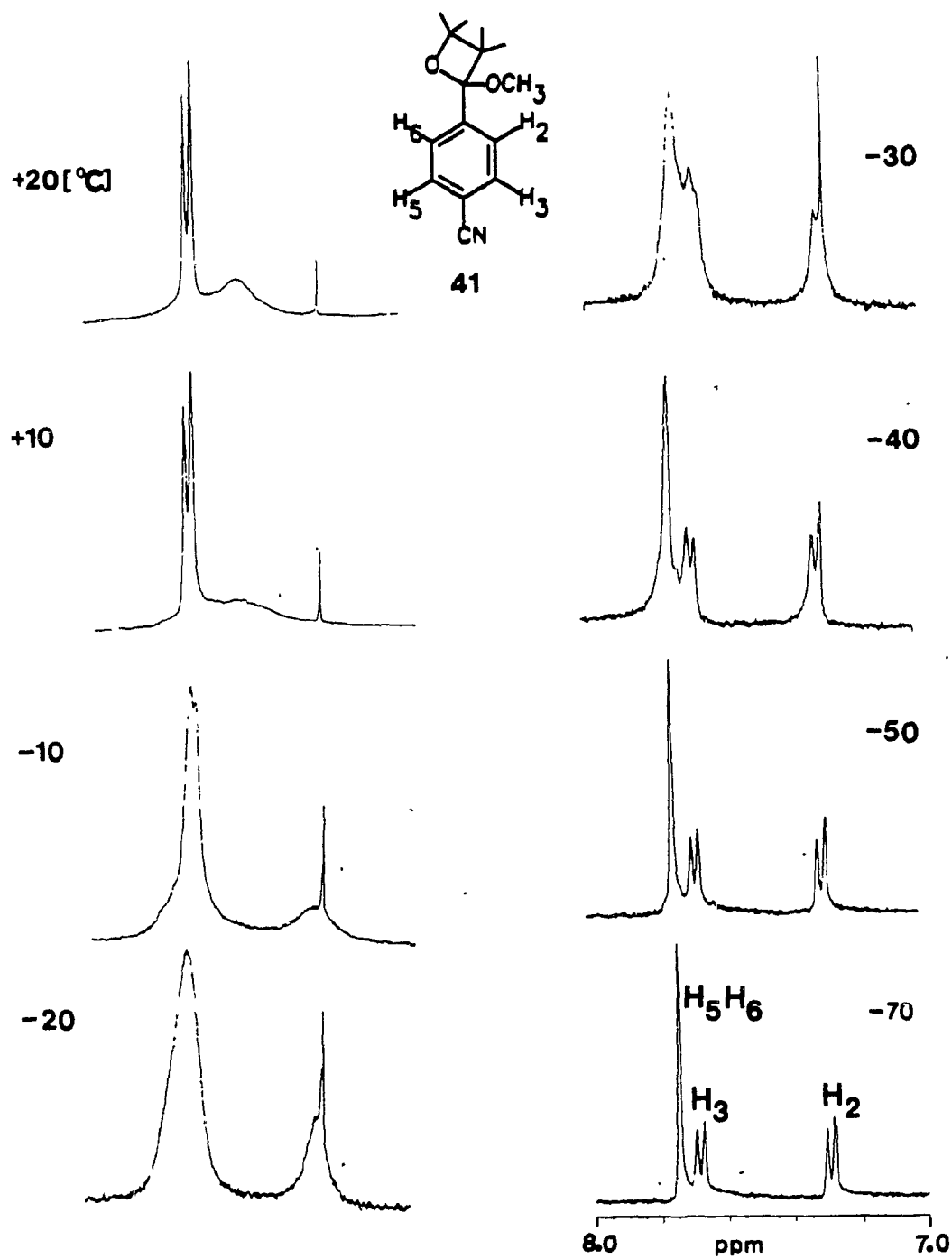


Figure 2.10 Variable temperature <sup>1</sup>H nmr (360 MHz) study of oxetane 41 in CDCl<sub>3</sub>

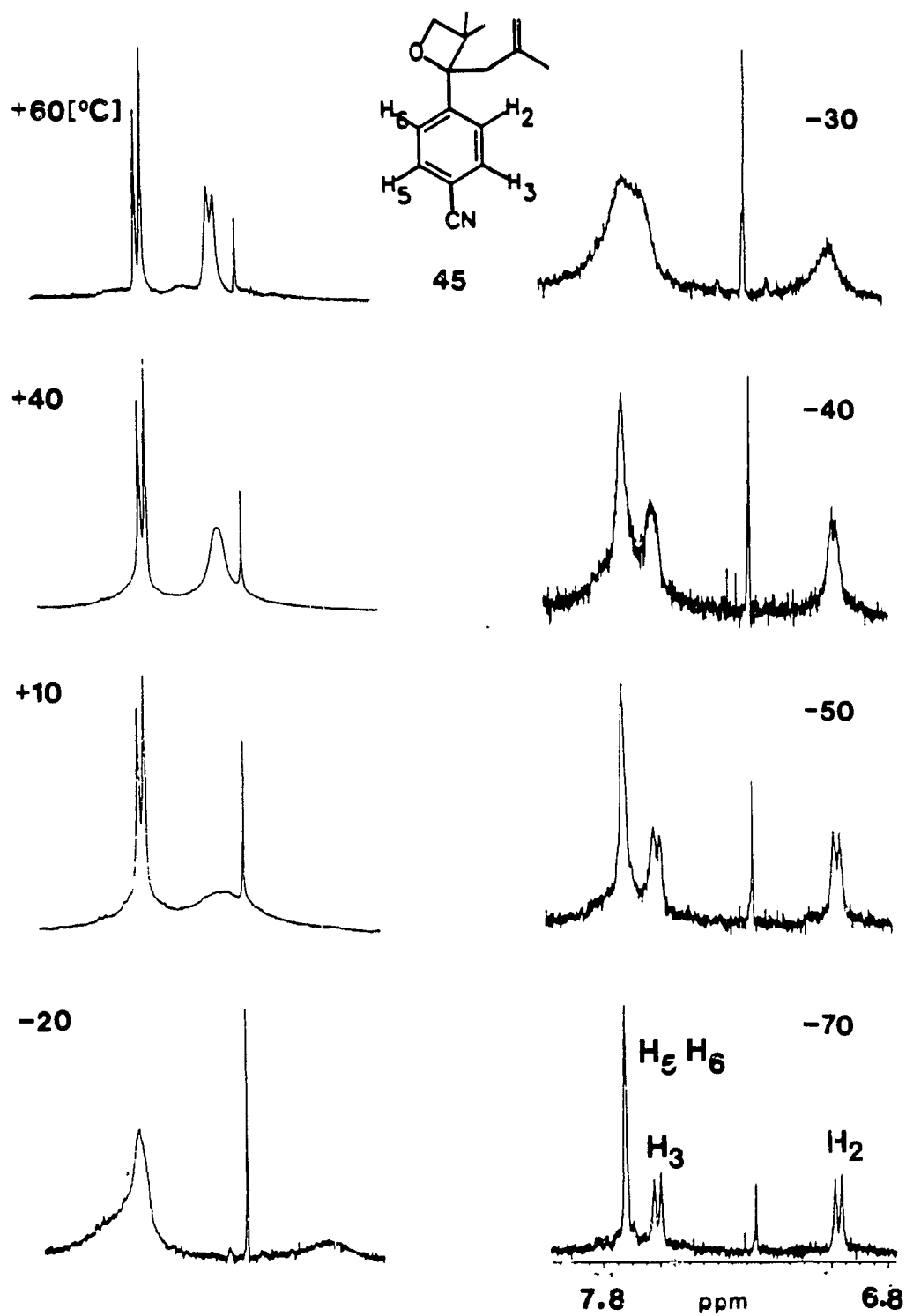


Figure 2.11 Variable temperature <sup>1</sup>H nmr (360 MHz) study of oxetane 45 in CDCl<sub>3</sub>

## 2.3 Discussion of the observed photochemistry of methyl 4-cyanobenzoate (22).

### 2.3.1 General considerations.

Calculations using the Rehm-Weller equation predict PET to occur between the acceptor **22** with olefins 2,3-dimethyl-2-butene (**2**), 1-methylcyclohexene (**19**), and cyclohexene (**38**) at the diffusion controlled rate, Table 2.7.

**Table 2.7** The calculated free energy change for the electron transfer process with the singlet excited state of methyl 4-cyanobenzoate (**22**) as acceptor

Donor	$E_{1/2}^{\text{ox}}$ (V)	$\Delta G_{\text{ET}}$ kcal mol <sup>-1</sup> (kJ mol <sup>-1</sup> )
<b>2</b>	1.62 <sup>a</sup>	-18.6 (-78.0) <sup>b</sup>
<b>19</b>	1.93 <sup>a</sup>	-11.5 (-48.1)
<b>38</b>	2.31 <sup>a</sup>	-2.7 (-11.4)

<sup>a</sup> $E_{1/2}^{\text{ox}}$  values taken from reference (30).

<sup>b</sup> $E_{\text{o,o}}$  (**22**) 95.3 kcal mol<sup>-1</sup> (50).

Irradiation of methyl 4-cyanobenzoate (**22**) with olefins **2**, **19**, and **38** in the presence of biphenyl (**12**) gave photo-NOCAS products in all three cases. Three types of 1:1:1 (nucleophile : olefin : aromatic) adducts are isolated in reaction [2.18] with olefin **2**. However, only one of these was a photo-NOCAS product, *i.e.*, where substitution has occurred with displacement of the cyanide ion. The other two products result from reaction at the carbonyl carbon of the ester group, with apparent displacement of the methoxide ion.

The two products **29** and **30** however, are still believed to be formed via an electron transfer process, since in both cases the methoxy group is found incorporated into the structure, *i.e.*, methanol has added to  $2^{+\bullet}$ . The alcohol **30** was initially thought to form by a hydrogen atom abstraction process involving the excited  $n,\pi^*$  triplet state of ketone **29**. However, irradiation of this ketone in acetonitrile-methanol appears to give a Norrish type 2 cyclobutenol product which was not characterised. An alternative pathway involves the formation of  $29-\bullet$ , by a second PET step. The reduction potential of the intermediate ketone should be less negative than that of the ester (compare that of 4-cyano acetophenone  $E_{1/2}^{\text{red}} = -0.65 \text{ V}$  (75). Reduction of the ketone by  $22-\bullet$  leads to the ketone radical anion  $29-\bullet$  which can now readily undergo protonation. This is followed by hydrogen atom abstraction to give the alcohol (**30**).

Irradiation of **22** with 1-methylcyclohexene (**19**) in the presence of biphenyl (**12**), gives a product distribution of photo-NOCAS products similar to that observed when 1,4-dicyanobenzene (**1**) is employed as the electron acceptor with **19** (**30**). Three of the four possible structural isomers were isolated: *trans anti*-Markovnikov (**32**) and the *cis*- and *trans*-Markovnikov products (**34**, **33**). The *cis anti*-Markovnikov was not isolated in this reaction, although it was found as a minor product in the irradiation mixture with **1**. The *trans anti*-Markovnikov product (**32**) is formed as the major product. Formation of products with the aryl group in the equatorial positions is favoured.

Irradiation of **22** with cyclohexene (**38**) gives only one of the two possible photo-NOCAS products (retaining the ester group) (**39**). The reaction also gives a 1:1 (olefin : aromatic) adduct (**40**). Due to the enhanced acidic nature of the olefin radical cation, there is now a competition between deprotonation of  $38^{+\bullet}$  vs. methanol addition to  $38^{+\bullet}$ . This type of 1:1 adduct formation is observed with **1** and **38** in acetonitrile (**43**).

### 2.3.2 Formation of Photo-NOCAS adducts with methyl 4-cyanobenzoate (**22**):

#### mechanistic considerations

The irradiation mixtures of 2,3-dimethyl-2-butene (**2**) and 1-methylcyclohexene (**19**), with **22**, contain two ketone products **29** and **35**. These are formed by the addition of the  $\beta$ -alkoxy alkyl fragment to the carbonyl of the ester. Ketone **35** is formed with the same stereo- and regioselectivity generally observed for the formation of photo-NOCAS products. Addition favours the formation of the *trans anti*-Markovnikov 1:1:1 adduct. This suggests that the ketones are formed by a similar process, although addition also occurs at the carbonyl. The observation of ketone formation raises many questions concerning the mechanistic scheme previously proposed.

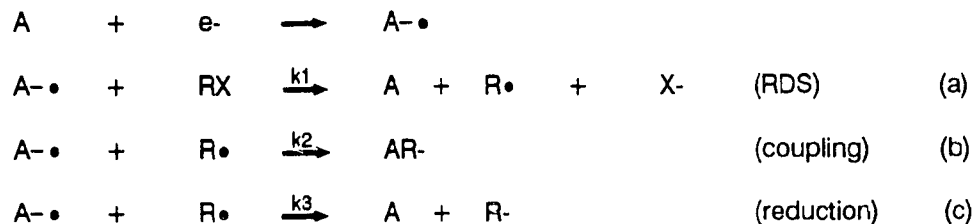
Is our original proposed mechanism, Scheme 2.2, still valid in describing the outcome of the photo-NOCAS reaction? In light of these findings, it becomes apparent that while the general scheme can account for the observed chemistry, some extension is necessary to explain the formation of ketones. At the simplest level, one could envisage ketone formation by anionic attack of the  $\beta$ -alkoxy alkyl anion at the carbonyl carbon with displacement of the ester methoxide ion. In the photo-NOCAS reactions using 1,4-dicyanobenzene (**1**) with either olefin **2** or **19**, no addition at the nitrile has been observed. If the attack does occur by an anionic pathway, how readily would the alkyl anion form under the photo-NOCAS conditions, and why is attack observed at the carbonyl of **22** with olefins **2** and **19** and not with cyclohexene (**38**)? Can the previously proposed mechanism also explain why no attack was observed at the nitrile carbon of **22** and **1**?

A key step in our proposed reaction mechanism involves the attack of an alkyl radical at the *ipso*-position of the radical anion of the electron acceptor, Scheme 2.2 (step 4). This addition is conceptually similar to the attack of an alkyl anion on the neutral acceptor. However, anionic attack is known to occur at the nitrile carbon of **1**, and at the more reactive carbonyl in the case of the ester. The relative reactivity of the ester carbonyl

and nitrile can be estimated by comparison of the relative ease of reduction of the two functional groups using lithium aluminium hydride. Under similar conditions, esters are reduced much faster than the corresponding nitriles (76).

The only difference in the two modes of addition (anion/neutral, radical/radical anion) is the position of an electron. In the above examples (reactions [2.20] and [2.21]) there appears to be a competition between these two pathways. This work reiterates a dichotomy in reaction mechanisms observed in other systems, e.g., the Grignard reaction (77), and the reactions between electrochemically generated radical anions and alkyl halides (78). There is no well defined distinction between a 'polar' (anionic) pathway and a 'radical' (single electron transfer, SET) pathway. In many incidences they occur in competition, and can be considered as two extremes of a mechanistic spectrum.

This competition can be demonstrated in the reaction between electrochemically generated radical anions and alkyl halides (RX). The reaction in many cases can result in coupling or reduction of RX. Lund has attempted to correlate this divergent behaviour with the redox potentials of the system (78b). The reactions involved in this system are shown in Scheme 2.3



Scheme 2.3

Lund has defined a competition parameter  $q = k_3/k_2 + k_3$ . When  $q = 0$ , only coupling is observed, and when  $q = 1$ , reduction is the only process involved. The degree

of partitioning between the two processes can be estimated by preparative reduction and isolation of the products. The reactions between benzyl chlorides and a series of radical anions of aromatic acceptors are found to depend on the reduction potential of the acceptor and a formal potential  $E_{1/2}^q$  (i.e. the potential of an electron acceptor where  $q = 0.5$ ). When  $E_{1/2(A)}^{\text{red}} \ll E_{1/2}^q$  reduction of  $R^\bullet$  is observed, and when  $E_{1/2}^{\text{red}}(A) \gg E_{1/2}^q$  only coupling is found. The degree of partitioning between the polar and SET pathways is highly dependent on the reduction potential of the aromatic acceptor. In contrast to our work, the reaction described by Lund follows two competing pathways that result in different products, so it becomes relatively easy to estimate the extent of each process.

In the photo-NOCAS reaction using **22**, we see a strong parallel between our divergent mechanisms and the quandary faced by chemists studying the Grignard reaction. This is perhaps the archetypical example of a reaction where there can be a competition between two mechanistic pathways depending on the position of one electron. The mechanism of this reaction has received considerable attention over the last twenty years, and will be briefly discussed below. In many respects the reactions of Grignard reagents is closely related to that of alkyl lithium reagents.

The key mechanistic work on the Grignard reaction has been summarised in two comprehensive reviews (79,80). The 'radical' nature of this reaction was proposed as long ago as 1929. Grignard reagents were found not only to add to benzophenone at the carbonyl, but were also able to reduce the ketone to the alcohol (81). Much of the ensuing key work on this reaction has been centred largely around the study of substituted benzophenones.

Convincing evidence has been given by Holm, that the rate determining step of the reaction of *tert*-BuMgCl with benzophenone follows an initial electron transfer step from the Grignard reagent to the aromatic acceptor, described as an SET process (82). Four



different reactions are observed in this case leading to 1,2-, 1,4- and 1,6- addition, as well as pinacol formation. A linear Hammett plot of the  $\log k$  ( $k$  is the pseudo first order rate constant for the sum of the four reactions above) versus  $\sigma$  is obtained, with a reaction constant  $\rho = + 3.0$ . The overall rate is also found to be independent of steric factors. Holm suggested that the reactions proceeded initially via a common SET step, implying that the electron transfer constitutes the major, 'if not the only reaction mechanism'. Holm went on to speculate that an SET mechanism may also be important for reactions of secondary, primary, and aromatic Grignard reagents.

To further examine the radical nature of this reaction, Ashby incorporated radical probes into the Grignard reagents (83). The 'free' radical nature of the reaction would be demonstrated by the observation of cyclisation and isomerisation of the alkyl group in the final products. The primary Grignard reagent, 5-hexenylmagnesium bromide, gives 52% 1,2-addition with no cyclisation and no 1,6-addition. The reaction appears to proceed via a polar pathway, or at least, if it does involve a SET pathway, no 'free' radical nature is observed. In the tertiary case, 1,1-dimethyl-5-hexenylmagnesium chloride, while both 1,2- and 1,6- addition are found (38% and 62% respectively) only cyclisation is observed during 1,6-addition (74%). The absence of cyclisation accompanying the 1,2-addition can be explained by two factors: (a) the alkyl radical  $R^\cdot$  is not 'free' in nature, but is still bound to the magnesium ion, or (b), the addition occurs in an ionic manner,  $R^-$ . Collapse of the radical ion pair then leads to 1,6-addition or escape from the cage gives pinacols. Attempts to trap the radical anion of benzophenone during the reaction, using *para*-dinitrobenzene, have proved unsuccessful, although the out of cage pinacol formation is eliminated under these conditions (84). In the tertiary case, the radical ion complex is considered to be unstable due to the formation of the more stable tertiary radical making the escape pathway more competitive. This escape leads to radical cyclisation and 1,6-addition.

Grignard reactions of primary, secondary and tertiary reagents adding to the

sterically hindered dimesityl ketone, where there is no possibility of 1,2-addition, have also been examined (85). In the case of the tertiary reagent, a strong ESR signal (radical concentration 80%) is observed. A strong band at 640 nm, assigned to the ketyl, was compared to that for the ketyl formed under different conditions. While there was no true 'free' ketyl or radical formed during the Grignard reaction, the 'radical' nature was clearly demonstrated.

The idea of the oxidation/reduction potentials of the reagents playing an important role in the reaction was investigated by Holm (80) and Lund (86). Lund studied the electrochemical butylation of substituted benzophenones by adding *tert*-butyl bromide to the substrate during the cyclic-voltammetric experiment. Electron transfer from the substrate radical ion or the dianion to the halide followed by rapid C-Br bond cleavage produces *tert*-butyl radical. Coupling then occurs between the radical and the neutral substrate or its radical anion. Electrochemical *tert*-butylation of benzophenone gives 60% 1,2-addition (addition at the carbonyl) and 8% 1,6-addition (addition at the *para*-ring position). 4-Cyanobenzophenone on the other hand gives 33% 1,2- and 50% 1,6- addition with displacement of the cyano group. 4,4'-Dimethoxybenzophenone gives exclusively 1,2-addition. As the reduction potential of the benzophenone becomes less negative, the radical nature of the addition dominates. The study gives a good indication as to the role of ring substituents on the direction of addition. Addition is favoured at the *para*-position where the spin density is concentrated in the radical anion. An electron-withdrawing group at the *para*-ring position favours attack at the ring, while 1,2-addition occurs with electron-donating groups. Not only does the reduction potential play a significant role, but the stabilisation of the resulting radical ion by substituents also appears to be important.

Holm recognised a correlation between the anodic oxidation potential for several Grignard reagents and the rates of reaction with benzophenone (80). He attempted to distinguish between a two-step mechanism (SET followed by radical recombination) and a

polar one-step anionic attack on the neutral ketone (polar mechanism). In the polar concerted case, the rates of the reaction should follow the trend *tert* < *sec* < *prim*, based on steric arguments. However, a two-step SET mechanism should show a reverse trend in the reaction rates due to the radical stability. A good correlation is found between the oxidation potential of the Grignard reagent and the log *k* (*k* is the pseudo first-order rate constant). As the oxidation potential becomes more negative the reaction rate increases, favouring the ET process.

Other rate studies of Grignard reactions offer further evidence of the span of the polar and SET reactions as a function of the ketone type (79). When the ketone substrate becomes difficult to reduce, a polar mechanism is evoked, *i.e.*, the reaction should occur by anionic attack, and the trend should follow: *prim*(1114) > *sec*(272) > *tert*(9), (the relative rates in parentheses). However, when benzophenone is used the trend in rate is reversed: *prim*(30) < *sec*(4027) < *tert*(5363). The factors found to be important as to which mechanistic path is followed during the Grignard reaction are also believed to be important in the photo-NOCAS reaction: (a) the oxidation of the 'carbanionic' Grignard reagent (reduction of the  $\beta$ -alkoxy alkyl radical), (b) the reduction potential of the substrate (aromatic acceptor), and furthermore (c), the solvent in which the reaction is carried out.

In this study, the reactions of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**) with primary and tertiary alkyl reagents in THF were examined, reactions [2.24]-[2.27]. The results of these reactions are shown in Table 2.3. 1,4-Dicyanobenzene (**1**) reacts with CH<sub>3</sub>MgBr and CH<sub>3</sub>Li to give only products resulting from attack at the nitrile group, forming imine **47**. This imine is readily hydrolysed to the 4-cyanoacetophenone (**49**). No substitution of the cyano group is observed. The *tert*-butyl analogues, on the other hand, are found to attack predominantly at the *ipso*-carbon of the aromatic ring, C-1, with displacement of cyanide ion, to give 4-*tert*-butylbenzonitrile (**51**) (42%). Significant attack is

found to occur at the C-2 position of the ring, to give a 1,4-diene product, (50), in 25%. To a lesser extent attack at the nitrile is observed to yield the imine (46), which is readily hydrolysed to the corresponding ketone (48).

The oxidation potentials of the Grignard and lithium reagents have been measured (87).<sup>3</sup> One must remain circumspect in using the reported oxidation potentials of such reagents. There are difficulties in making these measurements, and the situation is compounded by the complexity of the structures of these reagents in solution, since they are known to form aggregates such as dimers and tetramers (88). The values are usually reported in ethereal solution and are not easily standardised. They are of limited thermodynamic significance since they are non-reversible. However, the results do provide a reasonably good relative scale of oxidation potential even though the absolute numbers have little meaning, and should only be used in a qualitative sense.

The negative reduction potential of **1** ( $E_{1/2}^{\text{red}} = -1.66 \text{ V vs SCE (30)}$ ) ensures that the methyl reagents ( $\text{CH}_3\text{MgBr}$ ,  $E_{1/2}^{\text{ox}} = -0.25 \text{ V}$ ;  $\text{CH}_3\text{Li}$ ,  $E_{1/2}^{\text{ox}} = -0.5 \text{ V}$ ) exhibit 'anionic' character. A SET process would not be expected to occur, and hence addition is only observed at the nitrile, via a polar pathway to form imine **46**. The oxidation potential of the *tert*-butyl analogues are found to be significantly more negative (*tert*-BuMgBr,  $E_{1/2}^{\text{ox}} = -1.07 \text{ V}$ ; *tert*-BuLi,  $E_{1/2}^{\text{ox}} = -2.30$ ). This increase in the potential facilitates the radical nature of the reagents, and allow the reaction with **1** to proceed with electron transfer from the reagent to the electron accepting aromatic system to form the alkyl radical and **1-•**. The reaction is considered to proceed by two competitive pathways, polar and SET processes. *Ab initio* calculations for **1-•**, at the STO-3G level, Figure 2.8, show the spin density to be concentrated primarily at the ring C-1 positions, with a significant amount of spin at the C-2 positions. It can be argued that the majority of the products, **50** and **51** (total 67%), is

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<sup>3</sup>Oxidation potentials are usually quoted for the alkyl Grignard and lithium reagents. This refers to the process  $\text{RMgX}/\text{RMgX}^{+\bullet}$  or  $\text{R}^\bullet/\text{R}^+$

formed through the SET process. The remaining 23% of product can be assumed to form through the polar mechanism, where the alkyl anion attacks the electrophilic centre of the nitrile to give ultimately ketone **48**.

The 1,4-diene **50** bears a remarkable resemblance to the types of products obtained through the Birch reduction of aromatics (89). This reaction normally proceeds with formation of the non-conjugated 1,4-diene product, by a process involving electron transfer to the intermediate radical ion aromatic (90). Reaction generally stops at the diene stage, due to the more negative reduction potential of the diene. We can envisage formation of **50** by a similar SET process. Addition of the *tert*-butyl radical at the C-2 position of **1-**, a centre of relatively high spin density, gives the anionic intermediate with a large degree of the negative charge localised at the C-5 position. This anion can be stabilised by the presence of the metal counter ion. Protonation during work-up gives product **50**.

The chemistry observed when methyl 4-cyanobenzoate (**22**) reacts with the alkyl reagents is rather more complex, and it becomes increasingly more difficult to discern the two mechanistic pathways, Table 2.3. Further difficulties arise in attempting to relate the chemistry of the *tert*-butyl reagents to the spin and charge densities of the acceptor. Reactions with methyl reagents again show exclusive attack at the carbonyl in an anionic fashion to give alcohol **54** using methyl Grignard, and a mixture of this alcohol and 4-cyanoacetophenone (**49**) with methyl lithium. The more negative reduction potential of the ester ( $E_{1/2}^{\text{red}} = -1.76 \text{ V, SCE}$ ) (30) ensures that the reagents function in an ionic manner, undergoing nucleophilic addition to the more reactive ester carbonyl. However, the *tert*-butyl analogues undergo substitution at the carbonyl and displacement of the nitrile (**48** and **52** respectively). A considerable amount of disubstituted product (**53**) is also observed. Two competing pathways are again assumed, although the anionic pathway now dominates due to the more negative reduction potential of the ester (**22**). However, it becomes much harder to distinguish between the paths responsible for ketone formation.

*Ab initio* calculations for **22**-• show the spin density of the radical anion to be concentrated at the carbonyl carbon and at the C-2 and C-4 ring positions. The highest concentration is observed at the C-1. Pulse radiolysis studies of alkyl benzoates suggest the spin and charge density distribution to be similar in many respects to that observed for the substituted benzylic radicals,  $R_2\dot{C}Ph$  (91). We therefore cannot rule out the formation of ketones **48** and **53** by a radical-radical anion coupling process. Complexation by the metal ion at the carbonyl oxygen can further increase the spin density at the carbonyl carbon centre. A parallel complexation can be envisioned in the photo-NOCAS reaction between **22**-• and the methanol solvent to increase the spin at the ester carbonyl. While the detailed nature of the mechanism for product formation from the ester is still unknown, the evidence points to a competition between the polar and SET processes. The exact boundary between polar and SET mechanism remains ill-defined, and as a result, it is not easy to distinguish between the two in the case of the *tert*-butyl reagents.

In light of the above observations, and the growing number of examples of this competition between polar and SET pathways, the mechanism proposed for the photo-NOCAS reaction must be extended to account for the possibility of reduction of the  $\beta$ -alkoxy alkyl radical during the reaction, when stronger reductants (e.g., **22**-•) are generated. It is important to consider how readily the ester **22**-• can reduce alkyl radicals during the photo-NOCAS reaction. Saveant has recently measured alkyl radical reduction potentials using cyclic voltammetry of butyl iodides at an inert glassy carbon electrode. Potentials were found to follow the order: *tert*-butyl, -1.60; *sec*-butyl, -1.5; *n*-butyl, -1.4 V vs. SCE) (92). It becomes apparent that **22**-•, being a stronger reducing agent than **1**-•, is potentially able to reduce the *tert*-butyl radical to the anion, which can then lead to anionic attack on the neutral acceptor. Even in the presence of strong reductants the SET process is still observed due in large part to the activation energy for the reduction step. For example, a similar competition between radical addition to radical anion and reduction of the attacking

radical by the radical anion is observed in the alkylation of naphthalene in the presence of sodium (93). It was originally proposed, that the reaction proceed by an  $S_N2$  displacement on the alkyl halide by the electrochemically generated radical anion of naphthalene. Not only did the reaction give several alkylated products (61%), it also gave a substantial amount of reduction products (22%), where the alkyl radical was reduced by radical anion, which was then protonated by the solvent. Naphthalene has a high reduction potential (-2.53 V vs. SCE) (94), and the radical ion would be very capable of reducing alkyl radicals. On going from the planar radical to the pyramidal anion the intrinsic barrier due to the solvent reorganisational energy ( $\lambda$ ) has been estimated to be 13.4 kcal mol<sup>-1</sup> (56.0 kJ mol<sup>-1</sup>) (93b). This may help limit the extent of reduction during the photo-NOCAS reaction.

There is some additional evidence for the reduction of the  $\beta$ -alkoxy alkyl radical, a key intermediate in the photo-NOCAS reaction. Ethers **36** (*cis* and *trans*) and **37**, are formed during the photo-NOCAS reaction of **22** and 1-methylcyclohexene (**19**). These ethers have been observed in the photo-NOCAS reaction using **1** (30), but have been assumed to form by a hydrogen atom abstraction process following methanol addition to the olefin radical cation. When the photo-NOCAS reaction of **22**, **19**, and biphenyl (**12**) is carried out in acetonitrile-methanol-*d* (3:1), deuterium is incorporated into all three ethers: *trans* **36** (18%), *cis* **36** (25%), and **37** (7%), as observed by SIM, see experimental section, Table 5.1. This suggests that protonation of the anion is a major pathway to ether formation, since no incorporation should be observed if the methanol addition occurs exclusively by a radical process.

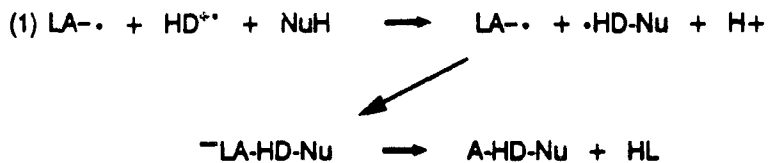
From the work carried out on the alkyl reagents, and the observation of deuterium incorporation into the ethers, there does appear to be competition between the two pathways: radical adding to the radical ion of **22** and anion adding to the neutral molecule. This apparent lack of chemistry observed for **1** during the photo-NOCAS reaction may be a reflection of the lower reducing power of **1**-•. *Ab initio* calculations for the ester radical

anion point to a high degree of spin density at the carbonyl; coupling of the radical anion and  $\beta$ -alkoxy alkyl radical is also probable, facilitated by the protic solvent. In order to account for these new pathways, not previously considered, the mechanistic scheme has been extended (Scheme 2.4).

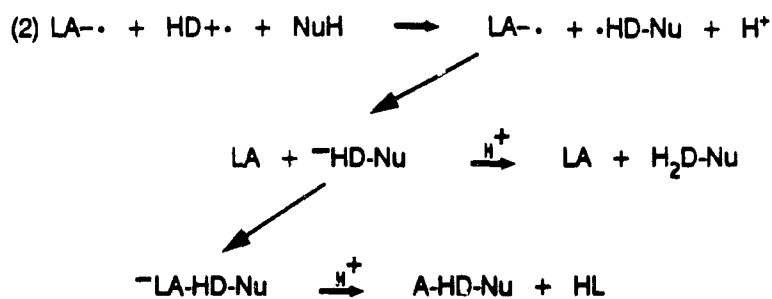


**Mechanism**

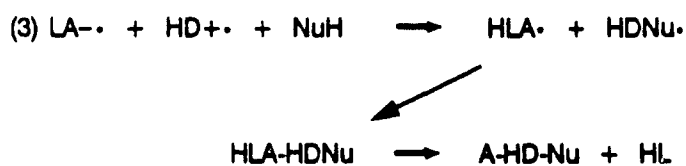
Options:



This is the mechanism originally proposed for the photo-NOCAS reaction involving methanol, 1,4-dicyanobenzene and 2,3-dimethyl-2-butene.



The radical anion of the electron acceptor may be able to reduce the intermediate radical.



The radical anion may be protonated at an early stage in the reaction.

**Key**    LA    = electron acceptor with leaving group (aromatic nitrile)  
           NuH   = protic nucleophile (methanol)  
           HD    = electron donor (olefin)

**Scheme 2.4**

### 2.3.3 Direct excitation of methyl 4-cyanobenzoate (22) and 2 or 5 in acetonitrile-methanol (3:1)

When biphenyl (12) is omitted from the photo-NOCAS irradiation mixture with methyl 4-cyanobenzoate (22) as the electron acceptor, there is a dramatic change in the observed photochemistry. When olefin 2,3-dimethyl-2-butene (2) is employed as the donor, only one product, a cyclic imine (23) is formed in high yield. Only a trace amount of this compound is observed when the reaction is carried out in the presence of 12, along with a trace of the corresponding amine (31). The amine is thought to form from the imine, by a second PET reduction process. Protonation of 23<sup>-•</sup>, followed by hydrogen atom abstraction of the resultant radical, gives the amine. To gain further insight into the mechanism for cyclisation, and also to examine the scope of this reaction as regards the olefin, 1-methylcyclohexene (19) was used. Surprisingly, only one major product, imine 25, is formed. There is however, some evidence (GC-MS) for the existence of trace amounts of three possible stereo- and regioisomers. Imine formation using olefins 2 and 19 is effectively quenched by the addition of biphenyl (12) to the irradiation mixture. The irradiation was also carried out with a second ester, 22a, and again only one cyclic imine is observed as the major product. Because of the observed stereo- and regioselectivity of the reaction, it was initially believed that the imine is formed via an exciplex/excited charge-transfer (CT) complex. In contrast, no such cyclic imine formation has been observed in the photo-NOCAS reactions involving 1,4-dicyanobenzene (1), even though it shows the existence of a ground-state CT complex with olefin 2. Attempts to selectively irradiate the 1:2 CT complex, by use of a 1,4-dicyanobenzene solution filter proved unsuccessful. Only the photo-NOCAS product is observed.

These observations prompted a study of the absorption characteristics of the acceptors 1, 22, and 22a, in the presence of olefins, 2,3-dimethyl-2-butene (2) and 1-methylcyclohexene (19).

Several methods exist to determine the extent of association between an electron acceptor and an electron donor in solution in the ground state (95); for example, nmr (96), calorimetry (97) and spectrophotometry (98). The spectrophotometric method, ultraviolet absorption spectroscopy, was used in this study. In order to determine the extent of the complexation in the ground state, the equilibrium constants for this association were measured. A Benesi-Hildebrand analysis (99) was used to determine the association constant ( $K_a$ ) and extinction coefficient ( $\epsilon_\nu$ ) for the complex from the absorption data. In this treatment only one bimolecular equilibrium association was assumed, equation [2.2].



D = donor, A = acceptor, C = complex

The absorbance of the complex,  $A_c$ , in a region where only the complex absorbs, is given by Beer's law, and is measured by uv spectroscopy.

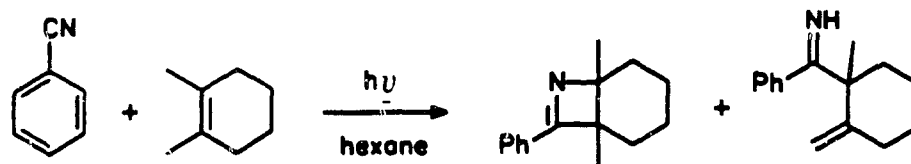
$$A_c = \log I_0/I = \epsilon_\nu [C]l \quad \text{equation [2.3]}$$

When the concentration of the olefin donor  $[D]_0$  is very much greater than the concentration of the acceptor  $[A]_0$ , and in cases where complex formation is relatively weak, equation [2.4] can be used to determine the association constant  $K_a$  and the extinction coefficient  $\epsilon_\nu$  of the complex. The approximations used above are not valid for  $K_a > 100 \text{ l mol}^{-1}$  (100). The Benesi-Hildebrand treatment allows the evaluation of the product term  $K_a \epsilon_\nu$ . From a plot of  $\epsilon[A]_0/A_c$  vs  $1/[D]_0$ ,  $K_a$  and  $\epsilon_\nu$  can be calculated from the slope and intercept.

$$\epsilon[A]_0/A_c = 1/K_a \epsilon_\nu [D]_0 + 1/\epsilon_\nu \quad \text{equation [2.4]}$$

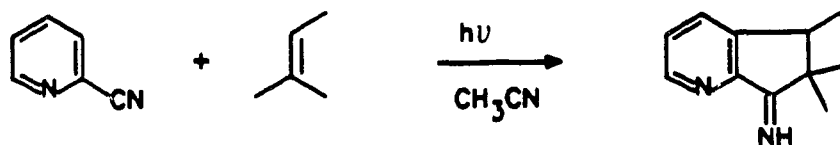
The Benesi-Hildebrand study was used to determine the extent of CT formation for **1**, **22**, and **22a** with olefin **2**, and also **22** with both **2** and **19**. In all cases, (**1:2**, **22:2**, **22:19**, and **22a:2**), the association constant is found to be significant ( $K_a \approx 0.4$ ), which implies that the excitation of the ground state CT complex is expected to compete with the excitation of the free acceptor during the photo-NOCAS irradiation. The extinction coefficients for the complexes are found to be small ( $< 100$ ), however, these were not measured for the maxima, which are hidden under the absorbance of the acceptor. There is considerable error in the determination of the association constant for **22** in the presence of olefin **19**. This is due to the low absorbance found at 310 nm. The degree of CT formation between **1** and **2** is found to be significantly smaller than that measured for the ester **22** with the same olefin. These observations have led to the suggestion that the imine product is formed by the selective excitation of the CT complex.

The chemical literature holds few examples of photochemical formation of cyclic imines similar to that found for methyl 4-cyanobenzoate (**22**). Cantrell has reported the formation of an imine during the irradiation of benzonitrile with 1,2-dimethylcyclohexene in hexane, reaction [2.28] (101). However, no cyclisation into the aromatic ring is observed. The reaction proceeds to give the azetine product along with 24% of an imine product. Cantrell explained this formation by a process involving hydrogen atom abstraction by the excited benzonitrile, followed by cross-coupling of the resulting radicals, similar in outcome to the 'ene' reaction. The irradiation, Cantrell has argued, involves only the excited singlet of the benzonitrile and proceeded with formation of the exciplex. The alternate mechanism of charge-transfer excitation was ruled out, although enhanced absorption was observed on the tail of the uv spectrum of benzonitrile with added olefins. No attempt was made to measure the magnitude of this association.



[2.28]

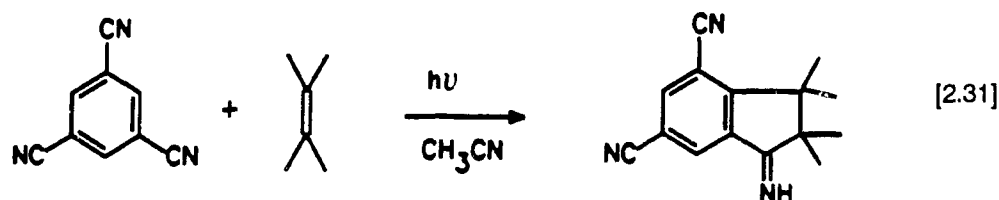
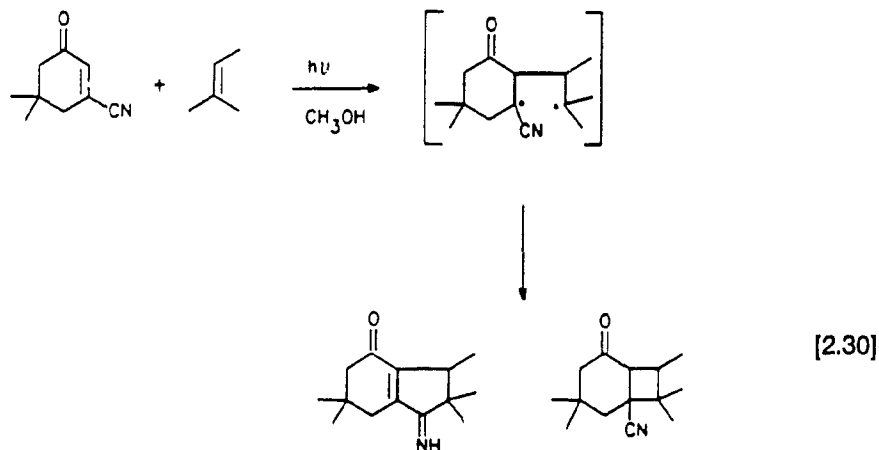
Photochemical cyclic imine formation, on the other hand, is observed in the irradiation of 2-cyanopyridine with 2-methyl-2-butene in acetonitrile, reaction [2.29] (102). This leads to the regioselective formation of an imine as the major product (16%). The addition is found to occur with the dimethyl fragment of the olefin  $\alpha$  to the imine group, as observed with ester **22**. The reaction is accompanied by the formation of a considerable amount of polymeric olefin product, which leads to the proposal of a biradical intermediate. Closure of this biradical to form the iminium species, followed by disproportionation, gives the cyclic imine. No mention of closure to cyclobutane products was made. This pathway may be disfavoured by a high activation energy. A PET process was not considered as a mechanistic possibility, although the Rehm-Weller equation predicts a favourable electron transfer step.



[2.29]

Saito has exploited the same type of cyclic imine formation in the photoannulation of  $\alpha,\beta$ -unsaturated nitriles (103). The reaction was studied using 3-cyano-5,5-dimethyl-2-cyclohexenone to gather information on the regiochemistry of the addition, reaction [2.30]. The cyclisation to form the imine, [3+2] addition, is generally found in competition with the expected cyclobutane ring formation, [2+2] cycloaddition. In cases where cyclohexene and cyclopentene are used, no such cyclic imine is found. Only when a trisubstituted olefin is employed, is this observed. Irradiation of a solution of the enone and 2-methylpropene (**44**) or 1-methylcyclohexene (**19**) leads to regioselective ring formation, where the closure occurs to give the more heavily substituted alkylated carbon of the olefin  $\alpha$  to the imine group. The reaction shows little solvent dependency, unlike that observed with our irradiations. The ratio of [3+2]:[2+2] cycloaddition products remains constant with changes in the solvent polarity, although the formation of the imine is reported to be much 'cleaner' in the presence of alcohols. In our study, when the reaction with **22** and **2** is carried out in benzene, only oxetane **41** is formed, reaction [2.21]. Irradiation of a benzene solution of the *tert*-butyl ester (**22a**) does not give an oxetane, due largely to the steric effect of the bulky *tert*-butyl group, but gives imine **23a**, reaction [2.13].

A mechanism, similar to that formulated for the 2-cyanopyridine example, was proposed to explain the enone reactivity. The triplet enone reacts with the olefin, to form a biradical intermediate. In the case where 2-methyl-2-butene is used, the reaction proceeds with formation of the more sterically hindered (more stable) radical. Ring closure could occur in either of two ways. This closure is found to be temperature dependent. As the temperature of the irradiation mixture is increased, the proportion of imine product also increases. Presumably more activation energy is provided at elevated temperatures to allow coupling to occur at the nitrile, as opposed to the coupling of two tertiary radical centres. No stereochemical information was given on the addition process.



More recently, cyclic imine formation was found to occur during the irradiation of 1,3,5-tricyanobenzene and **2** in acetonitrile, although attempts to repeat this reaction with other olefins failed, reaction [2.31] (104). The Rehm-Weller equation suggests that a diffusion-controlled PET process ( $\Delta G_{\text{ET}} = -27.7 \text{ kcal mol}^{-1}$ ,  $-116 \text{ kJ mol}^{-1}$ ) is feasible, but the mechanistic steps in the ring closure were not discussed.

Irradiation of acetonitrile-methanol solutions of **22** and **2** or **22** and **19** is predicted to proceed by a diffusion-controlled PET step on the basis of the Rehm-Weller equation, assuming this involves the singlet excited ester. In order to experimentally determine if this is the case, (*i.e.*, the excited ester is quenched at the diffusion-controlled rate by the olefin), a fluorescence study was undertaken. No fluorescence emission is observed from **22**, nor could the lifetime of the ester be measured using a single-photon counting apparatus. The lifetime ( $\tau_s$ ) of the ester is therefore thought to be much less than 2.0 ns, the lower limit of

this technique. This fact poses a major discrepancy, since the reaction was initially thought to go via a singlet excited state of the ester upon direct irradiation. Generally aromatic esters show little or no emission. This has been attributed to rapid intersystem crossing to an  $n,\pi^*$  triplet state slightly above the  $\pi,\pi^*$  triplet state (105). Only with large bulky groups on the ester is the fluorescence emission enhanced (106). If the intersystem crossing to the triplet state is efficient, then the lowest triplet of the ester is obtained, from which electron transfer becomes an endothermic process on the basis of the Rehm-Weller equation. There have been reports in the literature where the anomalous singlet behaviour has been ascribed to the formation of singlet exciplex/excited CT complex formation (107). Indeed, our evidence (uv) points to the involvement of a CT complex.

This idea of reaction from a singlet exciplex has been proposed to explain the apparent singlet behaviour of aromatic esters in the photoisomerisation of olefins (107b). Direct photoisomerisation of *cis*-cyclooctene is found to give a photostationary state of the alkene with a high *trans* : *cis* ratio (0.96). When the irradiation is triplet sensitised, a much lower ratio of *trans* : *cis* (0.05) is observed. However, in the presence of methyl benzoate, an unusually high ratio of 0.25 is found. It was suggested that this occurs through the formation of a singlet exciplex, in which the olefin is able to rotate about the C=C bond by an angle  $\pi = 90^\circ$ . Collapse of the exciplex to the nearby twisted ground state of the olefin results in the observed isomerisation. The excited singlet state of the olefin cannot be obtained directly by energy transfer from the excited ester by a vertical Frank-Condon transition, that is, energy transfer from the ester to the planar ( $\pi = 0^\circ$ ) olefin in  $S_1$  state is endothermic. The excited singlet surface ( $\pi = 0^\circ$ ) for disubstituted olefins is around 130 kcal mol<sup>-1</sup> above the ground state (107b), much higher than the singlet energy of the ester (95.4 kcal mol<sup>-1</sup>). However, a non-vertical transition can occur in which the energy is transferred to the potential surface of the twisted excited singlet olefin, which is at a lower energy. A twisted singlet complex has been proposed to account for the observed



photoisomerisation. Experimentally non-vertical transitions of this type are possible when there is a high degree of flexibility about the olefin C=C bond (108). This would be impossible for cyclobutenes but possible for cyclohexenes, which would then form a reactive twisted state. The probability of non-vertical transitions is also believed to increase when there is significant electronic interaction associated with the sensitiser and the olefin (108). The possibility that CT excitation could bring about the photoisomerisation was not considered.

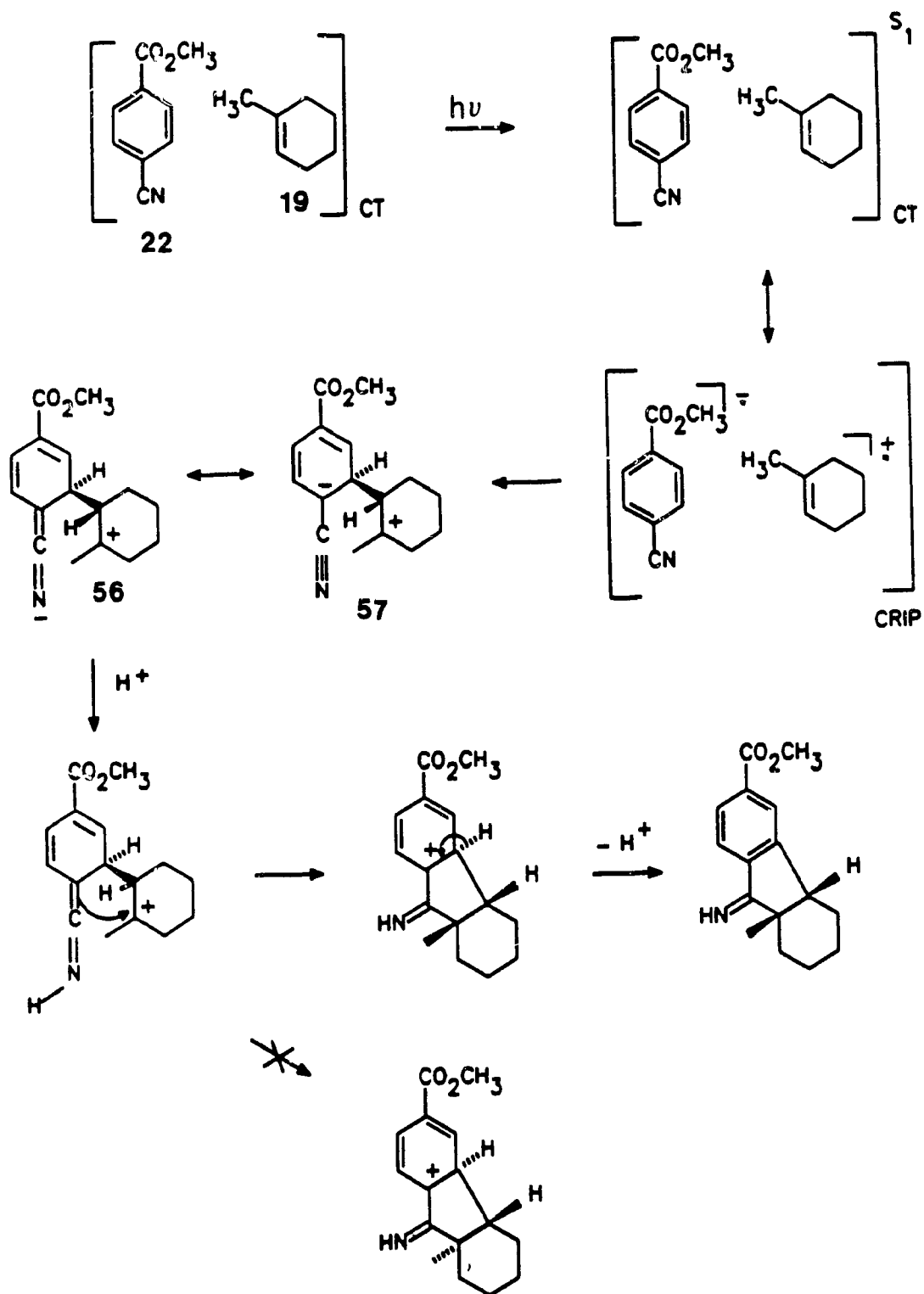
Initially it was thought that the observed addition and subsequent imine formation between **22** and 1-methylcyclohexene (**19**) was due to a rigid excited charge-transfer complex in which the olefin is held tightly on the surface of the ester in a specific conformation. Cantrell has also considered the degree of this interaction in the exciplex in describing the two possible modes of addition of olefins to benzonitriles (101). He argued that the cycloaddition occurred at the nitrile to form azetines, or at the C-1 and C-2 aromatic positions to form bicyclo[4.2.0]octadienes, depending on the orientation within the exciplex. The more electron rich olefins, which show azetine formation, according to this work, are held over the nitrile group, while the electron deficient olefins lie over the aromatic ring, to give bicyclo products. However, experimental evidence suggests this type of interaction is weak and devoid of the rigidity necessary to explain any regioselectivity (109). While the ground state CT complex obviously exhibits interaction between the aromatic  $\pi$  system and the olefin  $\pi$  bond (the components are held in close proximity, at the van der Waals contact distance (3.5 Å)), the interaction is not rigid, and there is movement between the planes. The orientation effects of ring substituents are known to play a minor role; the stability of the complex is influenced by the redox characteristics of the acceptor and donor (109c). Several years ago Hammond addressed the problem of the magnitude of this interaction in the excited state in his discussion on the attempts to enantio-differentiate chiral olefins during photochemical isomerisations (110). The observed enantiomeric excess (e.e.) is low

(7%), and it is concluded that the interaction is weak. Other workers have attempted to increase this selectivity using chiral aromatic esters, but with little success (107a). Only when the temperature is lowered does the selectivity increase significantly (40% e.e., -88°C) (111).

If this orientation is weak in the ground and excited state of the charge-transfer complex, with no apparent orientation preference, the regio- and stereoselectivity observed during imine formation must be accounted for by a different mechanism. Since no out of cage products are observed in the irradiation of methyl 4-cyanobenzoate (22) and 2 or 19, the formation of the free solvated radical-ions must be negligible. A mechanism has been proposed to account for this behaviour, Scheme 2.5. The first step in the mechanism is the selective excitation of the ground state CT complex to form the excited singlet complex. Photocycloadditions of olefins to benzene generally involve the excited singlet state and commonly reaction occurs through the exciplex or excited charge-transfer complex (112). As a general rule, the singlet complex formation favours concerted and stereoselective cycloaddition products (113).

The extent of charge separation in the excited state of the complex is expected to be high, forming an essentially pure contact radical-ion pair (CRIP) (114). In polar solvents, it is suggested that the exciplex can be considered as a CRIP. Although the degree of electron transfer is high, there is some mixing of locally excited states  $A^*D \leftrightarrow A-\bullet D+\bullet$ . The excited state of the complex can be described by the following wavefunction (115):

$$\Psi_{AD} = a^* \psi_1(D+\bullet/A-\bullet) + b^* \psi_2(DA^*) + \dots \quad \text{equation [2.5]}$$



Scheme 2.5

This describes the complex as the sum of a contribution from the 'no bond' wavefunction [ $\psi_2(DA^*)$ ] from the locally excited states and a 'dative bond' wavefunction [ $\psi_1(D^+ \bullet / A^- \bullet)$ ].

We estimate the extent of ET character within the excited complex from the measured energetics of the system, *i.e.*, from the difference between the sum of the redox potentials of the acceptor-donor pair, and the available excitation energy  $E_{0,0}$ , equation [2.6]. This relationship is very similar to the Rehm-Weller equation although the columbic attraction term has not been included. The efficiency of formation of the CRIP is found to vary as a function of the exothermicity of the ET formation process ( $\Delta G_{ET}$ ) (116).

$$\Delta G_{ET} \approx [E_{1/2}^{ox}(D) - E_{1/2}^{red}(A)] - E_{0,0}(A^*)^1 \quad \text{equation [2.6]}$$

As  $\Delta G_{ET}$  becomes more negative, the contribution from the dative bond wavefunction increases  $a^* \gg b^*$ , *i.e.* the electron transfer character increases. This dependence however is offset by the increase in the efficiency of SSRIP formation from the CRIP with increasing exothermicity. This is true for situations where the exothermicity for the electron transfer process is less than the total reorganisational energy ( $\lambda$ ) [43.8 kcal mol<sup>-1</sup> (183.3 kJ mol<sup>-1</sup>) (29)] for the process (114, 117). The efficiency of the SSRIP formation, the precursor to the free solvated ions, is found to increase in polar solvents (118). The  $\Delta G_{ET}$  is found to be more negative in the case of **1** with **2** (-21.9 kcal mol<sup>-1</sup>, -91.7 kJ mol<sup>-1</sup>), than **22** with **2** (-17.3 kcal mol<sup>-1</sup>, -72.4 kJ mol<sup>-1</sup>). The extent of free radical ion formation is estimated to be greater in the former case. Indeed, reaction with **1**, following direct excitation appears to result in formation of separated radical ions. Products of this mechanism are absent for excitation of **22**, when biphenyl (**12**) is omitted from the irradiation mixtures.

Before escape of the radical ions from the cage, addition of the oxfin radical cation occurs at the C-3 ring position *ortho* to the nitrile group in the ester radical anion. There are two ways in which this can add: addition can occur to form either a secondary or a

tertiary cation. The initial addition is believed to occur with formation of the more stable cation. This step controls the regioselectivity of the cycloaddition.

There are two possible pathways for closure of the zwitterionic intermediate (**55**): closure can occur from the same side as the initial addition to give the *syn*-addition product, or from the opposite face of the ring system to give the *anti*-addition product. These modes give the *cis*- and *trans*-ring junctions respectively. Molecular modelling (PC-Model, Version 4) demonstrates the considerable strain necessary to attack in the *anti*-manner. Closure to give the observed *cis*-junction is therefore a kinetically controlled process. The addition is also thermodynamically controlled, giving the more stable product (on the basis of molecular modelling). If it is assumed the negative charge to be delocalised through the C-C-N system, there are three nucleophilic sites for the cation to attack. Kinetically controlled ring closure favours five-membered ring formation. The linearity of the C-C-N fragment makes it almost impossible for cyclisation to occur to give the six-membered ring due to the considerable strain energy necessary to bring the cation in proximity to the nitrogen. Again molecular modelling confirms this.

Irradiation of a mixture of **22** and **2** was also carried out in acetonitrile to determine if the imine hydrogen was obtained by an intramolecular hydrogen migration from the aromatic ring. Formation of imine **23** is found to be less efficient under these conditions, leading to the suggestion that protonation of the nitrile at the radical ion stage may play an important role. When the reaction is carried out in acetonitrile-methanol-*d* (3:1), deuterium is found incorporated into the product, but rapid exchange of the imine hydrogen in solution, observed in the  $^1\text{H}$  nmr spectrum, make it impossible to pin-point the source. After the formation of the olefin-aromatic ring bond the negative charge can become delocalised over the C-C-N fragment. Two resonance structures (**56**, **57**) are drawn, Scheme 2.5. Protonation of the nitrogen gives an electron rich carbon centre at the nitrile, and ring closure can lead to the imine directly. Finally, deprotonation at the C-3 ring position

restores the aromaticity and regenerates the acid catalyst.

The key step in the overall mechanism for imine formation is the selective irradiation of the CT complex between ester (**22**) and the olefin. This allows direct formation of the CRIP, from which it is believed the imine is formed. Addition of biphenyl to the reaction mixture effectively quenches the direct formation of the CRIP. Instead, reaction proceeds with the formation of the freely solvated radical ions, and formation of the 1:1:1 adducts. Biphenyl (**12**) is known to have an effect on the reaction efficiency in photo-NOCAS reactions with **1** but does not change the overall chemistry. Differences in the observed chemistry from the geminate (CRIP) and the free radical ions have been reported in the past (119). Interception of the geminate pair has a significant advantage regarding increases in the efficiencies of these reactions.

Biphenyl (**12**) has a slightly higher singlet energy ( $E_{o,o} = 95.9 \text{ kcal mol}^{-1}$  (120)) than methyl 4-cyanobenzoate (**22**). Irradiation of a solution containing both **12** and **22** will result in the formation of the excited singlet state of the ester by energy transfer. This singlet excited state is known to be short-lived ( $< 2 \text{ ns}$ ) and will be quenched rapidly to give the ground state or the lower energy triplet state. Biphenyl however, does not absorb far beyond 280 nm. Therefore, ester **22** is expected to absorb most of the light during irradiation. To account for PET between biphenyl and ester, the formation of a second charge-transfer complex is proposed. Our absorption studies show the existence of this between **12** and **22**. The oxidation potential of biphenyl is similar to that of the olefins. The excitation mechanism therefore follows that described for imine formation: however, instead of reaction within the CRIP, solvation of the radical ions becomes more efficient, and reaction occurs from the freely solvated ions. The use of the CT complex allows us to bypass the low extinction coefficient of biphenyl at wavelengths longer than 280 nm, the lower singlet energy of the biphenyl, and the short lifetime of the ester.

A second mechanism can be postulated to account for the apparent singlet reactivity

from the short-lived ester: static quenching (121). Due to the short singlet lifetime of ester **22**, the efficiency of diffusional quenching of the excited ester by the olefin would be expected to be low. At the relatively high concentrations of olefin used in the photo-NOCAS reaction (0.2 M), it is not hard to imagine, that at the moment ester **22** is excited, it will be in proximity to some molecules of the olefins, or biphenyl. Before the ester can begin the diffusional process electron transfer can occur with the nearest neighbour. This mechanism allows the ester to react from the singlet excited state in the presence of biphenyl or olefin, without requiring a diffusional process, which will lead to rapid decay of the excited ester by ISC or energy transfer.

## 2.4 Conclusions.

While there are some similarities between the photochemistry of 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate, contrasting results have been observed under similar irradiation conditions. Biphenyl (**12**) is known to have a marked effect on the reaction efficiency for irradiations involving **1**. However, its absence in reactions of **22** has a dramatic effect on product formation. Although ester **22** has a short-lived singlet excited state ( $\tau_s < 2$  ns) (compare to **1**,  $\tau_s = 9.6$  ns), the observed chemistry in polar solvent appears to involve an electron transfer process to the excited singlet state of the ester. A mechanism involving the excitation of the ester-olefin charge transfer complex has been proposed. This leads to novel formation of cyclic imine products with no incorporation of methanol. A charge transfer complex between biphenyl and ester **22** has also been proposed to account for reactions where the co-donor (**12**) is added. Under these conditions, photo-NOCAS product formation is observed.

Irradiation of mixtures containing ester **22** and olefin **2** and **19** leads to formation of ketone 1:1:1 (methanol : olefin : aromatic) adducts, where addition at the carbonyl carbon is observed. Deuterium is also found incorporated into the ether by-products by an anionic

process. These observations have led us to extend the mechanistic scope of the photo-NOCAS reaction to cases where the aromatic radical anion is capable of reducing the intermediate  $\beta$ -alkoxy alkyl radical. A similarity has been drawn between the radical-anion/radical coupling step of the photo-NOCAS reaction and competition observed in the Grignard reaction. *Ab initio* calculations at the STO-3G level adequately explain the coupling mechanism possible at this stage of the reaction.

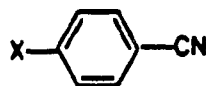


## Chapter 3

### Examination of Other Substituted Benzonitriles as Potential Electron Acceptors in the Photo-NOCAS Reaction.

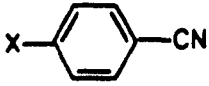
#### 3.1 Introduction

The study of the photo-NOCAS reaction was extended to include four other *para*-substituted benzonitriles (**58-61**). An indication as to the synthetic potential of the acceptors was obtained by employing 2,3-dimethyl-2-butene (**2**) as the olefin to screen the acceptors. This olefin has the advantage of having a relatively low oxidation potential [1.62 V (SCE) in  $\text{CH}_3\text{CN}$ ], thereby being relatively susceptible to photoinduced electron transfer with the chosen acceptors. The expected products from the reaction are relatively simple. The normal photo-NOCAS conditions were employed, and all reactions were examined in the presence and absence of biphenyl (**12**). On the basis of the Rehm-Weller equation, all four acceptors were predicted to undergo electron transfer with the olefin at the diffusion controlled rate,  $\Delta G_{ET} < -4 \text{ kcal mol}^{-1}$  ( $-16.7 \text{ kJ mol}^{-1}$ ). The same was true for cases where biphenyl (**12**) was employed as a co-donor, except for **59** which was slightly endothermic ( $1.9 \text{ kcal mol}^{-1}$ ,  $7.9 \text{ kJ mol}^{-1}$ ). Some of the characteristics of the acceptors are shown in Table 3.1.



<b>58</b>	<b>X = <math>\text{SO}_2\text{CH}_3</math></b>
<b>59</b>	<b>= F</b>
<b>60</b>	<b>= <math>\text{CF}_3</math></b>
<b>61</b>	<b>= <math>\text{N}(\text{CH}_3)_3</math></b>

**Table 3.1** Characteristics of potential acceptors **58-61**.



<b>X =</b>	<b>SO<sub>2</sub>CH<sub>3</sub></b>	<b>F</b>	<b>CF<sub>3</sub></b>	<b>N(CH<sub>3</sub>)<sub>3</sub>I</b>
	<b>58</b>	<b>59</b>	<b>60</b>	<b>61</b>
$E_{o,o}$ (kcal mol <sup>-1</sup> ) <sup>a</sup>	100.2	104.4	102.0	103.1
$E_{1/2}^{red}$ (V, SCE) <sup>b</sup>	-1.55	-2.48	-2.03	-1.85
$\Delta G_{ET}(2)$ (kcal mol <sup>-1</sup> ) <sup>c</sup>	-28.4	-11.1	-19.1	-24.4
	(-20.0)	(1.5)	(-8.9)	(-13.0)
$E_{1/2}^{ox}$ (V) <sup>d</sup>	2.7	1.9	2.3	2.5

<sup>a</sup>Singlet energies are taken from reference (123).

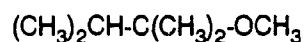
<sup>b</sup>Reduction potentials were measured by cyclic voltammetry, in acetonitrile using Pt electrode (0.1M, TEAP). Full details of the apparatus used are given in the experimental section.

<sup>c</sup>Energies were calculated using the Rehm-Weller equation. Oxidation potential of 2,3-dimethyl-2-butene (**2**) is 1.62 V (30), coulombic attraction term = 1.29 kcal mol<sup>-1</sup>. The values in parentheses were derived using the singlet energy of biphenyl, 95.9 kcal mol<sup>-1</sup> (120);  
 $E_{ox}^{ox}(\mathbf{12}) = 1.80$  V (SCE) (4d)

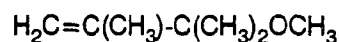
<sup>d</sup>This value represents the maximum oxidation potential of the olefin with which the excited acceptor can undergo a photoinduced electron transfer process at the diffusion controlled rate ( $\Delta G_{ET} = -4$  kcal mol<sup>-1</sup>, -16.7 kJ mol<sup>-1</sup>).

### 3.2 Results of the photo-NOCAS irradiations.

Irradiation of 4-(methylsulphonyl)benzonitrile (**58**) and 2,3-dimethyl-2-butene (**2**) in acetonitrile-methanol solution in the presence of biphenyl (**12**) gives benzonitrile as the major product. Also formed in this reaction are the two possible 1:1 (methanol : olefin) adducts, (**62**) and (**63**), in equal amounts. Two of the three possible olefin dimer products are also observed. In the irradiation in the absence of co-donor **12**, only trace amounts of all the above products are detected after a much longer irradiation period. There is no evidence for photo-NOCAS product formation or any olefin : aromatic (1:1) adducts with or without added co-donor.



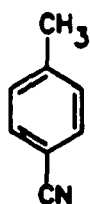
**62**



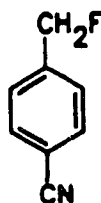
**63**

Irradiation of an acetonitrile-methanol solution of 4-fluorobenzonitrile (**59**) and olefin **2** again gives benzonitrile and a 1:1 mixture of ethers **62** and **63**. There is no evidence (GC-MS) of the formation of photo-NOCAS products under both irradiation conditions.

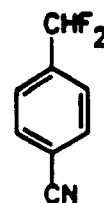
The 4-(trifluoromethyl)benzonitrile (**60**), on the other hand, gives only products resulting from the loss of fluoride ion. Without added co-donor (**12**), 4-tolunitrile (**64**) is the only product observed, while, in the presence of **12**, monofluoro- (**65**), difluoro- (**66**), and 4-tolunitrile (**64**) are all identified (known compounds). After prolonged irradiation with added biphenyl, 4-tolunitrile is the only product observed.



**64**

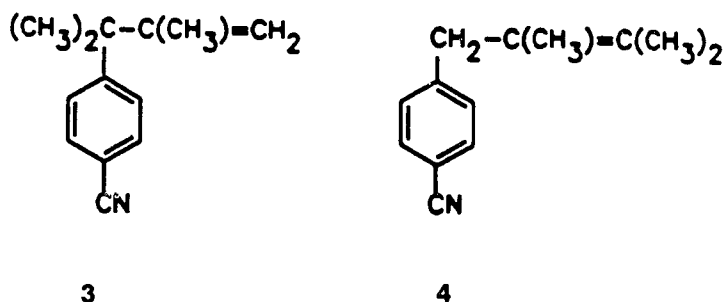


**65**



**66**

(4-Cyanophenyl)trimethylammonium iodide (**61**), on the other hand, while giving benzonitrile, also gives a small amount of a 1:1 (olefin : aromatic) product, 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (**3**). Only one of the two possible 1:1 adducts is observed. No evidence is found for the existence of 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (**67**). There also appears (GC-MS) to be a small amount of the reduced form of the adduct **3**, although this has not been isolated and the structure remains unconfirmed.



In these last three examples, the yields and efficiencies of the reactions are all low. No photo-NOCAS products or cyclic imine products are found with any of the acceptors.

### 3.3 Discussion

In general, the photochemistry of aryl sulphones, particularly that of photoinduced electron transfer, has received little attention; however, as in most areas of PET, the interest is growing (122). On the basis of our understanding of the photo-NOCAS reaction, 4-(cyanophenyl)methylsulphone (**58**) appears at the onset to be a potentially good candidate as an electron acceptor for the reaction. It has a relatively high singlet energy (100.2 kcal mol<sup>-1</sup>, 419 kJ mol<sup>-1</sup>) (123), and the Rehm-Weller equation predicts an exothermic diffusion controlled electron transfer process to occur when 2,3-dimethyl-2-butene (**2**) is used as the electron donor; -28.4 kcal mol<sup>-1</sup> (-118.8 kJ mol<sup>-1</sup>), and -20.0 kcal mol<sup>-1</sup> (-83.7 kJ mol<sup>-1</sup>) with biphenyl as co-donor. From the Stern-Volmer plot, the excited state of the sulphone is

found to be quenched at the diffusion controlled rate by the olefin ( $\tau = 5.2$  ns,  $k_q = 1.26 \times 10^{10} \text{ s}^{-1}$ ), Figure 3.1.

The measured reduction potential of **58** [-1.55 V (SCE) in  $\text{CH}_3\text{CN}$ ] is found to be less than that of 1,4-dicyanobenzene (**1**) [-1.65 V (SCE)]. This gives a higher threshold to the maximum oxidation potential of the olefin (2.7 V) with which electron transfer will occur, where the excited sulphone is involved, Table 3.1.

Irradiation of the sulphone, while not giving photo-NOCAS products, resulted in an electron transfer process. The formation of the 1:1 (methanol : olefin) adducts **3** and **4** is a clear indication of the generation of the radical-cation of olefin **2**. The two possible addition products, **3** and **4**, are formed in essentially a 1:1 ratio, indicative of a possible disproportionation pathway of the resultant  $\beta$ -alkoxy alkyl radical, see Scheme 2.2. Since the olefin radical-cation ( $2^{+\bullet}$ ) is known to be acidic, deprotonation occurs before methanol addition. This is followed by coupling of the radicals to give the olefin dimers.

If the reaction is clearly going by a PET mechanism, why is there only adduct products from the olefin cation, and why is benzonitrile the major product, not phenyl methylsulphone? An insight into the reaction mechanism for this acceptor can be gained by examination of the general electrochemical behaviour of aromatic sulphones.

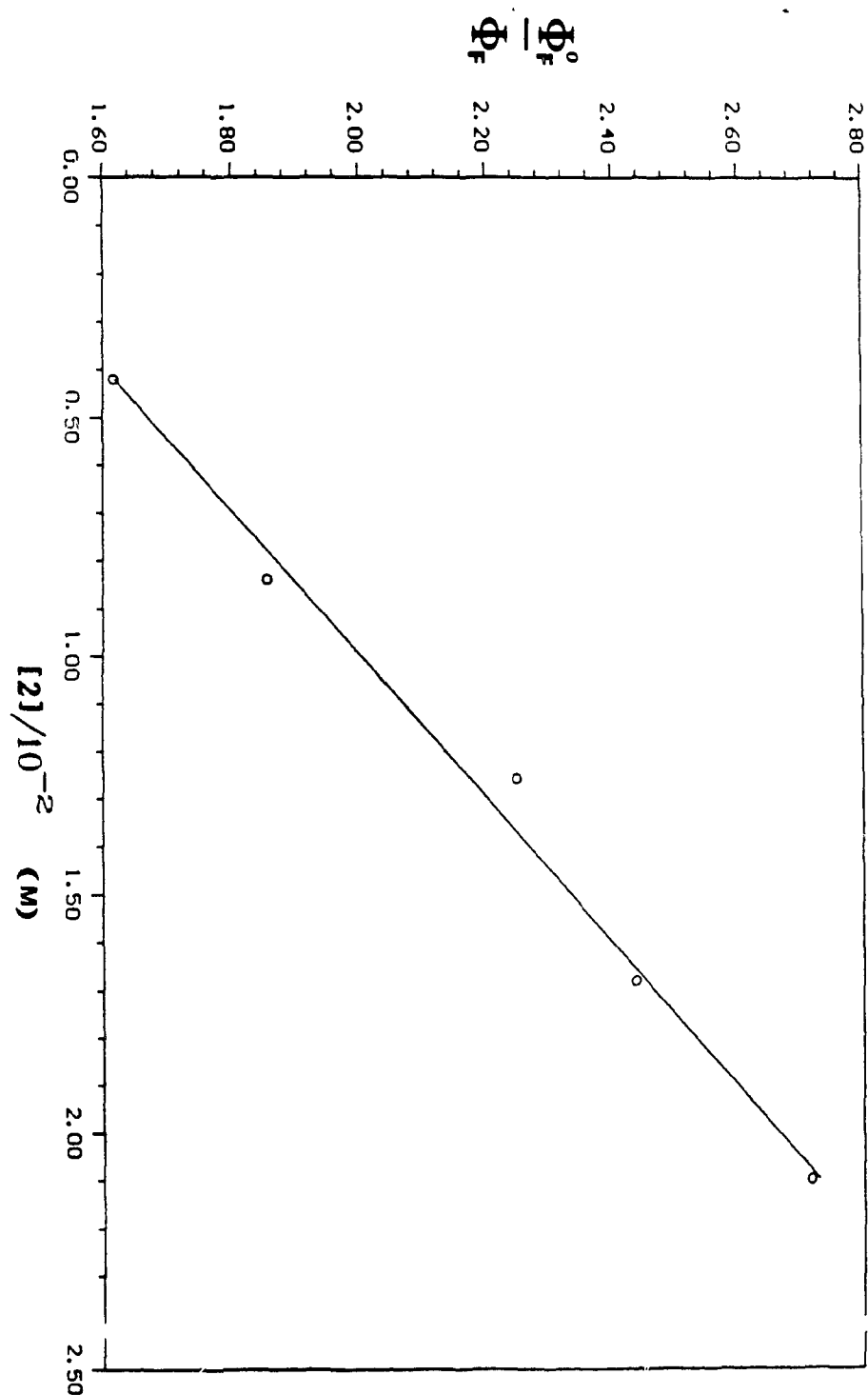
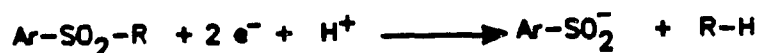


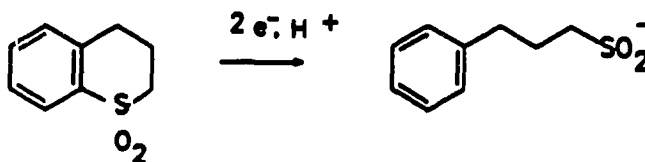
Figure 3.1 Stern-Volmer quenching study of 4-(methylsulphonyl)benzonitrile (58).

### 3.3.1 Electrochemical behaviour of Sulphones.

Cleavage of alkyl-, alkoxy- and halo-substituted aryl sulphone is known to occur in protic solvents electrochemically in the manner shown in reaction [3.1](124). An exception to this 'rule of thumb' is the electrochemical cleavage of cyclic aryl sulphones(125), where the aryl-sulphur bond is cleaved, reaction [3.2].



[3.1]



[3.2]

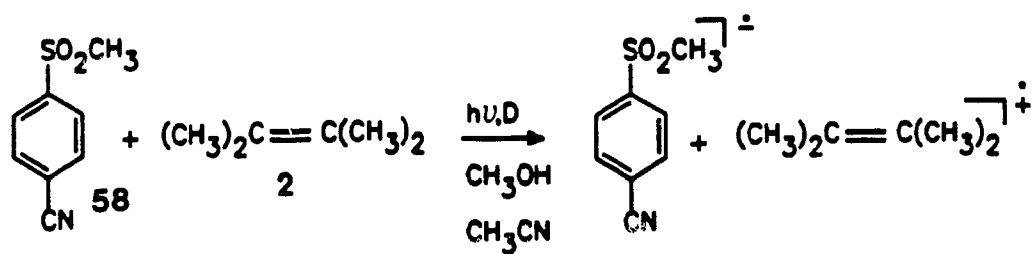
Only in the presence of strong electron-withdrawing groups does the cleavage take place across the aryl-sulphur bond (126). Zuman, in his study of the electrochemistry of substituted phenyl methyl sulphones(4), found that in the presence of electron-withdrawing groups, e.g., 4-CN, 4-COOH, 4-CONH<sub>2</sub>, and 4-COOCH<sub>3</sub>, cleavage occurs exclusively at the aryl-sulphur bond. The authors proposed a mechanism involving the initial formation of the sulphone radical-anion, followed by two possible pathways, e.e.c. or e.c.e. The first pathway involves protonation of the radical-anion, followed by a second electron transfer to give the anion, which can then lose methylsulphonyl ion, CH<sub>3</sub>SO<sub>2</sub><sup>-</sup>. The second pathway involves initial formation of the di-anion by two successive electron transfer steps, which then

undergoes protonation. Cleavage then occurs to give what appears as an overall 'hydride displacement'. The authors however, were unable to distinguish between these pathways.

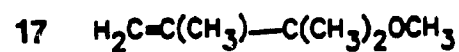
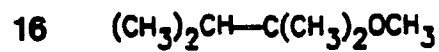
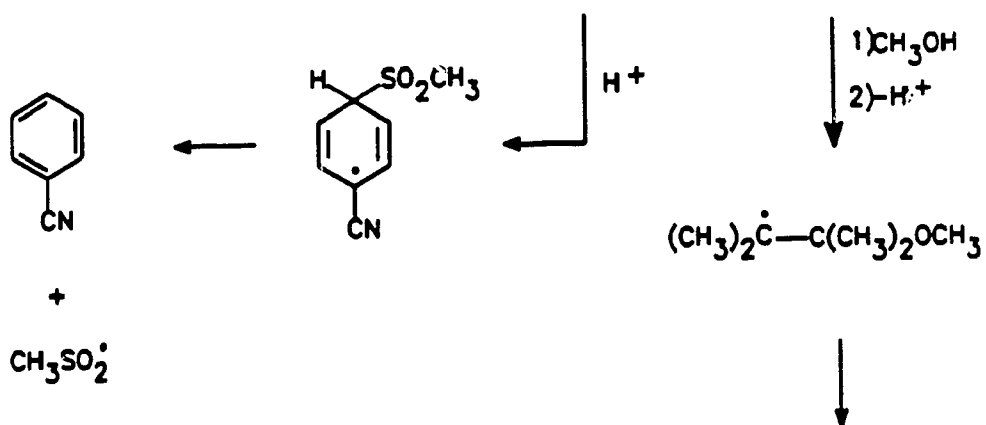
The radical-anion of **58**, was found in this study to be stable, reversible during the cyclic voltammetric sweep ( $100 \text{ mV s}^{-1}$ ). Photo-NOCAS conditions involving sulphone **58**, are believed to proceed via formation of the radical-ions by a PET process. The initially formed sulphone radical-anion undergoes protonation, and then cleavage of the aryl-sulphur bond occurs to give benzonitrile and the methylsulphonyl radical. No products, via dimerisation or hydrogen atom abstraction by the sulphonyl radical, are observed under our method of analysis (GC-MS). In contrast to the electrochemical cleavage, only one electron transfer step is possible under the photochemical conditions. To confirm that protonation of the radical-ion precedes cleavage of aryl-sulphur bond, the reaction is carried out in  $\text{CH}_3\text{CN}/\text{CH}_3\text{OD}$  (3:1), Scheme 3.1. Analysis by (GC-MS, SIM) shows 93.4% deuterium incorporation in the benzonitrile. This effectively rules out cleavage of the radical-anion to give 4-cyanophenyl radical, since benzonitrile formed shows complete deuteration.

Semi-empirical molecular orbital theory (HMO) has been used to elucidate the polarographic behaviour of substituted phenyl sulphones and predict the direction of cleavage (127). At this simple level, the aryl-sulphur bond order shows a marked decrease, while that of the aryl-carbon nitrile bond remains essentially constant (127). In our study the radical ion of **58** shows (AM1) a high negative charge concentration at the *ipso* carbon adjacent to the sulphur where protonation is found to occur, Figure 3.2.

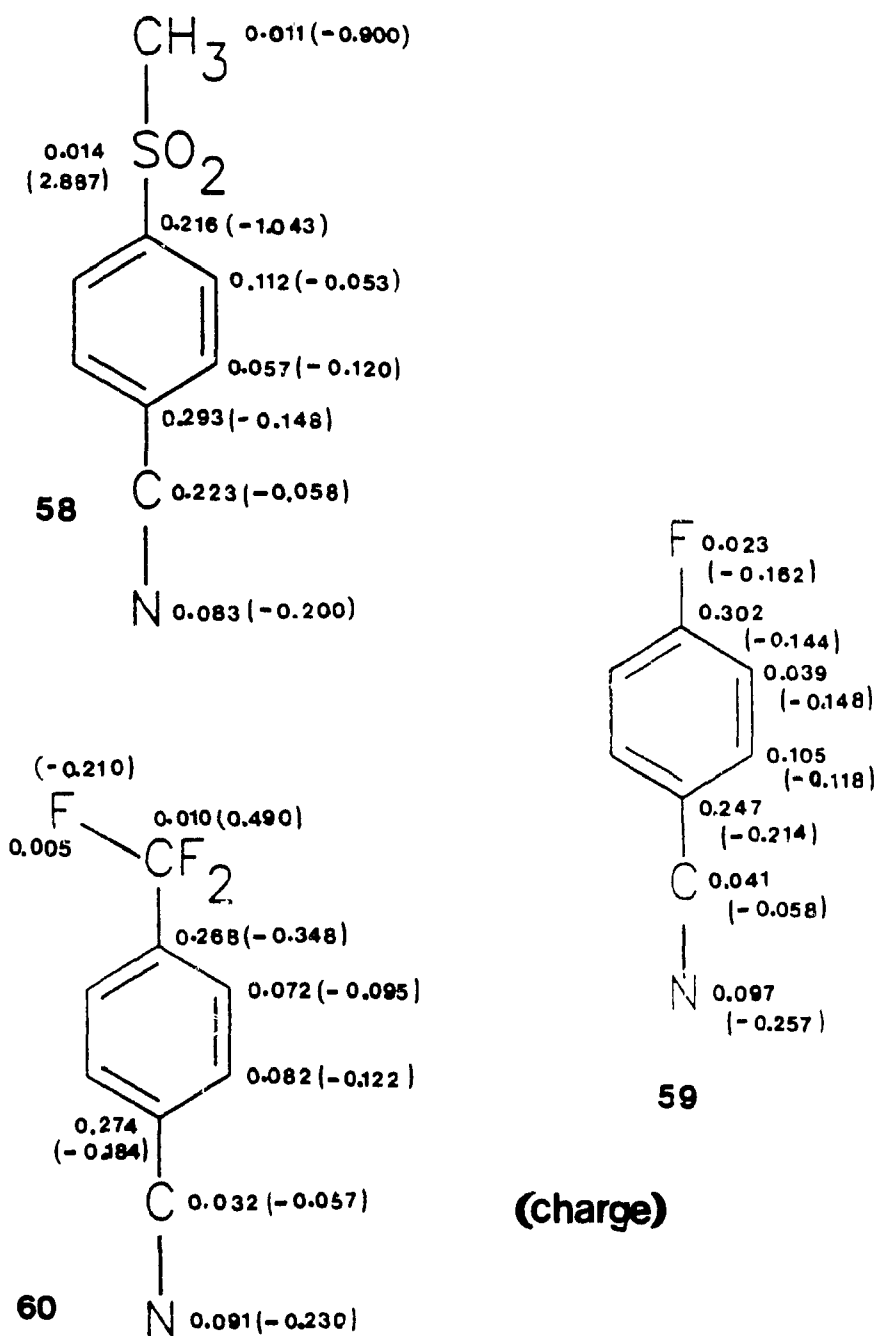




D = biphenyl



Scheme 3.1



**Figure 3.2** Spin and charge densities (STO-3G) for radical anions of 4-(methylsulphonyl)benzonitrile (58), 4-fluorobenzonitrile (59), and 4-(trifluoromethyl)benzonitrile (60).

### 3.3.2 Mechanistic discussion of the reactions of 59, 60 and 61

Ethers **3** and **4** are also observed during the irradiation of 4-fluorobenzonitrile (**59**), indicating that the reaction is preceded by a PET process. However, the exact nature of benzonitrile formation in this case was at first unknown. Is it formed in the same manner observed for sulphone **58**, or does cleavage of the aryl-fluorine bond occur at the radical-anion stage to give the 4-cyanophenyl radical and fluoride ion? The reduction potential of **59** is found to be the most negative of all the acceptors studied,  $[-2.48 \text{ V (SCE) in } \text{CH}_3\text{CN}]$ . The reduction step is also found to be irreversible at  $100 \text{ mV s}^{-1}$ . Reversibility has only been observed at very rapid scan rates,  $30 \text{ V s}^{-1}$  ( $i_{p,a}/i_{p,c} = 1$ ) (128). Subsequent rapid chemistry, after electron transfer, makes it impossible to observe the radical-anion oxidation. The number of electrons involved in this reduction step is difficult to estimate due to the *in situ* formation of benzonitrile which has a slightly less negative reduction potential than **59**.

Attempts have been made to measure the ESR signal of this radical-anion. Reigler found that the electrolytically generated radical-ion rapidly decomposes. Instead, what is observed by ESR spectroscopy, is a signal due to the radical-ion of 4,4'-dicyanobiphenyl (129). This is believed to form by either coupling of 4-cyanophenyl radicals or by dimerisation of the radical-anion. Kemp, however, was able to measure the ESR signal with considerable difficulty, using  $\text{Na}/\text{NH}_3(\text{t})$  reductive conditions and a fast mix-flow technique (130).

When the photo-NOCAS reaction of 4-fluorobenzonitrile (**59**) and **2** is carried out in  $\text{CH}_3\text{CN}/\text{CH}_3\text{OD}$  (3:1) only 16.4% deuterium is incorporated into the benzonitrile product in contrast to 93.4% for sulphone **58**. This puts an upper limit on the importance of a protonation step involving the radical-anion. Cleavage of the radical-anion (**58**-•) before protonation appeared to be the dominant process, but the protonation cannot be ruled out completely since there is some degree of charge concentration at this centre. The radical coupling product, 4,4'-dicyanobiphenyl, is not observed during the photolysis in this study,

although this may be a reflection of the low radical concentrations formed during the irradiation. Although the deuterium incorporation was small, it is still significant. One cannot completely rule out the possibility that the 4-cyanophenyl radical is reduced by a second radical-anion of **58**. This of course is expected to play a minor role due to the low concentrations of radical-anions produced during the course of the reaction. No reliable value for this reduction potential is known, however, the oxidation potential has been measured for phenyl lithium [ $< -0.1$  V, THF/HMPA(30%)] (**3a**). There is little thermodynamic significance to this value, but it does allow an estimation of the ease of reduction of the phenyl radical to the anion. Reduction of the 4-cyanophenyl radical by **58**• may account for a very small amount of deuterium incorporated benzonitrile.

At the AM1 level of calculation, the bond order for the aryl-fluorine bond is found to decrease after reduction reflecting a considerable weakening of this bond. The negative charge appears to be highly concentrated on the aryl carbon attached to the nitrile, thus diminishing the role of protonation at the *ipso* carbon adjacent to the fluorine, Figure 3.2.

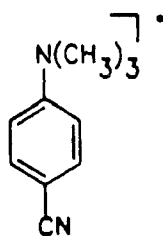
The results obtained from irradiation of **59** can be explained in part on the basis of the electrochemical behaviour of the radical-anion. The reduction potential is found in this study to be irreversible. The C-F bond cleavage is known to be efficient at a lead cathode in methanol (131). In fact, it is difficult to stop the reduction after only one bond fission. After the first C-F bond cleavage and formation of **66**, the remaining C-F bond strength decreases, and diminishes further after the second C-F bond has been broken (132). Of course, this cleavage occurs at the surface of the electron rich cathode and it is impossible to stop the second and third electron transfers. In the PET process only one electron can be transferred at a time. However, this process leads to the formation of all three substituted products. After the electron has transferred, bond fission is believed to occur with the formation of the cyano-stabilised benzylic radical. AM1 calculations show that the radical-anion of **60** has a very large, negative charge concentration at the *ipso* carbon

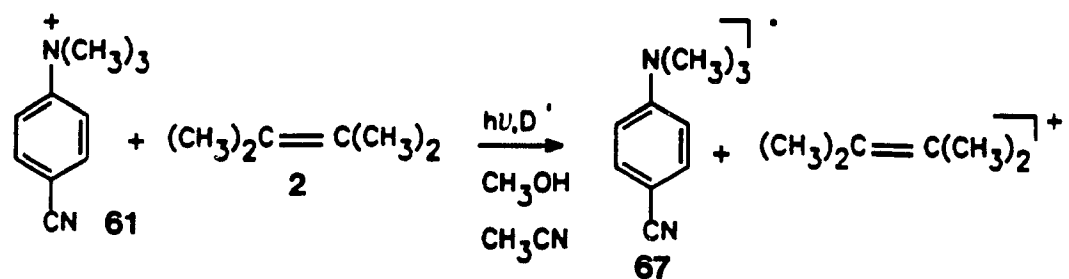
adjacent to the  $\text{CF}_3$  group, while the spin density is localised equally at both the ring C-1 and C-4 ring positions, Figure 3.2. Hydrogen atom abstraction or reduction of the benzylic radical followed by protonation can account for the observed products. As before, the reduction pathway can be assumed to be insignificant due to the low radical-anion concentrations.

This facile benzylic-halogen cleavage by electron transfer has been exploited in the alkylation by substitution at hindered saturated benzylic carbon centres (133). For example, reaction involving the sodium salt of 2-nitropropane with 4-nitrobenzyl chloride gives 92% of product  $4\text{-NO}_2\text{PhCH}_2\text{C}(\text{CH}_3)_2\text{NO}_2$ . This reaction is believed to follow a SET step from the carbanion to the aromatic system. This forms a benzylic radical-anion, which after facile C-Cl cleavage, couples with the nitropropane radical to give a 1:1 adduct.

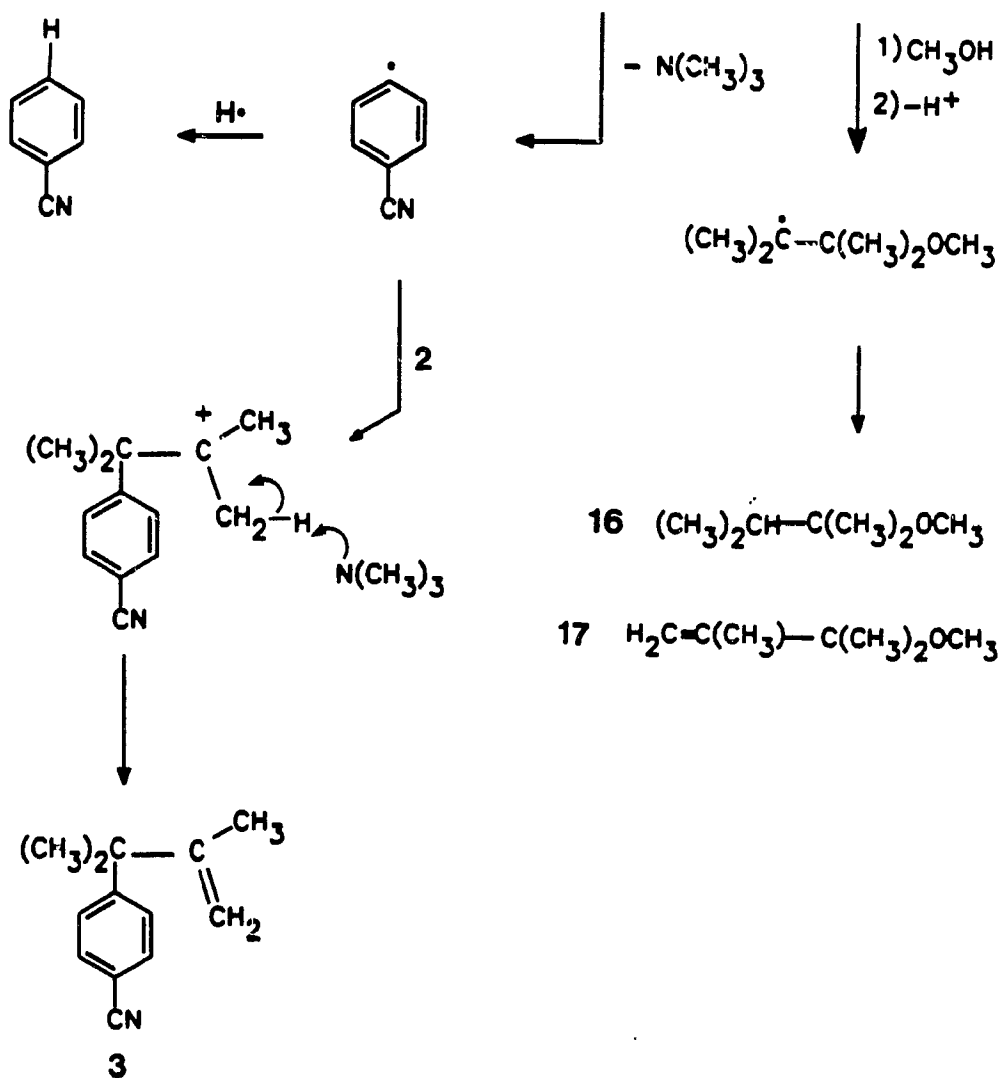
While no photo-NOCAS products are observed in the irradiation mixture using (4-cyanophenyl)trimethylammonium iodide (**61**), this example raised some interesting synthetic possibilities. Benzonitrile is formed during this reaction, as observed for **58** and **59**, as well as a 1:1 (olefin : aromatic) adduct, 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (**3**), as a minor product. Repeating the reaction in  $\text{CH}_3\text{CN}-\text{CH}_3\text{OD}$  (3:1) leads to only 3.0% deuterium incorporation in the benzonitrile. It appears that after electron transfer has occurred between the acceptor and olefin **2**, cleavage of the resulting radical **67** is rapid giving 4-cyanophenyl radical and trimethylamine, Scheme 3.2. In the irradiation mixture of 1,4-dicyanobenzene (**1**) and **2** in acetonitrile both 1:1 adducts **3** and **4** are observed. These result from the coupling of the ambident radical and 1,4-dicyanobenzene radical-anion, followed by loss of cyanide ion. With the ammonium salt (**61**) however, it is apparent that the radical of the ammonium cation ( $\text{61}^+$ ) is unstable, and the resulting 4-cyanophenyl radical adds to the radical-cation of the olefin. Addition results in the formation of the tertiary cation, which in the presence of amine undergoes deprotonation to give the observed product. A PET mechanism is implied by the observation of the ethers **3** and **4**.

Anilinium salts of this type have been studied in the past. (4-Methylphenyl) trimethylammonium iodide is found to react by a PET process with methoxy substituted benzenes to give a similar mode of radical addition (134). The reaction is also found to proceed with rapid aryl-nitrogen cleavage following the electron transfer step.





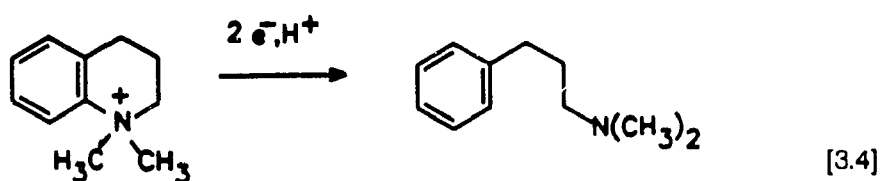
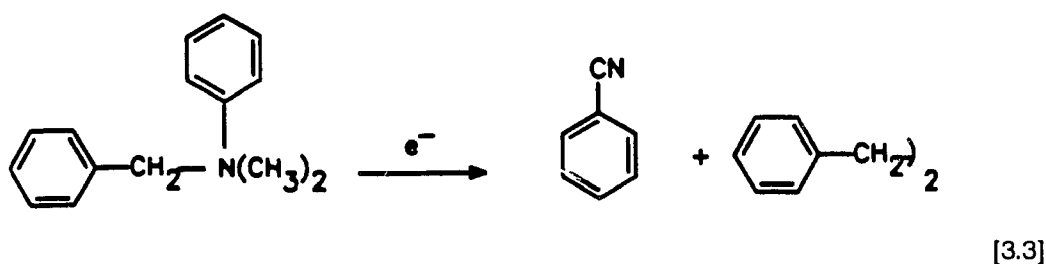
D' = biphenyl



Scheme 3.2

### 3.3.3 Electrochemical behaviour of anilinium salts

Reductive cleavage of the ammonium alkyl cations is very similar to that of the alkyl halides (135). The anilinium salts normally cleave at the aryl-N bond. The stability of the incipient radical directs the cleavage of the radical-anion (136). This cleavage is best demonstrated by the mixed benzyl phenyl alkyl system, where the benzylic dimer was observed, reaction [3.3]. The benzylic radical has been observed by ESR spectroscopy (137). Radical formation is further demonstrated when the optically active salt  $\text{PhCH}(\text{CH}_3)\text{N}(\text{CH}_3)_3$  is observed to give the racemic 2,3-diphenyl butane product (136a). This type of cleavage has been exploited on the preparative electrochemical scale in the opening of cyclic aromatic quaternary amines (138). Electrolysis leads to the open tertiary amine in high yield (88%), reaction [3.4].



### 3.4 Conclusions

While the screening process shows that none of the compounds **58-61** are useful electron acceptors for the photo-NOCAS reaction, *i.e.*, no 1:1:1 (nucleophile : olefin : aromatic) adducts are observed, they do give useful information regarding the overall synthetic scope of the reaction. All the acceptors exhibit electron transfer character. The



Rehm-Weller equation still remains a useful model in selecting potential electron accepting candidates. An important characteristic necessary in defining a good acceptor is the formation of a relatively stable radical-anion. This can be readily assessed by cyclic voltammetry and ESR spectroscopy. The electrochemical method was used in this study. 1,4-Dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**) both exhibit reversible reduction in acetonitrile (50,139), and both react to give photo-NOCAS products. Compounds **59-61** exhibit irreversible reductions under the same conditions. In contrast, compound **58** showed a reversible reduction. This gives an early indication that protonation and bond cleavage can compete during the photo-NOCAS irradiation. Of course, one must remain cautious in relating the stability of a radical-anion during the cyclic electrochemical sweep ( $100 \text{ mV s}^{-1}$ ) with the reactivity of the radical-anion during the irradiation process, unless the rates of these competing processes are known. 4-(Methylsulphonyl)benzonitrile (**58**), while showing reversibility in the CV study, did undergo rapid protonation at the radical-anion stage to give benzonitrile as the major product.

AM1 calculations were employed as a useful tool in predicting the feasibility of radical coupling and electrophilic attack (protonation). In our model compound, 1,4-dicyanobenzene (**1**), this level of calculation predicts high spin density at the ipso carbon positions where attack by the  $\beta$ -alkoxy alkyl radical occurs. However, this site also has a high degree of negative charge density and could readily undergo protonation during the irradiation. No benzonitrile has been detected in reactions of **1**. This protonation may, however, occur in a reversible manner. The AM1 calculations also allow an insight into the positions of radical/radical-anion coupling. In the case of ester **22**, the centres of high spin and charge density are observed at the ipso carbons as well as at the carbonyl carbon. Even though the greatest spin density is adjacent to the ester carbonyl, no coupling or protonation was observed due largely to the nature of the leaving groups,  $^-\text{CO}_2\text{CH}_3$  or  $^{\bullet}\text{CO}_2\text{CH}_3$ .

Sulphone **58** is driven to lose the methylsulphonyl radical by the extreme basic nature of the ipso carbon adjacent to the sulphur group. The C-F bond cleavage of **59**• and **60**• is known to be rapid, and this process completely dominates during the irradiations.

The study of ammonium salt **61**, while showing no formation of 1:1:1 photo-NOCAS products, did uncover some interesting possibilities with regards to the synthetic potential of this class of compound. The reaction appears to proceed by the addition of the 4-cyanophenyl radical to the olefin radical-cation at the tertiary position of the olefin cation, leading to an intermediate tertiary cation. In the presence of strong base, trimethylamine, the cation undergoes deprotonation to give the 1:1 product **66**. This route offers a second pathway to the formation of photo-NOCAS products, if the intermediate cation can be trapped by added nucleophiles before deprotonation by the amine can occur. The range in reduction potentials of ammonium salts coupled with their high singlet energies make them attractive as electron acceptors for a wider range of olefins in the photo-NOCAS reaction.

## Chapter 4

### The Study of 4-Cyanobenzaldehyde and 4-Cyanobenzophenone as Electron Acceptors in the Photo-NOCAS Reaction

#### 4.1 Introduction

With the encouraging results obtained using methyl 4-cyanobenzoate (**22**) as an electron acceptor in the photo-NOCAS reaction, the study was extended to include other benzonitriles containing the carbonyl functional group: 4-cyanobenzaldehyde (**68**) and 4-cyanobenzophenone (**69**). The same screening process used with the previous examples was employed. 2,3-Dimethyl-2-butene (**2**) was used as the electron donating olefin.

Both compounds are known to undergo efficient and rapid intersystem crossing from the excited singlet state to the triplet excited state. The triplet energies are therefore used to determine the feasibility of a PET process involving olefin **2**, using the Rehm-Weller equation. The results are shown in Table 4.1. The electron transfer process is predicted to occur at less than the diffusion controlled rate in both cases. The  $\Delta G_{ET}$  for this process is found to be slightly positive for the aldehyde but becomes more positive for the ketone due to the more negative reduction potential. On this basis, the electron transfer process is assumed to be in competition with other process occurring from the triplet state.

#### 4.2 Results

Irradiation of an acetonitrile-methanol solution of **68** and 2,3-dimethyl-2-butene (**2**), gives four products (combined yield 60%): two 1:1 (olefin : aromatic) adducts **70** (15%) and **71** (5%), an oxetane 1:1 (olefin : aromatic) adduct **72** (25%), and a 1:1:1 (nucleophile : olefin :aromatic) adduct **30** (15%), reaction [4.1]. Addition of biphenyl to this reaction mixture has no effect.

**Table 4.1** Characteristics of 4-cyanobenzaldehyde (**68**) and 4-cyanobenzophenone (**69**), and the free energy for the electron transfer process involving 2,3-dimethyl-2-butene (**2**).

	<b>68</b> <sup>a</sup>	<b>69</b> <sup>b</sup>
$E_{o,o}$ (kcal mol <sup>-1</sup> )	67.4	66.4
$E_{1/2}^{red}$ (V, SCE)	-1.40	-1.47
$\Delta G_{ET}^c$ (kcal mol <sup>-1</sup> )	0.9 (4.0) <sup>e</sup>	3.6 (14.9) <sup>e</sup>
$E_{1/2}^{ox}$ (V, SCE) <sup>d</sup>	1.4	1.3

<sup>a</sup>Reference (123)

<sup>b</sup>Reference (140)

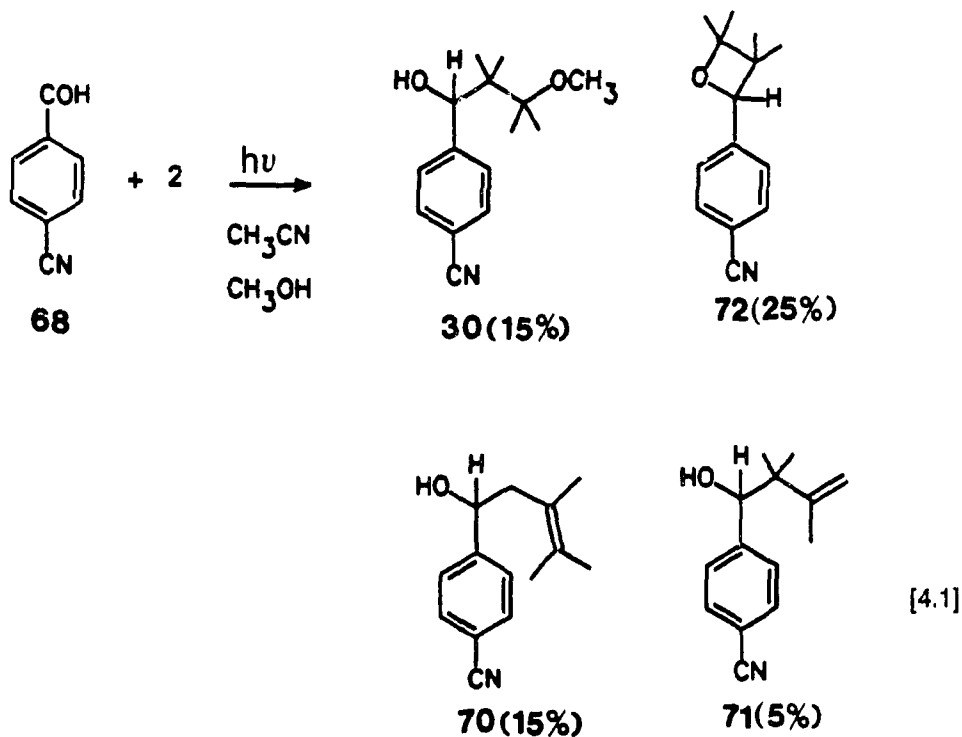
<sup>c</sup> $E_{1/2}^{ox}$  (**2**) = 1.62 (30); values given in kcal mol<sup>-1</sup>.

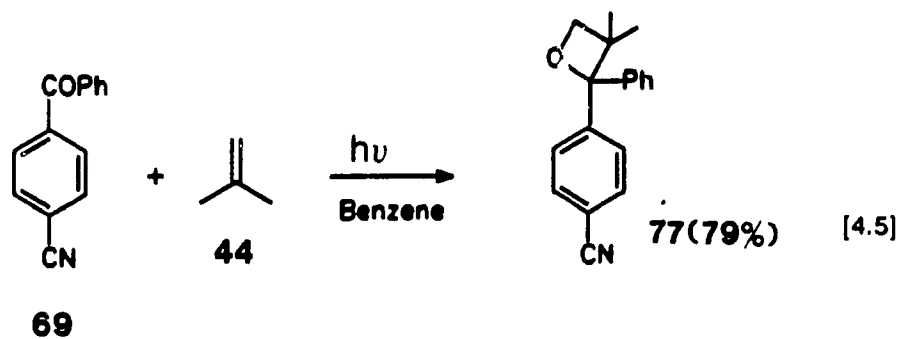
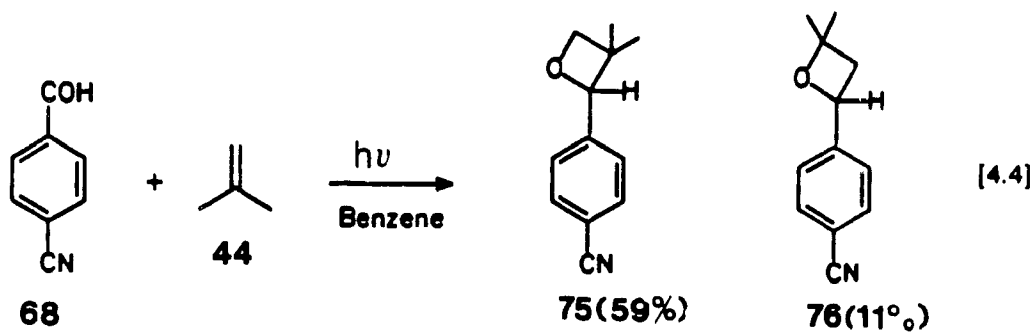
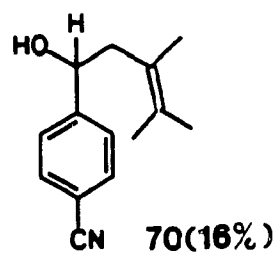
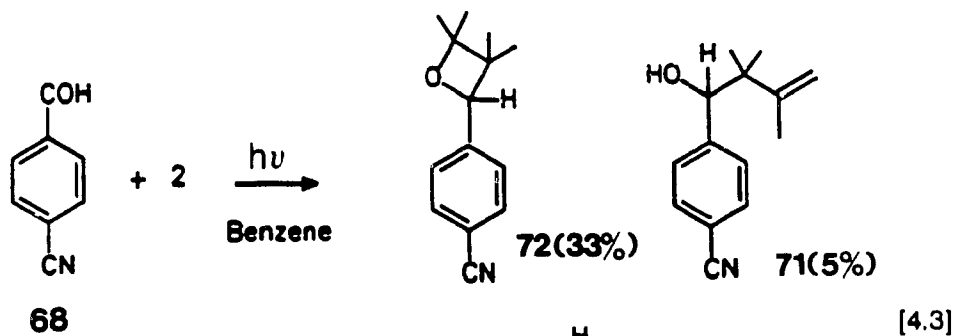
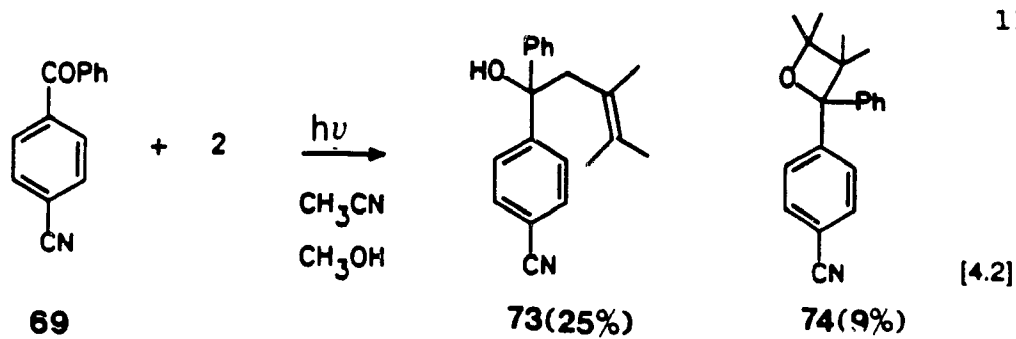
<sup>d</sup>This value represents the maximum oxidation potential of olefin with which the excited acceptor can undergo a photoinduced electron transfer process at the diffusion controlled rate ( $\Delta G_{ET} = -4$  kcal mol<sup>-1</sup>).

<sup>e</sup>kJ mol<sup>-1</sup>

Under similar irradiation conditions, a mixture of **69** and **2** in acetonitrile-methanol gives two 1:1 (olefin : aromatic) adducts, alcohol **73** (25%), and oxetane **74** (9%). No 1:1:1 adducts are observed, reaction [4.2].

The irradiations were repeated in benzene solvent. Irradiation of a solution of **68** and **2** gives three products: **70** (16%), **71** (5%), and **72** (33%), reaction [4.3]. All these products are obtained in reaction [4.1]. A mixture of **69** and **2** in benzene produces oxetane **74** (25%) as the major product, along with alcohol **73** as a minor product (8%). Irradiations of mixtures of **68** and 2-methylpropene (**44**), and **69** and **44**, leads only to formation of oxetanes in high yields, **75** (59%) and **76** (11%), reaction [4.4], and **77** (79%), reaction [4.5].





### 4.3 Structural Determination

Structural determination is based largely on  $^1\text{H}$ ,  $^{13}\text{C}$  nmr and mass spectroscopy. Structure **30**, a (1:1:1) adduct, is a product from the irradiation of acetonitrile-methanol solution of methyl 4-cyanobenzoate (**22**) and **2**, reaction [2.18]. The structural determination of **30** is described in Chapter 2.

The infrared spectra of compounds **70** and **71** both show strong O-H stretching frequencies, 3480 and 3500  $\text{cm}^{-1}$  respectively. There is no evidence of a carbonyl group. The presence of a hydroxyl group in both compounds is confirmed by  $^1\text{H}$  nmr spectra; exchangeable ( $\text{D}_2\text{O}$ ) protons are observed at 2.68 and 2.34 ppm, for **70** and **71** respectively. The sharp absorption band at 2260 and 2240  $\text{cm}^{-1}$  for these compounds confirms that the nitrile is still present.

The multiplet at 4.79 ppm in  $^1\text{H}$  nmr of **70** corresponds to a benzylic hydrogen coupled to an adjacent methylene group ( $J = 8.6$  and  $5.3$  Hz). The methylene protons (2.58, 2.27 ppm) show strong geminal coupling and a corresponding coupling to the benzylic position. The presence of the methylene is confirmed by  $^{13}\text{C}$  nmr (44.91 ppm, triplet). This suggests a structure where the olefin is coupled through the terminal carbon to the carbon on the aromatic carbonyl. A major loss of 84 and 83 amu in the mass spectrum of **70** correspond to the loss of an allylic fragment ( $\text{C}_6\text{H}_{11}$  and  $\text{C}_6\text{H}_{12}$ ).

The benzylic hydrogen (4.65 ppm) in the  $^1\text{H}$  nmr spectrum of **71** is not coupled which suggests that it is adjacent to the dimethyl-substituted methylene carbon. Only two singlet resonances (0.95 and 0.94 ppm) are observed in the aliphatic region of the  $^1\text{H}$  nmr spectrum. There is however a doublet of doublets (3H) observed at higher frequency (1.86 ppm,  $J = 1.5, 0.7$  Hz). This third methyl group is coupled to two hydrogens of the terminal methylene. The presence of the methylene is confirmed by a triplet observed at high frequency (114.02 ppm) in the  $^{13}\text{C}$  spectrum. The aromatic 1,4-disubstitution in compounds **70** and **71** is indicated by an AA'XX' coupling pattern observed in the aromatic region of the  $^1\text{H}$  nmr spectra.

Compound **72** shows a characteristic C-O stretching frequency ( $1035\text{ cm}^{-1}$ ) in the infrared spectrum, indicative of an oxetane (**73**). Four singlet resonances were observed in the  $^1\text{H}$  nmr spectrum in the aliphatic frequency region. This pattern is consistent with the presence of a chiral centre in the structure; the methyl groups are non-equivalent. No coupling is observed for the benzylic hydrogen (5.43 ppm) which allows a structure for a [2+2] cycloaddition product between the carbonyl and the olefin double bond to be drawn. Mass spectral fragmentation shows a dominant loss of 58 amu (loss of acetone). This is a characteristic cleavage across the oxetane ring.

A broad band ( $3510\text{ cm}^{-1}$ ) observed in the infrared spectrum of compound **73**, accompanied by an exchangeable proton ( $\text{D}_2\text{O}$ ) in the  $^1\text{H}$  spectrum are indicative of an alcohol. A methylene group  $\text{CH}_2$  (geminal coupling 13.4 Hz) is apparent from the  $^1\text{H}$  nmr and  $^{13}\text{C}$  (46.40, t) spectra. Only three methyl groups are observed by nmr. A very sharp absorption ( $2250\text{ cm}^{-1}$ ) confirms the presence of the nitrile.

Compounds **75**, **76**, and **77**, all oxetanes, are identified by the characteristic C-O stretching frequency in the infrared spectra. The mass spectra fragmentation is also indicative of this functionality; the molecular ions of **75** and **77** both show strong loss of 30 amu (loss of formaldehyde). The molecular ion of **76** shows loss of 58 amu (loss of acetone). The regiochemistry of oxetanes **75** and **76** is determined on the basis of coupling exhibited by the benzylic hydrogen and the methylene protons. Only compound **76** shows a coupled benzylic hydrogen. The methylene group of **77** exhibits a large geminal coupling (10.8 Hz) as well as coupling to the benzylic hydrogen ( $J = 8.3$  and  $7.4\text{ Hz}$ ). A reciprocal coupling is found for the benzylic hydrogen. A structure where the methylene  $\text{CH}_2$  is  $\alpha$  to the benzylic position is assigned to compound **76**.

The regiochemistry of oxetane **77** is assigned on the basis of the chemical shift of the methylene hydrogens. When they are  $\alpha$  to the oxygen they are found at higher frequency (4.29, 4.26 ppm, AB quartet,  $J = 5.3\text{ Hz}$ ).



All three oxetanes, **75**, **76**, and **77**, were found to retain the nitrile group, evident from the carbon-nitrogen stretching frequency in the infrared spectra.

#### 4.4 Discussion

The observed products in reaction [4.1] indicate that more than one pathway to product formation is involved. Compound **30**, a 1:1:1 adduct, implies that an electron transfer is in operation, *i.e.*, the irradiation proceeds with formation of a radical-ion pair. The mechanistic details for the formation of **30** have been discussed before, Chapter 2. Where **30** is formed from methyl 4-cyanobenzoate (**22**), an intermediate ketone is proposed as a precursor, which can undergo photoreduction to the alcohol. The addition of  $\beta$ -alkoxy alkyl radical at the carbonyl can be accounted for by a coupling between the alkyl radical with the radical-anion of the aldehyde, or by addition of the reduced form of the alkyl radical to the neutral aromatic. This latter coupling process can be ruled out due to the low reduction potential of the electron accepting aldehyde. If the coupling proceeds through radical-anion formation, there is a high probability that this radical-ion will undergo protonation at the carbonyl oxygen. *Ab initio* calculations at the STO-3G level point to a high degree of spin density at the carbonyl carbon (0.2172), with the highest negative charge found on the carbonyl oxygen (-0.2726). We believe this protonation to be rapid, since the aldehyde **68** shows an irreversible reduction electrochemically. Protonation also serves to increase the spin density at the carbonyl carbon position. No aromatic substitution is found with the aldehyde.

Formation of oxetane **72** as the major product occurs by a competing photocycloaddition pathway. The Paterno-Büchi reaction (141), as it is sometimes referred to, has been extensively examined and has wide synthetic application (142). Formation of oxetanes is generally thought to proceed through an  $n,\pi^*$  triplet (or singlet) excited state of the ketone. The reaction occurs in a non-specific manner due to the relatively poor

molecular orbital overlap (143). In the  $n,\pi^*$  excited triplet state, the electrophilic oxygen can react with the olefin, to form an intermediate biradical. Where an asymmetric olefin is used in the reaction, closure occurs through the formation of the more stable biradical. Biradicals have been detected during oxetane formation by ESR spectroscopy (144). The regioselectivity of oxetane formation, due to the more stable biradical precursor, is observed in our irradiation mixtures of **68** or **69** and 2-methylpropene (**44**) in benzene, reactions [4.4] and [4.5]. Product formation results with ring closure with the more substituted olefinic carbon adjacent to the carbonyl carbon. However, the involvement of only a biradical intermediate has not always adequately explained product distributions in this reaction. Experimental evidence supports the initial involvement of an exciplex (145).

In reaction [4.1] three competing pathways are possible. Hydrogen atom abstraction by the ketone followed by ketyl-alkyl radical coupling results in the formation of alcohols **70** and **71**. Photocycloaddition and electron transfer leads to products **72** and **30** respectively. The ratio of cycloaddition to hydrogen atom abstraction products is dependent on the relative rates for these two processes. Rate constants for hydrogen atom abstraction by  $n,\pi^*$  triplet excited states are on the order  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  (146). The rate for quenching by the olefin through an electron transfer process or exciplex formation is expected to be slower than the diffusion controlled rate. Some degree of competition is expected. We can assume that the rate constant for quenching of the excited triplet by electron transfer and exciplex formation is slightly greater than the hydrogen atom abstraction process in reaction [4.1]. Two pathways exist for the formation of radical-ions. These can form through the exciplex or from an encounter complex. The degree of CT character within the exciplex of **69** and **2** is expected to be less than in reactions involving excited methyl 4-cyanobenzoate (**22**) and 1,4-dicyanobenzene (**1**). Where the oxidation potential of the donor is low, the electron transfer becomes possible and the radical-ion pair can be detected (147). Increasing the  $E_{1/2}^{\text{ox}}$  of the donor favours hydrogen atom abstraction, resulting in the

formation of ketyl radicals (148).

The formation of **30** would appear to be dependent on the solvent polarity. The efficiency of the free radical-ion formation should become negligible in non-polar solvents. When the irradiation is carried out in benzene oxetane **72** and radical coupling products **70** and **71** are observed.

The extent of charge transfer character in the irradiation of 4-cyanobenzophenone (**69**) is expected to be less significant due to the slightly greater endothermic electron transfer process, as predicted by the Rehm-Weller equation. There is no evidence of electron transfer occurring. Both products from the irradiation in acetonitrile-methanol, **73** and **74** can be adequately explained by a hydrogen atom abstraction and subsequent radical coupling process. There is no evidence of product formation occurring through the formation of free radical-ions. The reaction shows little solvent dependency, although the relative yields of oxetane (**74**) and alcohol (**73**) are reversed in benzene; oxetane (**74**) becomes the major product. Only one ketyl-olefin coupling products is observed during the irradiations of **69** in both solvent systems. The second possible coupling product, where coupling occurs through the tertiary radical, is excluded, presumably due to the steric congestion at the carbonyl centre.

#### 4.5 Conclusion

The Rehm-Weller equation has proved to be a useful guide in determining the extent of an electron transfer process involved during the irradiation of substituted-benzonitrile/olefin mixtures in polar solvent. In the study of methyl 4-cyanobenzoate (**22**) and 1,4-dicyanobenzene (**1**), electron transfer processes are estimated to be extremely exothermic, and the formation of radical-ion pairs is expected to be efficient. However, in the above examples, **68** and **69**, the free energy for electron transfer in the excited state ( $\Delta G_{ET}$ ) becomes slightly endothermic, and therefore, the rate constant for this process becomes

less than diffusion-controlled. Other processes, hydrogen atom abstraction, subsequent radical coupling, and photocycloaddition, can now compete. We feel that products **70-73** are formed through the exciplex and by hydrogen atom abstraction processes, since the same products are observed in the non-polar system. In contrast to ester **22**, the reaction is believed to occur exclusively from the  $n, \pi^*$  triplet excited state. When electron transfer does occur during the irradiation of **68** no photochemical aromatic substitution is observed. Radical-anion/ $\beta$ -alkoxy alkyl radical coupling, aided by protonation of **68**•<sup>-</sup>, occurs at the carbonyl carbon.

Only products from the exciplex and by hydrogen atom abstraction-radical coupling are found with **69**. The increased endothermicity for the electron transfer process ensures that the competing radical-ion formation is negligible (rate constant  $\ll 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ). It is obvious from these examples how important the solvent polarity is in effecting the efficiency of free radical-ion formation. This solvent dependency has also been observed for 1,4-dicyanobenzene (**1**) and methyl 4-cyanobenzoate (**22**).

## Perspective

Several factors have been recognised which allow the synthetic potential of a substituted aromatic to be evaluated as an electron acceptor in the photo-NOCAS reaction.

1. Since the first step in the overall reaction scheme involves the photochemical transfer of an electron, it is important to assess the thermodynamic feasibility of this process. The Rehm-Weller equation proves to be a useful tool in determining the possibility of electron transfer occurring. In this work  $-4 \text{ kcal mol}^{-1}$  has been used as the limit of exothermicity. Where this value is more negative, PET becomes competitive, *i.e.*, faster than other competing processes. This competition is best demonstrated by 4-cyanobenzophenone (69) and 4-cyanobenzaldehyde (68). In both examples PET is expected to occur at less than the diffusion controlled rate, and product formation in the latter case occurs via freely solvated radical-ions, as well as by hydrogen atom abstraction process. The Rehm-Weller equation predicts a diffusion controlled electron transfer process to occur between methyl 4-cyanobenzoate (22) and olefin 2. In this case, all products can be accounted for by formation of radical-ions.

2. The stability of the intermediate radical-anion of the acceptor plays a crucial role in determining the outcome of the irradiation process. Cyclic voltammetry (CV) and electrochemical studies have been used extensively to determine the stability of these intermediates. ESR spectroscopy can also give some information regarding the stability. Where photo-NOCAS 1:1:1 adduct formation is observed, (1,4-dicyanobenzene (1) and methyl 4-cyanobenzoate (22)), reversible reduction of the acceptor is observed in acetonitrile by CV. Reaction of the radical-ions occurs to give adducts before bond cleavage or irreversible protonation can occur.

3. *Ab initio* and semi-empirical calculations give some indication of the sites of addition of the intermediate  $\beta$ -alkoxy alkyl radical to radical-anions. These have been useful

in describing the product distribution found in the irradiation mixtures of methyl 4-cyanobenzoate (**22**), and 4-cyanobenzaldehyde (**58**), with olefin **2**.

4. The singlet lifetime of the excited singlet state of the acceptor must be sufficiently long-lived to allow efficient electron transfer. We recognise a second possible pathway which allows reaction to occur in situations where the lifetime is short. Excitation of a charge-transfer complex has facilitated PET in the case of ester **22**. Selective excitation has also allowed a quite different pathway to be followed, resulting in cyclic imine formation. This is an area that requires further investigation and exploitation.

It is evident that there are several criteria that must be met in order for a substituted aromatic to be employed as an electron acceptor in the photo-NOCAS reaction. This places a significant restriction on the scope of the reaction. However, only a limited series has been studied.

## Chapter 5

### Experimental

#### *General Information*

The  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were recorded on a Nicolet 360 NB, a Varian EM-360L, or a Bruker 300 MSL spectrometer. Chemical shifts are reported in parts per million (ppm) down-field relative to tetramethylsilane. Infrared spectra (ir) were recorded on an air-purged Perkin-Elmer 180 grating spectrometer and are reported in wavenumbers ( $\text{cm}^{-1}$ ). The spectra were calibrated against the  $1601.4\text{ cm}^{-1}$  absorption band of polystyrene film. Mass spectra were recorded on a Hewlett-Packard 5970 series mass selective detector and are reported as  $m/z$  with the relative intensities in parentheses. Exact mass determinations were carried out using a ZAB-E spectrometer. Elemental analyses were carried out by Canadian Microanalytical Service Ltd., B.C. The melting points were determined using a Cybron Corporation Thermolyne apparatus linked to a digital thermocouple, and are corrected. Singlet lifetimes were measured using a PRA (Photochemical Research Associates Inc.) fluorescence lifetime system 3000. A model 510 lamp (hydrogen discharge) was used. Data was collected and analysed using a multi-channel analyser with software developed by Brian Millier (Dalhousie University). Fluorescence quenching and emission was recorded using a P-E (Perkin-Elmer) MPF-66 fluorescence spectrophotometer interfaced to a P-E 7500 professional computer. Samples were degassed prior to use using three freeze-pump thaw cycles. Ultraviolet absorption spectra were recorded on a Cary Varian 219 spectrometer and are reported in nm. X-ray data was collected on an Enraf-Nonius CAD4 four cycle diffractometer. The structure was solved using SHELX-86; calculations and refinements were performed by using SHELX-76, see Appendix. *Ab initio* calculations were carried out using a Stardent(Stellar)/GS2500 computer. The author is indebted to Drs. R. J. Boyd and T. S.

Cameron for their technical expertise and the use of their facilities. Product analyses were determined by gas chromatography using either a Hewlett-Packard 5890 GC, fitted with a 5% phenyl methyl silicone fused silica WCOT column (25 m x 0.20 mm, 0.33- $\mu$ m film thickness), coupled to a H-P mass selective detector; or a H-P 5890 GC, fitted with a DB 1701 fused silica WCOT column (30 m x 0.25 mm, 0.25- $\mu$ m film thickness), with a flame ionisation detector. Preparative-GC was carried out using Varian Aerograph models A-700 and 920, fitted with either 10% FFAP SW 60/80 or 10% QF-1 Chromasorb P 60/80 column. Preparative medium-pressure liquid chromatography (MPLC) was carried out using a 2.5 cm x 1 m column packed with tlc grade silica gel (without binder) (Merck, Kieselgel 60 PF<sub>254</sub>) at 15 psi helium (1 psi = 6.9 kPa). The chromatograms were generally developed with a hexanes-methylene chloride linear solvent gradient and the eluent was monitored, collected by a uv spectrometer-fraction collector. Dry column flash (DCFC)(149) and flash chromatography were performed using tlc grade silica gel (Merck) and silica gel (Aldrich, 230-400 mesh 60A) respectively.

Irradiations were carried out at 10°C using either a CGE 1-kW or an Hanovia 450-W medium pressure mercury vapour lamp contained in a quartz immersion well. Solutions were degassed by nitrogen ebullition prior to irradiation.

### Materials

Solvents were fractionally distilled immediately before use. Acetonitrile was purified by the reported method (60). Anhydrous diethyl ether (Mallinckrodt) was used without further purification. THF (Anachemia, ACS grade) was refluxed for 24 h over LiAlH<sub>4</sub> then fractionally distilled directly into reaction vessels under nitrogen. Thiophene-free benzene was distilled from sodium/benzophenone under nitrogen. Hexane used for uv studies was stirred with H<sub>2</sub>SO<sub>4</sub> (conc.) to remove alkenes, washed with water, dried over MgSO<sub>4</sub> and fractionally distilled from NaH. Olefins were fractionally distilled from CaH<sub>2</sub> prior to use.



Methyl 4-cyanobenzoate (Aldrich) was sublimed and recrystallised twice from methanol.

1,4-Dicyanobenzene (Aldrich) was purified by the previously reported method (30). Grignard and lithium reagents were obtained from Aldrich and used immediately.

#### *Cyclic voltammetric measurements*

Oxidation potentials were obtained by cyclic voltammetry using a PAR (Princeton Applied Research) 173 potentiostat in combination with a PAR 175 universal programmer and a PAR 179 digital coulometer. Controlled potential electrolyses were performed with the use of the PAR 173 potentiostat. The working electrode was a platinum sphere (1 mm diameter), while the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE), which was connected to the solution by a Luggin capillary. The electrolyte was TEAP (0.1 M) and the solvent was acetonitrile. Substrate concentrations were typically 0.005 M. If the anodic wave was not reversible, the half-wave potential was taken as 0.028 V before the anodic peak potential (150).

*The photo-NOCAS reaction: methanol, methyl 4-cyanobenzoate (22), and 2,3-dimethyl-2-butene (2).*

A solution of methyl 4-cyanobenzoate (**22**) (0.65 g,  $4 \times 10^{-3}$  mol) and 2,3-dimethyl-2-butene (**2**) (1 mL,  $8.4 \times 10^{-3}$  mol) in acetonitrile:methanol (3:1, 40 mL) was irradiated through quartz using a 450-W lamp. The irradiation was terminated after 70 h (35.6% conversion, based on recovered **22**). The volatile components were removed from the photolysate by distillation at reduced pressure, leaving a yellow oil, which was purified using flash chromatography (silica gel,  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ ). The imine (**23**) (0.29 g, 83%) was analysed immediately. *ir* (liq. film)  $\nu$ : 3400(m, broad), 3240(m), 2960(s), 2870(m), 1720(s), 1645(s), 1590(m), 1380(s);  $^1\text{H}$  nmr (60 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.6(b, 1H, exch.), 8.2-7.7(m, 3H), 3.9(s, 3H), 1.2(s, 6H), 1.1(s, 6H);  $^{13}\text{C}$  nmr (90.79 MHz,  $\text{CDCl}_3$ )  $\delta$ : 188.23(s), 166.75(s), 156.84(s),

139.12(s), 133.34(d, 5.0 Hz), 128.62(d, 163.3 Hz), 124.29(d, 167.2 Hz), 122.42(d, 165.9 Hz), 52.28(q, 147.1 Hz), 52.01(s), 46.35(s), 25.68(q, 127.4 Hz), 25.40(q, 126.6 Hz); ms  $m/z$ : 246(3), 245(18), 244(3), 231(39), 230(100), 215(24), 171(23), 128(10), 115(10), 77(5).

*Hydrolysis of the imine (23) to the ketone (24).*

A sample of the imine (**23**), in  $\text{CDCl}_3$  solution, was slowly hydrolysed to the corresponding ketone (**24**). Hydrolysis of (**23**) (0.29 g) was carried out in aqueous MeOH (50 mL) HCl (1 mL, 6M). The MeOH was removed by distillation at reduced pressure, and the residue was diluted with  $\text{H}_2\text{O}$  (50 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 25 mL). The combined organic layers were washed with aq.  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ , dried over  $\text{MgSO}_4$  and evaporated to give a yellow oil. The ketone (**24**) was isolated by flash chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ ) as a colourless solid (0.20 g, 69%). Recrystallisation of **24** from 95% EtOH afforded fine needles; mp 69.4-70.4°C; ir (KBr)  $\nu$ : 2980(m), 2940(m), 2880(w), 1730(vs), 1625(w), 1595(w), 1450(m), 1340(m), 1290(s), 1250(s), 1200(s), 985(s), 760(s);  $^1\text{H}$  nmr (361.03 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15(s, 1H), 8.03(d, 1H,  $J = 7.9$  Hz), 7.76(d, 1H,  $J = 8.1$  Hz), 3.97(s, 3H), 1.26(s, 6H), 1.10(s, 6H);  $^{13}\text{C}$  nmr (90.79 MHz,  $\text{CDCl}_3$ )  $\delta$ : 210.59(s), 166.47(s), 161.45(s), 136.73(s), 135.47(s), 128.69(d, 164.0 Hz), 124.68(d, 163.5 Hz), 123.88(d, 164.1 Hz), 54.15(s), 52.49(q, 147.4 Hz), 44.95(s), 26.22(q, 127.0 Hz), 21.57(q, 127.5 Hz); ms  $m/z$ : 247(5), 246(25), 232(19), 231(100), 215(5), 172(6), 128(11), 115(11), 91(5); Anal. calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_3$ : C 73.15, H 7.35; found: C 73.14, H 7.37.

*The photo-NOCAS reaction: methanol, methyl 4-cyanobenzoate (22), 1-methylcyclohexene (19).*

A solution of **22** (0.65 g,  $4.03 \times 10^{-3}$  mol), biphenyl (**12**) (0.62 g,  $4.02 \times 10^{-3}$  mol) and **19** (1 mL,  $8.45 \times 10^{-3}$  mol) in acetonitrile:methanol (3:1, 40 mL) was degassed and irradiated through quartz (1-kW) at 10°C. Progress of the reaction was followed by GC-FID and when

conversion of the ester was essentially complete (12 h) the reaction was stopped. Removal of the volatile components of the mixture by distillation under reduced pressure gave a yellow oil (2.10 g). This mixture was separated using MPLC ( $\text{CH}_2\text{Cl}_2$ -hexanes gradient, followed by  $\text{CH}_2\text{Cl}_2$ ). When necessary, combined fractions were further purified using DCFC. The isomeric photo-NOCAS products **32-34** and the ketone **35** were obtained.

Isomer **32**, 31%: ir (liq. film, NaCl)  $\nu$ : 2970(m), 2930(s), 2860(m), 2810(w), 1725(vs), 1610(s), 1440(s), 1280(vs), 1190(s), 1105(vs), 760(s), 700(s);  $^1\text{H}$  nmr (300.13 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.99(d, 2H,  $J = 8.4$  Hz), 7.49(d, 2H,  $J = 8.5$  Hz), 3.88(s, 3H), 3.48(dd, 1H,  $J = 9.6$  Hz, 3.6 Hz), 3.14(s, 3H), 1.88-1.46(m, 8H), 1.31(s, 3H);  $^{13}\text{C}$  (75.47 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.12(s), 154.89(s), 129.37(dd, 161.8 Hz, 6.0 Hz), 127.49(s), 126.22(dd, 157.2 Hz, 6.8 Hz), 84.12(d, 139.3 Hz), 57.02 (dq, 140.6 Hz, 4.3 Hz), 51.88(q, 147.0 Hz), 43.37(s), 37.88(t, 126.8 Hz), 25.90(t, 127.4 Hz), 23.73(t, 125.4 Hz), 21.78(t, 125.4 Hz), 19.54(qm, 127.1 Hz); ms  $m/z$ : 263(11), 262(71), 231(36), 230(100), 176(43), 145(42), 143(87), 115(33), 91(22), 71(76), 59(22). Anal. calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_3$ : C 73.25, H 8.45; found C 72.99, H 8.51.

Isomer **33**, 5%: ir (liq. film, NaCl)  $\nu$ : 2950(s), 2880(m), 2840(w), 1740(vs), 1620(m), 1450(m), 1290(vs), 1200(m), 1130(s), 1080(m), 780(m), 720(m);  $^1\text{H}$  nmr (300.13 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.93(d, 2H,  $J = 8.4$  Hz), 7.29(d, 2H,  $J = 8.4$  Hz), 3.89(s, 3H), 3.13(s, 3H), 2.86(dd, 1H,  $J = 11.7$  Hz, 4.0 Hz), 1.98-1.26(m, 8H), 1.02(s, 3H);  $^{13}\text{C}$  nmr (75.47 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.34(s), 148.51(s), 129.55(d, 159.6 Hz), 128.69(d, 161.9 Hz), 127.94(s), 76.84(s), 51.89(q, 146.8 Hz), 51.80(d, 133.0 Hz), 48.52(q, 140.3 Hz), 37.01(t, 127.8 Hz), 29.53(t, 127.1), 26.28(t, 127.1 Hz), 23.81(t, 127.3 Hz), 16.94(q, 124.9 Hz); ms  $m/z$ : 262(21), 231(18), 230(63), 188(25), 171(22), 131(19), 129(48), 128(19), 115(14), 85(100), 72(37), 59(14), 55(24); Exact mass calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_3$ : 262.1569; found 262.1567.

Isomer **34**, 1%: ir (liq. film, NaCl)  $\nu$ : 2950(s), 2880(m), 2845(w), 1735(vs), 1625(m), 1450(m), 1290(s), 1120(m), 1090(m), 780(m);  $^1\text{H}$  nmr (300.13 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.91(d, 2H,  $J = 8.3$  Hz), 7.38(d, 2H,  $J = 8.3$  Hz), 3.89(s, 3H), 3.11(s, 3H), 2.47(dd, 1H,  $J = 12.8$  Hz, 3.3 Hz),

2.18-2.04(m, 2H), 1.83-1.13(m, 6H), 0.88(s, 3H);  $^{13}\text{C}$  nmr (75.47 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.25, 149.59, 129.74, 128.83, 127.75, 74.26, 55.25, 51.87, 48.28, 34.01, 28.99, 26.52, 23.42, 21.57; ms  $m/z$ : 263(7), 262(42), 247(2), 231(24), 230(74), 219(11), 188(37), 187(10), 171(18), 131(12), 129(48), 128(12), 115(12), 103(8), 91(10), 85(100), 77(10), 72(39), 55(21); Exact mass calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_3$ : 262.1569; found 262.1569.

Ketone **35**, 17%: ir (liq. film, NaCl)  $\nu$ : 3000(m), 2960(vs), 2890(s), 2840(w), 2260(s), 1700(vs), 1110(vs), 1475(m), 1280(m), 1260(m), 960(s), 850(s);  $^1\text{H}$  nmr (300.13 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.70(d, 2H,  $J$  = 8.3 Hz), 7.58(d, 2H,  $J$  = 8.2 Hz), 3.58(dd, 1H,  $J$  = 10.1 Hz, 3.9 Hz), 3.26(s, 3H), 1.97-1.62(m, 4H), 1.54-1.28(m, 4H), 1.24(s, 3H);  $^{13}\text{C}$  nmr (75.47 MHz,  $\text{CDCl}_3$ )  $\delta$ : 210.86(s), 144.84(s), 131.81(d, 167.8 Hz), 127.23(d, 172.2 Hz), 118.21(s), 113.46(s), 81.92(d, 143.1 Hz), 56.31(dq, 141.1 Hz, 4.2 Hz), 53.42(s), 34.70(t, 128.4 Hz), 24.85(t, 125.9 Hz), 23.44(t, 127.4 Hz), 20.91(t, 127.87 Hz), 16.01(qm, 127.7 Hz); ms  $m/z$ : 257(6), 225(67), 196(34), 127(25), 130(56), 95(100), 102(54), 71(54), 67(29), 59(50), 55(29); Anal. calcd. for  $\text{C}_{16}\text{H}_{19}\text{NO}_2$ : C 74.94, H 7.49, N 5.43; found C 74.68, H 7.44, N 5.44.

*The photo-NOCAS reaction: methanol, methyl 4-cyanobenzoate (22), cyclohexene (38).*

A solution of **22** (1.61 g,  $1.0 \times 10^{-2}$  mol), **12** (1.55 g,  $1.0 \times 10^{-2}$  mol) and **38** (2.1 mL,  $1.8 \times 10^{-3}$  mol) in acetonitrile:methanol (3:1, 110 mL) was degassed and irradiated through Pyrex (1-kW) at 10°C. After 206 h the reaction was stopped (38.6% conversion of **22**). Separation of the photolysate by MPLC (silica gel,  $\text{CH}_2\text{Cl}_2$ /hexanes gradient) gave the photo-NOCAS product (**39**), as a colourless oil, 0.08 g (8% yield), and the 1:1 adduct **40**, 0.10 g (12%).

**39**: ir (liq. film, NaCl)  $\nu$ : 2940(s), 2880(m), 2840(w), 1735(vs), 1620(m), 1030(w), 775(m), 710(m);  $^1\text{H}$  nmr (361.03 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.97(d, 2H,  $J$  = 8.32 Hz), 7.29(d, 2H,  $J$  = 8.30 Hz), 3.89(s, 3H), 3.27(td, 1H,  $J$  = 10.19, 10.18, 4.17 Hz), 3.09(s, 3H), 2.62-2.54(m, 1H), 2.29-2.24(m, 1H), 1.90-1.72(m, 3H), 1.53-1.20(m, 4H);  $^{13}\text{C}$  nmr (90.79 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.18,

150.47, 129.60(d, 162.7 Hz), 128.02, 127.58(d, 158.4 Hz), 82.97(d, 141.41), 56.65(q, 140.9 Hz), 51.92(q, 146.5 Hz), 51.24(d, 128.5 Hz), 34.10(t, 131.7 Hz), 31.30(t, 126.7 Hz), 25.98(t, 126.7 Hz), 24.90(t, 128.8 Hz); ms  $m/z$ : 249(7), 248(39), 217(15), 216(39), 157(24), 131(22), 129(48), 115(15), 103(13), 77(14), 71(100), 58(14); Exact mass calcd. for  $C_{15}H_{20}O_3$ : 248.1412; found 248.1415.

**49**: ir (liq. film, NaCl)  $\nu$ : 3030(w), 2940(s), 2870(m), 1730(m), 1620(m), 1410(m), 1285(s), 1110(m), 1025(w), 845(w), 765(m);  $^1H$  nmr (361.01 MHz,  $CDCl_3$ )  $\delta$ : 7.96(d, 2H,  $J$  = 8.24 Hz), 7.28(d, 2H,  $J$  = 8.22 Hz), 5.92(m, 1H,  $J$  = 9.93, 2.50 Hz), 5.69(dd, 1H,  $J$  = 9.9, 2.0 Hz), 3.90(s, 3H), 3.46(m, 1H), 2.10-1.49(m, 6H);  $^{13}C$  nmr (90.78 MHz,  $CDCl_3$ )  $\delta$ : 167.11(s), 152.08(s), 129.60(d, 165.86 Hz), 129.15(d, 153.54 Hz), 128.96(d, 162.88 Hz), 127.77(s), 127.71(d, 166.27 Hz), 51.96(q, 146.90 Hz), 41.85(d, 125.78 Hz), 32.36(t, 128.94 Hz), 24.92(t, 125.78 Hz), 21.04(t, 128.39 Hz); ms  $m/z$ : 218(1), 217(12), 216(66), 201(17), 185(17), 158(12), 157(88), 142(14), 131(16), 130(13), 129(100), 128(44), 115(32), 91(33), 79(13), 77(22), 59(14); Exact mass calcd. for  $C_{14}H_{16}O_2$ : 216.1150; found 216.1151.

*The photo-NOCAS reaction: methanol, methyl 4-cyanobenzoate (22), 2,3-dimethyl-2-butene (2).*

An acetonitrile:methanol (3:1, 20 mL) solution of the ester **22** (0.32 g,  $2.0 \times 10^{-3}$  mol), biphenyl (**12**) (0.31 g,  $2.0 \times 10^{-3}$  mol) and the olefin **2** (0.5 mL,  $4.2 \times 10^{-3}$  mol) was degassed and irradiated through quartz using a 450-W lamp. The reaction was stopped after 35 h, at 91.5% conversion of the ester. After the volatile components of the reaction mixture were removed under vacuum, the crude yellow oil was chromatographed using DCFC. Biphenyl was recovered (84%) using hexane as the eluent. The photo-NOCAS product **28** eluted with 5% diethyl ether/hexane as a colourless solid, 0.068 g (15%). Alcohol (**30**) was also isolated as a solid, 0.077 g (17%), using 10% acetone/ $CH_2Cl_2$  eluent.

**28**: recrystallised from MeOH to give fine needles mp 63.8-67.4°C; ir (KBr)  $\nu$ :

3000(m), 2970(w), 1720(s), 1600(w), 1445(m), 1280(s), 1200(m), 1120(m), 1105(s), 1060(m), 1015(m), 770(m), 705(m);  $^1\text{H}$  nmr (361.008 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.92(d, 2H,  $J = 8.49$  Hz), 7.52(d, 2H,  $J = 8.51$  Hz), 3.89(s, 3H), 3.10(s, 3H), 1.39(s, 6H), 1.00(s, 6H);  $^{13}\text{C}$  nmr (90.78 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.28(s), 153.06(s), 128.62(d, 159.46 Hz), 128.10(d, 128.12 Hz), 127.20(s), 78.82(s), 51.90(q, 146.56 Hz), 49.46(q, 140.40 Hz), 45.79(s), 24.35(q, 126.65 Hz), 19.88(q, 125.31 Hz); ms  $m/z$ : no mol. ion, 235(1.5), 219(0.7), 178(2.1), 163(3.2), 118(2.5), 117(2.5), 115(2.7), 103(1.5), 102(1.6), 91(2.5), 74(5.0), 73(100), 51(1.4); Anal. Calcd. for  $\text{C}_{15}\text{H}_{22}\text{O}_3$ : C 71.97, H 8.86, O 19.17; found C 71.71, H 8.87.

**30**: recrystallised from MeOH, mp 132.7-133.4°C; ir (KBr)  $\nu$ : 3450(b), 3055(m), 2970(m), 2260(s), 1625(m), 1490(m), 1415(m), 1390(w), 1340(w), 1220(m), 1075(s), 1020(m), 875(s), 860(s), 790(s), 640(s);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60-7.58(d, 2H,  $J = 8.45$  Hz), 7.49-7.47(d, 2H,  $J = 8.14$  Hz), 5.72(s, 1H, exch.), 4.98(s, 1H), 3.31(s, 3H), 1.42(s, 3H), 1.20(s, 3H), 0.90(s, 3H), 0.63(s, 3H);  $^{13}\text{C}$  nmr (90.784 MHz,  $\text{CDCl}_3$ )  $\delta$ : 147.64(s), 131.01(d,  $J = 165.17$  Hz), 129.44(d, 162.93 Hz), 119.08(s), 110.67(s), 83.24(s), 78.46(d,  $J = 143.97$  Hz), 40.03(q, 142.02 Hz), 44.02(s), 22.95(q,  $J = 125.18$  Hz), 19.70(q,  $J = 125.60$  Hz), 19.40(q,  $J = 125.59$  Hz), 14.74(q,  $J = 126.35$  Hz); ms  $m/z$ : no mol. ion, 130(12), 115(22.4), 104(8.5), 102(8.6), 85(12.5), 84(100), 83(28), 77(9.8), 73(89.7), 69(58.2); Anal. Calcd. for  $\text{C}_{15}\text{H}_{21}\text{NO}_2$ : C 72.84, H 8.56, N 5.66; found C 72.65, H 8.57, N 5.59.

When the irradiation described above was carried out to lower conversion (43% of the ester consumed after 3.5 h), along with **28** and **30**, two additional products, **29** and **31**, were detected.

Amine **19** was isolated as a colourless oil in 13.4% using EtOAc as eluent; ir (liq. film, NaCl)  $\nu$ : 3900(w, broad), 2960(s), 1720(s), 1615(w), 1585(w), 1435(m), 1290(s), 1240(m), 750(m);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.92(dd, 1H,  $J = 7.78, 1.55$  Hz), 7.79(d, 1H,  $J = 1.36$  Hz), 7.35(d, 1H,  $J = 7.86$  Hz), 4.10(s, 1H), 3.90(s, 3H), 1.46(broad s, 2H, exch.  $\text{D}_2\text{O}$ ), 1.24(s, 3H), 1.078(s, 3H), 1.06(s, 3H), 0.64(s, 3H);  $^{13}\text{C}$  nmr (90.78 MHz,  $\text{CDCl}_3$ )  $\delta$ : 167.40(s),

151.14(s), 149.83(s), 129.38(s), 128.38(d,  $J = 164.07$  Hz), 123.24(d,  $J = 159.93$  Hz), 122.82(d,  $J = 159.67$  Hz), 63.26(d,  $J = 135.58$  Hz), 51.98(q,  $J = 146.96$  Hz), 50.34(s), 46.27(s), 25.90(q,  $J = 125.67$  Hz), 22.062(q,  $J = 125.06$  Hz), 19.95(q,  $J = 125.16$  Hz), 17.74(q,  $J = 125.97$  Hz); ms  $m/z$ : 248(10), 247(68), 246(72), 232(62), 216(39), 215(100), 190(52), 188(38), 183(36), 171(25), 156(73), 155(29), 143(26), 141(29), 131(29), 130(38), 129(35), 128(38), 115(38), 70(31), 59(31), 58(29). Exact mass calcd. for  $C_{15}H_{21}NO_2$ : 247.1572; found 247.1572.

Ketone **29** was isolated from the reaction mixture, using 30% diethyl ether/hexane solvent system, in 4% yield; recrystallisation (3x) from MeOH gave fine needles, mp 64.5-65.5°C; ir (liq. film, NaCl)  $\nu$ : 2980(s), 2960(m), 2240(s), 1725(m), 1680(s), 1475(m), 1395(m), 1370(m), 1260(s), 1145(s), 1070(s), 975(m), 970(m), 855(m), 740(m);  $^1H$  nmr (361.01 MHz,  $CDCl_3$ )  $\delta$ : 7.77(d, 2H,  $J = 8.59$  Hz), 7.64(d, 2H,  $J = 8.46$  Hz), 3.22(s, 3H), 1.25(s, 6H), 1.21(s, 6H);  $^{13}C$  nmr (90.78 MHz,  $CDCl_3$ )  $\delta$ : 210.65(s), 145.66(s), 131.40(d,  $J = 167.45$  Hz), 128.48(d,  $J = 166.64$  Hz), 118.48(s), 113.16(s), 80.30(s), 54.75(s), 48.91(q,  $J = 141.24$  Hz), 23.56(q,  $J = 126.95$  Hz), 19.56(q,  $J = 125.28$  Hz); ms  $m/z$ : no  $M^{+*}$ , 230(1), 214(0.1), 131(8), 130(86), 115(9), 102(37), 84(48), 83(24), 75(10), 74(8), 73(100), 69(28), 55(25); Anal. Calcd. for  $C_{15}H_{19}NO_2$ : C 73.44, H 7.81, N 5.71, O 13.04; found C 73.22, H 7.58, N 5.68.

*The photo-NOCAS reaction: methanol, methyl 4-cyanobenzoate, (22) and 1-methylcyclohexene (19).*

An acetonitrile:methanol (3:1, 250 mL) solution of **22** (3.2 g, 0.02 mol) and **19** (4.73 mL, 0.04 mol) was degassed and irradiated through quartz at 10°C using a 450-W lamp for 17 h. Dilute aqueous HCl (10 mL) was added and the solution was stirred at room temperature for 7 h until the imine had hydrolysed (GC-MS). The solution was then concentrated under reduced pressure and the residual oil was chromatographed (MPLC, silica gel, 10% EtOAc/hexanes eluent). The ketone **26** was isolated as a colourless oil

(0.45 g, 17.5%, at 50% conversion of the starting ester).

**26**: ir (liq. film)  $\nu$ : 2955(s), 2880(m), 1735(vs), 1630(w), 1600(w), 1500(s), 1455(s), 1210(s), 1100(m), 980(w), 765(m);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.13(s, 1H), 8.04(d, 1H,  $J$  = 7.94 Hz), 7.80(d, 1H,  $J$  = 7.79 Hz), 3.97(s, 3H), 3.08(t, 1H,  $J$  = 5.24 Hz), 2.03-1.94(m, 2H), 1.58-1.20(m, 6H), 1.28(s, 3H);  $^{13}\text{C}$  nmr (90.78 MHz,  $\text{CDCl}_3$ )  $\delta$ : 209.93(s), 166.43(s), 155.36(s), 138.62(s), 135.09(s), 128.60(d,  $J$  = 167.04 Hz), 124.25(d,  $J$  = 165.91 Hz), 125.59(d,  $J$  = 163.43 Hz), 52.43(q,  $J$  = 147.34 Hz), 45.60(d,  $J$  = 132.10), 31.52(t,  $J$  = 127.40 Hz), 26.14(t,  $J$  = 127.31 Hz), 21.14(t), 21.01(t), 21.66(q,  $J$  = 127.34 Hz); ms  $m/z$ : 260(2), 259(13), 258(84), 244(17), 243(100), 240(21), 229(41), 227(19), 225(13), 217(41), 216(21), 203(21), 181(50), 171(16), 143(15), 142(12), 141(21), 129(25), 128(43), 127(19), 115(48), 77(19), 75(12), 59(24); Exact mass calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_3$ : 258.1256; found 258.1256.

*Preparation of the acid and the ammonium salt (27) from the keto ester (26).*

An aqueous NaOH solution (0.5 mL, 6.2 M) of the keto ester **26** (0.10 g,  $3.9 \times 10^{-4}$  mol) was heated under reflux for 20 minutes, after which time the ester had dissolved. The solution was cooled in an ice-bath, and  $\text{H}_2\text{O}$  (0.5 mL) was added. This solution was then acidified using HCl (conc.). A pale yellow solid was collected by filtration and washed with water. This solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and dried over  $\text{MgSO}_4$ . Evaporation of the solvent gave the acid, 0.08 g (88%), as a colourless solid. The  $^1\text{H}$  nmr showed the presence of an exchangeable hydrogen and the absence of the ester methoxy group;  $^1\text{H}$  nmr (361.009 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.21(s, 1H), 8.14(d, 1H,  $J$  = 7.95 Hz), 7.86(d, 1H,  $J$  = 7.95 Hz), 3.12(t, 1H,  $J$  = 5.32 Hz), 2.06-1.93(m, 2H), 1.30(s, 3H), 1.63-1.20(m, 6H). An exchangeable hydrogen was detected (EM360) at 8.6 ppm (this peak was not evident in the spectrum from the Nicolet).  $^{13}\text{C}$  nmr (90.784 MHz, acetone- $d_6$ )  $\delta$ : 170.42, 155.47, 139.40, 134.10, 129.28, 126.25, 124.50, 50.38, 45.65, 31.56, 26.24, 21.72, 21.21.

Ammonium salt **27** was formed by bubbling  $\text{NH}_3(\text{g})$  through a diethyl ether solution



of the acid at room temperature. The salt immediately precipitated from solution. The mixture was filtered; the solid was washed with diethyl ether to remove traces of unreacted acid, and dried under vacuum. The resulting colourless solid was then recrystallised from methanol, to give a sample (mp 183.4-184.8°C) from which a crystal was chosen for X-ray analysis.

*Preparation of ethers cis- and trans-1-methoxy 2-methylcyclohexane (36) and 1-methoxy 1-methylcyclohexane (37).*

The ethers were made from the commercially available alcohols (Aldrich) using the published procedure (151). The alcohol was treated with NaH in THF, and then with an excess of MeI. After work-up, the ethers were purified using prep-gc (QF1 column). 1-Methoxy 1-methylcyclohexane (**37**);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.18(s, 3H,  $\text{OCH}_3$ ), 1.69-1.21(m, 10H), 1.11(s, 3H,  $\text{CH}_3$ ). *cis*-1-Methoxy 2-methylcyclohexane (**36**);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.31(s, 3H,  $\text{OCH}_3$ ), 3.21(m, 1H), 1.79-1.25(m, 9H), 0.92(d, 1H,  $J = 7.19$  Hz). *trans*-1-Methoxy 2-methylcyclohexane (**36**);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.35(s, 3H,  $\text{OCH}_3$ ), 2.65(td, 1H,  $J_{aa} = 9.75, 9.75$  Hz,  $J_{ae} = 4.02$  Hz), 2.11-2.06(m, 1H), 1.78-1.03(m, 8H), 0.98(d, 3H,  $\text{CH}_3$ ,  $J = 6.48$  Hz).

*The photo-NOCAS reaction: methyl 4-cyanobenzoate (22), 1-methylcyclohexene (19), in acetonitrile-methanol-d.*

The photo-NOCAS reaction was carried out in deuterated methanol, and the ethers were analysed by GC-MS (SIM) to determine the percentage of incorporation. The results are shown in Table 5.1.

**Table 5.1** Mass spectral data for the ethers **36** *cis* and *trans*, and **37** formed during the photo-NOCAS reaction of methyl 4-cyanobenzoate (**22**) with 1-methylcyclohexene (**19**)

	<b>36 <i>trans</i></b>			<b>36 <i>cis</i></b>			<b>37</b>		
	<b>M<sup>+</sup></b>								
ions <i>m/z</i> <sup>a</sup>	128	129	130	128	129	130	128	129	130
expected %	100	8.8	0.6	100	8.8	0.6	100	8.8	0.6
authentic sample	100	8.2	0.5	100	7.8	0.7	100	8.5	-
in CH <sub>3</sub> CN:CH <sub>3</sub> OH	100	10	1	100	8	0.6	100	10	-
in CH <sub>3</sub> CN:CH <sub>3</sub> OD	100	31	3	100	43	4	100	17	2
% incorporation			18		25		7		

<sup>a</sup>The mass spectra were recorded using selective ion monitoring programme (GC-MS).

*Irradiation of methyl 4-cyanobenzoate (22) and 2,3-dimethyl-2-butene (2) in benzene.*

A solution of the **22** (2.40 g, 0.015 mol) and **2** (3.5 mL, 0.029 mol) in benzene (150 mL) was irradiated through Pyrex for 186 h. Separation of the mixture by MPLC (20% diethyl ether/hexanes) gave the oxetane (**41**) as a colourless oil (0.204 g,  $8.30 \times 10^{-4}$  mol, 12.4%, 45% conversion of the ester). On standing, the oxetane was readily converted into two ketones (**43:42**, 1:1.3) which were characterised.

**41**: ir (liq. film, NaCl)  $\nu$ : 3020(m), 2980(s), 2950(m), 2255(s, sharp), 1485(w), 1410(m), 1395(m), 1285(s), 1180(m), 1115(vs), 1040(m), 1020(s), 1005(s), 970(s), 945(m), 845(vs);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.67(d, 2H,  $J = 8.22$  Hz), 7.55(broad, 2H), 3.00(s, 3H,  $\text{OCH}_3$ ), 1.53(s, 3H), 1.29(s, 3H), 1.21(s, 3H), 0.67(s, 3H);  $^{13}\text{C}$  nmr (75.47 MHz,  $\text{CDCl}_3$ , DEPT)  $\delta$ : 144.95(s), 131.85(d), 127.62(d), 118.77(s), 111.80(s), 108.32(s), 85.07(s), 49.25(q), 46.58(s), 26.31(q), 24.55(q), 22.46(q), 17.79(q); ms  $m/z$ : 230( $\text{M}^{+}$ , 0.1), 214(2), 187(48), 186(37), 172(24), 156(9), 130(74), 116(23), 102(72), 84(100), 83(21), 75(20), 69(98), 55(32), 51(18).

**42**: mp 46.9–48.3°C [lit.(152) 45–47°C];  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.006 MHz)  $\delta$ : 8.04(d, 2H,  $J = 8.1$  Hz), 7.78(d, 2H,  $J = 8.1$  Hz), 3.53(septet, 1H,  $J = 6.8$  Hz), 1.23(d, 6H,  $J = 6.8$  Hz);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 90.784 MHz)  $\delta$ : 202.90(s), 139.46(s), 132.51(d), 128.71(d), 117.89(s), 116.21(s), 35.91(d), 18.83(q); ms  $m/z$ : 173(12), 131(16), 130(100), 103(22), 102(57), 76(16), 75(21), 51(18).

**43**: ir (liq. film, NaCl)  $\nu$ : 2990(m), 2940(w), 2235(s), 1685(vs), 1640(m), 1380(m), 1245(s), 960(m), 880(m), 835(m);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.33(d, 2H,  $J = 8.3$  Hz), 7.67(d, 2H,  $J = 8.3$  Hz), 5.11(s, 1H), 5.07(s, 1H), 1.75(s, 3H), 1.39(s, 6H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 75.47 MHz)  $\delta$ : 202.86(s), 148.69(s), 140.23(s), 131.97(d), 129.30(d), 118.04(s), 115.36(s), 111.75(t), 53.06(s), 25.54(q), 20.37(q); ms  $m/z$ : 214(3), 213( $\text{M}^{+}$ , 15), 198(27), 170(7), 130(66), 102(43), 83(100), 75(14), 55(88); Exact mass calcd. for  $\text{C}_{14}\text{H}_{15}\text{NO}$ : 213.1154, found 213.1150.

*Irradiation of tert-butyl 4-cyanobenzoate (22a) and 2,3-dimethyl-2-butene (2) in acetonitrile-methanol.*

A solution of (22a) (1.794 g,  $8.83 \times 10^{-3}$  mol) and 2 (2.14 mL,  $1.80 \times 10^{-2}$  mol) in acetonitrile:methanol (3:1, 90 mL) was irradiated through pyrex (450-W) for 120 h. The photolysate was distilled at reduced pressure, to give a residual red solid which was resolved using DCFC. Elution using 20% EtOAc/CH<sub>2</sub>Cl<sub>2</sub> solvent gave the starting ester (1.656 g, 7.7% conversion) and cyclic imine (23a) (0.070 g,  $2.43 \times 10^{-4}$  mol, 36%).

**23a:** ir (liq. film, NaCl)  $\nu$ : 3240(w, broad), 2980(m), 2980(m), 1720(vs), 1700(m), 1370(m), 1300(s), 1250(s), 1165(vs), 1115(m), 835(w); <sup>1</sup>H nmr (361.01 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.98(m, 2H, Ar-H and N-H), 7.84(d, 1H, J = 7.79 Hz), 7.77-7.76(m, 1H), 1.63(s, 9H), 1.20(s, 6H), 1.13(s, 6H); <sup>13</sup>C nmr (75.47 MHz, DEPT, CDCl<sub>3</sub>)  $\delta$ : 188.96(s), 165.39(s), 157.19(s), 138.11(s), 135.70(s), 128.52(d), 124.06(d), 122.70(d), 81.49(s), 52.15(s), 46.49(s), 28.15(s), 28.15(q, *tert*-butyl), 25.42(q), 22.58(q); ms *m/z*: 288(M<sup>+</sup>, +1, 4), 287(M<sup>+</sup>, 18), 272(28), 231(10), 217(39), 216(100), 214(24), 171(20), 57(24).

Amine (23a) (0.031 g,  $1.080 \times 10^{-4}$  mol) was stirred at room temperature in acetone (5 mL) with a trace amount of HCl (1M) for 15 minutes. The sample was evaporated at reduced pressure, dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and passed down a short silica column (Sep-pak®). Further elution was carried out using CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The collected solvent was evaporated to give ketone 24a as a colourless oil (0.0145 g, 46%).

**24a:** ir (liq. film, NaCl)  $\nu$ : 2980(m), 2940(w), 1720(vs), 1370(m), 1310(m), 1285(m), 1255(m), 1165(s), 960(w); <sup>1</sup>H nmr (361.01 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.09(s, broad, 1H), 7.97(dd, 1H, 8.00 Hz, 1.04 Hz), 7.73(d, 1H, 8.00 Hz), 1.62(s, 9H), 1.25(s, 6H), 1.09(s, 6H); <sup>13</sup>C nmr (90.78 MHz, CDCl<sub>3</sub>)  $\delta$ : 210.82(s), 165.18(s), 161.39(s), 137.42(s), 136.32(s), 128.53(d), 124.42(d), 123.70(d), 81.87(s), 54.16(s), 44.93(s), 28.15(q), 26.22(q), 21.61(q); ms *m/z*: 289(5), 288(M<sup>+</sup>, 24), 232(36), 218(24), 217(100), 215(24), 172(16), 129(18), 128(24), 115(21), 57(40); Exact mass calcd. for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>: 288.1725, found 288.1730. The *tert*-butyl ketone (24a) was

also converted to compound **24** by heating in MeOH/HCl (1M) at 70°C for 24 h. The product was identical (GC-MS, retention time and mass spectrum) to an authentic sample.

*Irradiation of tert-butyl 4-cyanobenzoate (22a) and 2,3-dimethyl-2-butene (2) in benzene.*

A solution of the **22a** (1.6 g, 0.008 mol) and **2** (2 eq.) in dry benzene (80 mL) was irradiated through Pyrex (1 kW lamp) for 105 h (9.6% conversion of the ester). Analysis (GC-MS) of the reaction mixture showed only the presence of the cyclic imine (**23a**) and ketone (**24a**).

*Irradiation of methyl 4-cyanobenzoate (22) and 2-methylpropene (44) in benzene.*

A solution of **22** (1.454 g,  $9.02 \times 10^{-3}$  mol) and **29** ( $2.0 \times 10^{-2}$  mol) in benzene (90 mL) was irradiated through Pyrex. Analysis of the photolysate indicated an inefficient reaction occurred. The product isolated in low yield by DCFC has been assigned structure **45**, (a colourless oil) 1%; ir (liq. film, NaCl)  $\nu$ : 2980(s), 28880(m), 2240(s, sharp), 1605(m), 955(s), 820(m);  $^1\text{H}$  nmr (361.01 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.64(d, 2H,  $J = 7.76$  Hz) (see description of the VT work chapter 2), 7.35(broad signal, 2H), 4.56(s, 1H), 4.42(s, 1H), 4.46(d, 1H,  $J = 5.51$  Hz), 4.12(d, 1H,  $J = 5.51$  Hz), 3.16(d, 1H,  $J = 13.95$  Hz), 2.56(d, 1H,  $J = 14.01$  Hz), 1.45(s, 3H), 1.34(s, 3H), 0.78(s, 3H);  $^{13}\text{C}$  nmr (75.47 MHz, DEPT,  $\text{CDCl}_3$ )  $\delta$ : 148.74(s), 141.21(s), 131.55(d), 126.00(d), 119.07(s), 114.95(t), 110.25(s), 92.94(t), 44.44(t), 42.88(s), 25.94(q), 23.75(q), 21.85(q); ms  $m/z$ : 241(0.1), 211(5), 196(22), 186(86), 168(20), 131(19), 130(100), 116(24), 102(83), 75(16), 56(49), 55(20), 51(19).

*Alkyl Grignard and lithium study.*

*Typical reaction*

The electron acceptor (1,4-dicyanobenzene (1), methyl 4-cyanobenzoate (22)) was dissolved in freshly distilled THF and cooled to  $-84^{\circ}\text{C}$  (EtOAc-liquid nitrogen slush bath). The Grignard or alkyl lithium reagent was added drop-wise under nitrogen atmosphere. The resulting solution was stirred at low temperature for 1 h, then at room temperature for 1h. The reaction was quenched by the addition of saturated ammonium chloride solution. The mixture was stirred for 15 minutes, extracted with  $\text{CH}_2\text{Cl}_2$ . The combined extracts were washed with  $\text{H}_2\text{O}$  and dried over  $\text{MgSO}_4$ . The solution was filtered and concentrated by rotary evaporation. The crude mixture was made up to 250 mL with  $\text{CH}_2\text{Cl}_2$ . A 25 mL aliquot, with a known amount of cyclododecane (approx. 0.013 g), was made up to 50 mL with  $\text{CH}_2\text{Cl}_2$ . This solution was then analysed by GC-FID.

The following samples were prepared for GC-FID calibration, in order to calculate the yields of the reactions. They were isolated from the crude reaction mixtures.

1-(4-cyanophenyl)-2,2-dimethyl-1-propanone (48): ir (liq. film, NaCl)  $\nu$ : 2980(m), 2245(m), 1685(s), 1480(m), 1280(m), 1195(m), 1175(w), 950(m), 840(m);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.027 MHz)  $\delta$ : 7.72(s, 4H), 1.34(s, 9H); ms  $m/z$ : 187(5), 131(19), 130(28), 103(22), 130(28), 103(22), 102(24), 75(12), 57(100).

50: recrystallisation from MeOH affords needles, mp  $86.6\text{--}87.3^{\circ}\text{C}$ ; ir (KBr)  $\nu$ : 2940(m), 2840(m), 2200(s), 1605(s), 1460(s), 1405(m), 1355(m), 1275(m), 1200(s), 1015(m), 995(m), 950(s), 900(s), 815(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 300.13 MHz)  $\delta$ : 6.83(m, 1H), 6.75-6.74(m, 1H,  $J = 4.7$  Hz), 3.05-3.00(m, 2H), 2.97-2.92(m, 1H), 1.06(s, 9H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 90.785 MHz)  $\delta$ : 143.94(d,  $J = 165.1$  Hz), 142.38(d,  $J = 166.4$  Hz), 119.16(s), 117.73(s), 113.13(s), 110.20(s), 48.61(d,  $J = 129.2$  Hz), 39.20(s), 29.12(t,  $J = 132.6$  Hz), 27.50(q,  $J = 125.2$  Hz); ms  $m/z$ : no  $\text{M}^{+}$ , 184(0.2, loss of  $\text{H}_2$ ), 169(1.5), 130(5), 129(16), 128(10), 102(11), 76(5), 75(6), 57(100), 51(8). Double irradiation experiments were performed in order to determine the

regiochemistry of the addition. The olefinic hydrogens collapsed to two singlets, and are therefore not coupled to each other, indicating a 1,4-diene. This was also in agreement with the uv spectrum which showed no long wavelength absorption.

Methyl 4-*tert*-butylbenzoate (**52**):  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.027 MHz)  $\delta$ : 7.97(d, 2H,  $J = 8.7$  Hz), 7.43(d, 2H,  $J = 8.7$  Hz), 3.88(s, 3H), 1.32(s, 9H); ms  $m/z$ : 193(4), 192(32), 178(24), 177(100), 161(21), 149(44), 145(10), 118(12), 117(16), 115(18), 105(24), 93(12), 91(25), 77(13), 59(21), 51(10).

Preparation of 1-[4-(1,1-dimethylethyl)phenyl]-2,2-dimethyl-1-propanone (**53**).

Procedure followed was that used by Pearson (153). Dry magnesium (2.43 g, 0.1 mol) and 1-bromo 4-*tert*-butylbenzene (21.7 g, 0.1 mol) in diethyl ether (75 mL) was placed in an ultrasonic bath for 1 h until all the metal had dissolved. Trimethylacetonitrile (8.3 g, 0.1 mol) in diethyl ether (10 mL) was added drop-wise to the solution. The mixture was refluxed for 2 h. An off-white precipitate was formed. The mixture was poured onto ice/HCl (6 M, 200 mL) and allowed to stand overnight. The organic layer was separated, and the aqueous layer was extracted with ether (3 x 100 mL). The combined organic layers were washed with dil. HCl (2 x 100 mL), sat. sodium bicarbonate (2 x 100 mL) and  $\text{H}_2\text{O}$  (2 x 100 mL). The solution was dried and concentrated at reduced pressure to give a yellow liquid. Fractional distillation at reduced pressure gave the desired ketone in 34% yield; bp 90-95°C, 0.1 mmHg [lit 103-106°C, 1 mmHg (153)]; ir (liq. film, NaCl)  $\nu$ : 2980(m), 2880(m), 1660(s), 1600(m), 1460(s), 1390(m), 1355(s), 1270(s), 1200(m), 1170(s), 1100(m), 945(s), 830(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.027 MHz)  $\delta$ : 7.40(d, 2H,  $J = 8.5$  Hz), 7.73(d, 2H,  $J = 8.5$  Hz), 1.36(s, 9H), 1.31(s, 9H); ms  $m/z$ : 218(3), 162(48), 161(100), 146(25), 118(24), 117(12), 115(12), 105(11), 91(24), 77(12), 57(21).

2-(4-Cyanophenyl)-2-propanol (**54**): ir (liq. film)  $\nu$ : 3450(s, broad), 2990(m), 2250(s), 1600(m), 1170(m), 1090(m), 945(m), 823(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 60 MHz)  $\delta$ : 7.6(s, 4H), 2.9(s, 1H, exch.), 1.6(s, 6H); ms  $m/z$ : 161(2), 147(11), 146(100), 102(11), 75(11), 59(14), 51(11).



*Ultraviolet absorption studies*

Ultraviolet absorption studies were carried out in acetonitrile:methanol (3:1) solution, (solvent system used in the photo-NOCAS reaction), to determine if there were charge transfer (CT) complexes present during the irradiations. A stock solution of acceptor (0.1 M) was used for this study. The absorptions were studied at 310 nm, where **1**, **22**, and **22a** show no absorbance at this concentration. The absorbance was studied as a function of increasing olefin concentration (0.0 M - 2.0 M).

In order to carry out the determination of the association constant, the concentration of the acceptor was made 0.010 M while the concentration of the olefin was varied over the range 0.101 - 0.404 M, in keeping with the assumption used in the derivation of the Benesi-Hildebrand equation. In order to maintain constant solvent characteristics, the total number of moles added to the stock solutions was kept constant by the co-addition of n-hexane. The total concentration of added alkene and hexane was 0.404 M, Table 5.2.

**Table 5.2** Experimental conditions used for Benesi-Hildebrand analysis of uv data.

Sample#	alkene		hexane		total added
	[ $\epsilon$ ]	mol/ $10^{-3}$	Vol/mL	mol/ $10^{-3}$	mol/ $10^{-3}$
1	0.101	1.01	0.53	4.04	4.04
2	0.202	2.02	0.40	3.03	4.04
3	0.303	3.03	0.26	2.02	4.04
4	0.404	4.04	0.13	1.01	4.04
5	0.505	5.05	0.00	0.00	4.04

5 mL of stock solution (0.02 M) was pipetted into 10 mL volumetric.

The alkene and hexane were then added. The solution was made up to the mark with  $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$  (3:1).

*Preparation of 4-(methylsulphonyl)benzonitrile (58)*

This was prepared using the thiol oxidation method of Bordwell (154). Hydrogen peroxide (30%, 30 mL, 0.26 mol) was added drpwise to a solution of 4-(methylthio)benzonitrile (Aldrich, 10.0 g,  $6.7 \times 10^{-2}$  mol) in glacial acetic acid (40 mL). After the addition, the mixture was heated for 2h at 85°C. The solution was cooled to room temperature and poured into water (250 mL). The sulphone was filtered and washed copiously with cold water. The dry solid was recrystallised twice from 95% EtOH to give the sulphone (58) as colourless needles (9.2 g, 76%): mp 143.8-144.8°C [lit. 141°C (155)]; ms  $m/z$ : 183(0.5), 182(1.5), 181(13), 166(19), 119(66), 102(100), 76(16), 75(31), 63(21), 51(22).

*Preparation of 4-(trifluoromethyl)benzonitrile (60).*

4-Bromobenzotrifluoride (18.0 g, 0.08 mol) and copper(I) cyanide (7.9 g, 0.09 mol) were heated in DMF (100 mL) at 100°C for 24 h. The mixture was cooled to room temperature and poured into conc. aqueous ammonia (100 mL). The mixture was extracted with diethyl ether (4 x 200 mL), and the combined organic extracts were washed with aqueous ammonia (3 x 200 mL) and H<sub>2</sub>O (3 x 200 mL). The ether layer was dried over MgSO<sub>4</sub> and evaporated to give 11.2 g of crude semi-solid. This was distilled (114-116°C) to give a colourless semi-solid (58) (7.8 g, 57%): ms  $m/z$ : 172(8), 171(100), 170(27), 121(61), 102(13), 76(13), 75(27), 69(13), 51(16).

*Preparation of (4-cyanophenyl)trimethylammonium iodide (61).*

4-(Dimethylamino)benzonitrile (2.00 g, 0.0137 mol) was refluxed in MeI (25 g) for 7 days, after which time no more starting material was present. The excess MeI was removed by rotary evaporation at reduced pressure. The crude remaining yellow solid was recrystallised twice from MeOH to give the desired salt (1.89 g, 48%): mp 159.6-160.4°C [lit. 181°C (156)]; ir (nujol, NaCl)  $\nu$ : 2240(w, sharp), 1605(w), 1120(m), 945(s), 930(s), 835(s), 805(m); <sup>1</sup>H nmr (D<sub>2</sub>O, 361.006 MHz)  $\delta$ : 7.94-7.89(A<sub>2</sub>B<sub>2</sub>, 4H), 3.57(s, 9H).

*The photo-NOCAS reaction: methanol, 4-cyanobenzaldehyde (68), and 2,3-dimethyl-2-butene (2).*

A mixture of 4-cyanobenzaldehyde (**69**) (2.098 g, 0.016 mol) and **2** (3.8 mL, 0.032 mol) in acetonitrile-methanol solution (3:1, 160 mL) was degassed and irradiated through Pyrex using a 1 kW lamp for 5 h. The reaction was stopped after 92% conversion of **69**, based on recovered aldehyde. The solvent was removed by evaporation at reduced pressure leaving a yellow gum (5.592 g). The mixture crude mixture was resolved using MPLC and DCFC. Four products were isolated: two 1:1 (olefin : aromatic) alcohols, **70** and **71**; oxetane **72**; and a 1:1:1 (nucleophile : olefin : aromatic) adduct **73**.

**70** (15%): ir (liq. film, NaCl)  $\nu$ : 3480(s, broad), 3010(m), 2885(m), 2940(s), 2260(vs), 1625(m), 1520(w), 1070(w), 1035(w), 845(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.008 MHz)  $\delta$ : 7.58(d, 2H,  $J$  = 8.3 Hz), 7.45(d, 2H,  $J$  = 8.1 Hz), 4.79(dd, 1H,  $J$  = 8.64, 5.3 Hz), 2.68(broad, 1H, exch.), 2.58(dd, 1H,  $J$  = 13.5, 8.7 Hz), 2.27(dd, 1H,  $J$  = 13.4, 5.2 Hz), 1.67(s, 6H), 1.57(s, 3H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 90.785 MHz)  $\delta$ : 149.82(s), 132.01(d), 129.94(s), 126.32(d), 122.81(s), 118.92(s), 110.75(s), 71.56(d), 44.91(t), 20.86(q), 20.56(q), 18.58(q); ms  $m/z$ : 216(0.1), 215( $M^+$ ., 0.6), 133(50), 132(23), 104(23), 102(9), 100(23), 84(76), 83(86), 77(22), 69(43), 67(11), 56(6), 55(100), 51(12); Exact mass: calcd. for  $\text{C}_{14}\text{H}_{17}\text{NO}$ : 215.1310; found 215.1308.

**71** (5.0%): ir (KBr)  $\nu$ : 3500(broad,s), 2980(s), 2900(m), 2240(vs), 1645(w), 1645(m), 1620(m), 1515(m), 1385(m), 1075(m), 885(m), 850(m);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.006 MHz)  $\delta$ : 7.59(d, 2H,  $J$  = 8.4 Hz), 7.44(d, 2H,  $J$  = 8.3 Hz), 5.06(m, 1H,  $J$  = 1.4, 1.5 Hz), 4.94(m, 1H,  $J$  = 1.4, 0.7 Hz), 4.65(s, 1H), 2.34(s, 1H, exch.), 1.86(dd, 3H,  $J$  = 1.5, 0.7 Hz), 0.95(s, 3H), 0.94(s, 3H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 90.784 MHz)  $\delta$ : 149.56(s), 145.81(s), 131.14(d), 128.58(d), 118.90(s), 114.02(t), 110.95(s), 76.74(d), 44.55(s), 23.86(q), 20.09(q), 19.70(q); ms  $m/z$ : 133(48), 132(22), 131(34), 130(58), 104(22), 103(11), 102(45), 84(77), 83(52), 77(27), 76(24), 75(20), 69(90), 67(14), 56(11), 55(100), 53(14), 51(25); Anal. Calcd. for  $\text{C}_{14}\text{H}_{17}\text{NO}$ : C 78.10, H 7.96, N 6.51; found C 77.72, H 7.83, N 6.44.

**72** (25%): ir (liq. film, NaCl)  $\nu$ : 3010(w), 3000(m), 2950(m), 2900(w), 2260(s), 1635(m), 1470(m), 1395(s), 1165(m), 1035(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.007 MHz)  $\delta$ : 7.64(d, 2H,  $J = 8.3$  MHz), 7.39(d, 2H,  $J = 8.0$  Hz), 5.43(s, 1H), 1.52(s, 3H), 1.30(s, 3H), 1.28(s, 3H), 0.69(s, 3H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 90.784 MHz)  $\delta$ : 146.02(s), 131.86(d), 125.74(d), 118.94(s), 110.69(s), 86.06(s), 85.94(d), 44.21(s), 25.03(q, 2 overlapping), 23.27(q), 20.03(q); ms  $m/z$ : 157(24, loss of acetone), 142(46), 131(19), 130(39), 116(20), 102(37), 84(100), 69(100).

**30** (15 %): structural determination above.

*Irradiation of a benzene solution of 4-cyanobenzaldehyde (69) and 2,3-dimethyl-2-butene (2).*

A solution of **68** (1.968g, 0.015 mol) and **2** (3.5 mL, 0.029 mol) in benzene (150 mL), was irradiated through pyrex for 7h. The yellow solution was decanted from the irradiation vessel leaving a white solid coating the inside of the Pyrex irradiation vessel. This solid was soluble in acetone and was removed from the glass (0.4413g). It remains unidentified. The photosylate was evaporated to yield a yellow oil. This was purified by MPLC (silica gel,  $\text{CH}_2\text{Cl}_2$ ), giving three products: two alcohols, **70** (16%), **71** (5%), and oxetane **72** (33%).

*The photo-NOCAS reaction: methanol, 4-cyanobenzophenone (69), and 2,3-dimethyl-2-butene (2).*

A solution of **69** (1.036 g,  $5.00 \times 10^{-3}$  mol) and **2** (1.19 mL,  $1 \times 10^{-2}$  mol) in acetonitrile-methanol (3:1, 50 mL) was degassed and irradiated through pyrex for 6.5 h (69.3% conversion, based on recovered **69**). Removal of the solvent at reduced pressure gave a yellow oil (1.497 g). The mixture was partially resolved using DCFC (silica gel, 15% diethyl ether/hexanes), then further resolved using MPLC (silica gel, 15% diethyl ether/hexanes). An oxetane **74** and an alcohol (**73**) 1:1 (olefin : aromatic) were isolated.

**73** (25%): ir (liq. film, NaCl)  $\nu$ : 3510(broad), 3080(w), 3015(m), 2940(m), 2875(m), 2250(vs, sharp), 1625(m), 1520(m), 1510(m), 1465(s), 1180(w), 1075(w), 835(s), 770(m),

735(m), 705(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.007 MHz)  $\delta$ : 7.63-7.23(9H, m), 3.24(d, 1H,  $J = 13.42$  Hz), 3.17(d, 1H,  $J = 13.42$  Hz), 2.85(s, 1H, exch.  $\text{D}_2\text{O}$ ), 1.68(s, 6H), 1.18(s, 3H);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 75.468 MHz)  $\delta$ : 153.19(s), 146.60(s), 132.77(s), 131.78(d), 128.29(d), 127.13(d), 126.76(d), 125.77(d), 122.70(s), 118.90(s), 110.29(s), 76.72(s), 46.40(t), 21.32(q), 21.06(q), 20.22(q); ms  $m/z$ : 273(15), 258(100), 243(22), 208(62), 130(65), 105(13), 102(27), 84(31), 77(19), 69(14), 55(12).

**74** (9%): ir (liq. film, NaCl)  $\nu$ : 3000(s), 2970(s), 2930(m), 2240(vs, CN), 1610(m), 1450(m), 1380(m), 1150(s), 1010(s), 845(m), 820(m), 720(s), 690(s);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361 006 MHz)  $\delta$ : 7.68-7.18(9H, m), 1.27(3H, s), 1.26(3H, m), 1.12(3H, m), 1.08(3H, s);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ , 75.468 MHz)  $\delta$ : 151.72(s), 144.77(s), 131.55(d), 127.88(d), 126.63(d), 126.20(d), 125.29(d), 118.92(s), 109.96(s), 88.88(s), 84.24(s), 47.01(s), 25.86(q, 2  $\text{CH}_3$ 's), 23.68(q), 23.55(q); ms  $m/z$ : 233(22), 218(19), 204(8), 190(9), 140(7), 130(6), 115(7), 105(9), 102(7), 84(100), 77(14), 69(62); ms  $m/z$ : no  $\text{M}^+$  observed, 233(9.4, loss of acetone), 218(11), 84(100), 77(10), 69(61).

*Irradiation of a benzene solution of 4-cyanobenzaldehyde (68) and 2-methylpropene (44).*

2-Methyl-2-propene (**44**) ( $3.736\text{ g}$ ,  $6.66 \times 10^{-2}\text{ mol}$ ) was bubbled into a degassed solution of **68** ( $1.178\text{ g}$ ,  $8.98 \times 10^{-3}\text{ mol}$ ) in benzene ( $90\text{ mL}$ ). The mixture was irradiated for 4h (78.1% conversion of **68**), through pyrex (450 W lamp). Evaporation of the solvent at reduced pressure gave a yellow oil ( $1.511\text{ g}$ ). This mixture was resolved using DCFC, 5% MeOH/ 20% EtOAc/ 75% hexanes. Oxetanes **75** and **76** (**75:76**, 5.2:1) were isolated with a combined yield 70%, ( $0.919\text{ g}$ ,  $0.906 \times 10^{-3}\text{ mol}$ , based on recovered starting material).

**75** (59%): ir (liq. film, NaCl)  $\nu$ : 2975(s), 2945(m), 2885(s), 2250(vs), 1615(m), 1510(m), 1470(m), 1000(m), 990(s), 975(vs), 950(m), 850(m), 840(m), 790(m);  $^1\text{H}$  nmr ( $\text{CDCl}_3$ , 361.007 MHz)  $\delta$ : 7.67(2H, d,  $J = 8.27\text{ Hz}$ ), 7.40(2H, d,  $J = 8.32\text{ Hz}$ ), 5.53(1H, s), 4.55(1H, d,  $J = 5.51\text{ Hz}$ ), 4.26(1H, d,  $J = 5.46\text{ Hz}$ ), 1.44(3H, s), 0.78(3H, s);  $^{13}\text{C}$  nmr ( $\text{CDCl}_3$ ,

90.785 MHz)  $\delta$ : 145.62(s), 131.99(d), 125.63(d), 118.86(s), 110.97(s), 90.65(d), 81.30(t), 40.75(s), 26.83(q), 22.48(q); ms  $m/z$ : 188(0.1), 187( $M^{+}$ , 0.3), 157(24,  $M^{+}$  - 30, loss of formaldehyde), 156(11), 142(41), 140(10), 132(37), 130(12), 116(20), 115(20), 102(19), 89(10), 76(11), 75(12), 63(10), 57(18), 56(100), 51(16); Anal. calcd. for  $C_{12}H_{13}NO$ : C 76.97, H 7.00, N 7.48; found C 76.75, H 7.01, N 7.39.

**76** (11%): ir (liq. film, NaCl)  $\nu$ : 2980(s), 2940(w), 2890(w), 2245(vs), 1610(m), 1510(w), 1510(w), 1450(w), 1370(s), 1270(m), 1145(m), 1000(s), 985(s), 965(s), 940(m), 835(s), 820(s);  $^1H$  nmr ( $CDCl_3$ , 361.007 MHz)  $\delta$ : 7.67(d, 2H,  $J$  = 8.3 Hz), 7.51(d, 2H,  $J$  = 8.4), 5.65(apparent triplet, 1H,  $J$  = 7.7 Hz), 2.85(dd, 1H,  $J$  = 8.3 Hz, 10.8 Hz), 2.33(dd, 1H,  $J$  = 7.4 Hz, 10.8 Hz), 1.60(s, 3H), 1.46(s, 3H);  $^{13}C$  nmr ( $CDCl_3$ , 90.784 MHz)  $\delta$ : 149.65(s), 132.28(d), 125.46(d), 118.88(s), 110.95(s), 81.15(s), 73.61(d), 42.26(t), 30.48(q), 28.87(q); ms  $m/z$ : 187( $M^{+}$ , 0.2), 132(15), 131(16), 130(31), 129(26,  $M^{+}$  - 50, loss of acetone), 103(8), 102(28), 76(14), 75(13), 56(100), 51(14).

*Irradiation of a benzene solution of 4-cyanobenzophenone (69) and 2-methylpropene (44).*

A solution of **69** (0.345 g,  $1.665 \times 10^{-3}$  mol) and 2-methylpropene (**44**) (0.5 mL, excess) in benzene (17 mL) was irradiated with a 1 kW lamp for 8.5 h (86.3% conversion of **69**). The solvent was evaporated at reduced pressure to give a yellow oil (0.444 g). This was resolved using DCFC (silica gel) with 10% ethyl acetate in hexane eluent. Oxetane **77** was isolated as an oil which solidified on standing.

**77** (79%): recrystallised from MeOH mp 78.4-79.1 °C; ir (liq. film, NaCl)  $\nu$ : 3070(w), 2980(m), 2940(m), 2880(m), 2245(s, sharp), 1610(m), 1510(w), 1500(w), 1470(m), 1450(m), 1410(w), 1395(w), 1375(w), 995(s, sharp), 975(s), 820(s), 745(s), 725(m), 695(s);  $^1H$  nmr ( $CDCl_3$ , 361.007 MHz)  $\delta$ : 7.64-7.20(m, 9H), 4.29(d, 1H, AB quartet,  $J$  = 5.29 Hz), 4.26(d, 1H, AB quartet,  $J$  = 5.29 Hz), 1.16(s, 3H), 1.11(s, 3H);  $^{13}C$  nmr ( $CDCl_3$ , 90.782 MHz)  $\delta$ : 149.77(s), 143.00(s), 131.78(d), 128.16(d), 127.01(d), 126.07(d), 125.07(d), 118.76(s),

110.52(s), 92.94(s), 78.66(t), 44.28(s), 25.67(q), 25.58(q); ms  $m/z$ : 234(20), 233(100), 232(15), 219(12), 218(62), 217(16), 208(47), 204(26), 203(20), 191(12), 190(25), 140(21), 130(23), 115(15), 105(23), 91(14), 77(15), 56(23); Anal. calcd. for  $C_{13}H_{17}NO$ : C 82.10, H 6.51, N 5.32; found: C 82.23, H 6.70, N 5.32.



## Appendix

15

### *Data Collection*

A suitable size crystal was mounted on a glass fibre. An Enraf-Nonius CAD4 diffractometer was used to measure the unit cell dimensions and to collect the data. The unit cell constants were obtained by least squares analysis of the diffractometer setting angles of 25 well centered reflections in the range  $2\theta = 24\text{--}30^\circ$ . The intensities were reduced to a standard scale using routine procedures (157). Lorentz and polarization corrections were applied and absorption corrections (158) were performed. Scattering factors for neutral atoms were taken from reference (159) and were corrected for the real part of anomalous dispersion. The structure was solved by using SHELXS-86 (160), calculations and refinements were performed by using SHELX-76 (161).

### *Structural analysis and refinement*

The systematically absent reflections confirmed the space group as  $P2_1/c$ . The positions of most atoms was determined from a E-map (SHELXS-86) and the remaining non-hydrogen atoms were located in subsequent difference-Fourier syntheses. The structure was refined initially by a full-matrix least-squares procedure with independent isotropic temperature factors on the atoms. Absorption corrections were then applied. Hydrogen atoms were placed in their geometrically calculated positions [ $d(\text{C-H}) = 1.08 \text{ \AA}$ ] and then refined riding on carbon atoms. The final refinements were with anisotropic temperature factors on the non-hydrogen atoms and individual isotropic temperature factors on the hydrogen atoms. A 2-block matrix least-squares method was employed. The function minimised was  $\sum w(|F_o| - |F_c|)^2$  where  $w$  is the weight. The different weighting schemes were tested but the best results were obtained when the unit weights were used during refinement. Final  $R = 0.0624$ ,  $R_w = 0.0559$ . No correction for extinction was applied. The final difference map had no recognizable residual features. The figures were produced with CHEMGRAF (162).

Table 5.3 Interatomic Distances (Å) for (C<sub>30</sub>H<sub>31</sub>O<sub>6</sub>)(NH<sub>4</sub>) (27)

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C(1)	-C(2)	1.479( 8)
C(1)	-O(1)	1.225( 7)
C(1)	-O(2)	1.290( 7)
C(2)	-C(3)	1.398( 8)
C(2)	-C(7)	1.393( 8)
C(3)	-C(4)	1.394( 8)
C(4)	-C(5)	1.389( 8)
C(5)	-C(6)	1.390( 8)
C(5)	-C(8)	1.464( 8)
C(6)	-C(7)	1.388( 8)
C(6)	-C(9)	1.510( 8)
C(8)	-C(14)	1.500( 8)
C(8)	-O(3)	1.226( 7)
C(9)	-C(10)	1.522( 8)
C(9)	-C(14)	1.535( 8)
C(10)	-C(11)	1.533( 9)
C(11)	-C(12)	1.517( 9)
C(12)	-C(13)	1.505( 9)
C(13)	-C(14)	1.569( 8)
C(14)	-C(15)	1.522( 9)

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Table 5.4 Interbond Angles (degrees) for  $(C_{30}H_{31}O_6)(NH_4)$  (27)

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C(2)	-C(1)	-O(1)	120.6 ( 5)
C(2)	-C(1)	-O(2)	115.8 ( 5)
O(1)	-C(1)	-O(2)	123.6 ( 6)
C(1)	-C(2)	-C(3)	121.8 ( 5)
C(1)	-C(2)	-C(7)	117.7 ( 5)
C(3)	-C(2)	-C(7)	120.5 ( 5)
C(2)	-C(3)	-C(4)	119.8 ( 5)
C(3)	-C(4)	-C(5)	118.9 ( 5)
C(4)	-C(5)	-C(6)	121.7 ( 5)
C(4)	-C(5)	-C(8)	129.8 ( 5)
C(6)	-C(5)	-C(8)	108.4 ( 5)
C(5)	-C(6)	-C(7)	119.1 ( 5)
C(5)	-C(6)	-C(9)	110.4 ( 5)
C(7)	-C(6)	-C(9)	130.4 ( 5)
C(2)	-C(7)	-C(6)	120.0 ( 5)
C(5)	-C(8)	-C(14)	107.7 ( 5)
C(5)	-C(8)	-O(3)	125.9 ( 5)
C(14)	-C(8)	-O(3)	126.3 ( 5)
C(6)	-C(9)	-C(10)	116.8 ( 5)
C(6)	-C(9)	-C(14)	103.4 ( 4)
C(10)	-C(9)	-C(14)	116.0 ( 5)
C(9)	-C(10)	-C(11)	112.4 ( 5)
C(10)	-C(11)	-C(12)	109.5 ( 5)
C(11)	-C(12)	-C(13)	110.5 ( 5)
C(12)	-C(13)	-C(14)	112.6 ( 5)
C(8)	-C(14)	-C(9)	103.2 ( 5)
C(8)	-C(14)	-C(13)	104.1 ( 5)
C(8)	-C(14)	-C(15)	115.0 ( 5)
C(9)	-C(14)	-C(13)	110.6 ( 5)
C(9)	-C(14)	-C(15)	113.4 ( 5)
C(13)	-C(14)	-C(15)	109.9 ( 5)

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Table 5.5 Torsional Angles (degrees) for  $(C_{30}H_{31}O_6)(NH_4)$  (27)

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O(1)	-C(1)	-C(2)	-C(3)	177.5 ( 4)
O(1)	-C(1)	-C(2)	-C(7)	-3.4 ( 7)
O(2)	-C(1)	-C(2)	-C(3)	-0.7 ( 7)
O(2)	-C(1)	-C(2)	-C(7)	178.4 ( 4)
C(1)	-C(2)	-C(3)	-C(4)	-178.9 ( 5)
C(1)	-C(2)	-C(7)	-C(6)	178.6 ( 5)
C(3)	-C(2)	-C(7)	-C(6)	-2.4 ( 7)
C(7)	-C(2)	-C(3)	-C(4)	2.1 ( 7)
C(2)	-C(3)	-C(4)	-C(5)	-1.5 ( 7)
C(3)	-C(4)	-C(5)	-C(6)	1.2 ( 7)
C(3)	-C(4)	-C(5)	-C(8)	178.0 ( 5)
C(4)	-C(5)	-C(6)	-C(7)	-1.4 ( 7)
C(4)	-C(5)	-C(6)	-C(9)	176.4 ( 4)
C(4)	-C(5)	-C(8)	-C(14)	167.1 ( 4)
C(4)	-C(5)	-C(8)	-O(3)	-10.7 ( 9)
C(6)	-C(5)	-C(8)	-C(14)	-15.8 ( 6)
C(6)	-C(5)	-C(8)	-O(3)	166.5 ( 6)
C(8)	-C(5)	-C(6)	-C(7)	-178.8 ( 5)
C(8)	-C(5)	-C(6)	-C(9)	-1.1 ( 6)
C(5)	-C(6)	-C(7)	-C(2)	1.9 ( 7)
C(5)	-C(6)	-C(9)	-C(10)	145.4 ( 5)
C(5)	-C(6)	-C(9)	-C(14)	16.7 ( 5)
C(7)	-C(6)	-C(9)	-C(10)	-37.2 ( 7)
C(7)	-C(6)	-C(9)	-C(14)	-165.9 ( 4)
C(9)	-C(6)	-C(7)	-C(2)	-175.3 ( 4)
C(5)	-C(8)	-C(14)	-C(9)	25.4 ( 5)
C(5)	-C(8)	-C(14)	-C(13)	-90.2 ( 5)
C(5)	-C(8)	-C(14)	-C(15)	149.5 ( 5)
O(3)	-C(8)	-C(14)	-C(9)	-156.9 ( 4)
O(3)	-C(8)	-C(14)	-C(13)	87.6 ( 5)
O(3)	-C(8)	-C(14)	-C(15)	-32.8 ( 7)
C(6)	-C(9)	-C(10)	-C(11)	-74.7 ( 6)
C(6)	-C(9)	-C(14)	-C(8)	-24.9 ( 5)
C(6)	-C(9)	-C(14)	-C(13)	86.0 ( 5)
C(6)	-C(9)	-C(14)	-C(15)	-150.0 ( 5)
C(10)	-C(9)	-C(14)	-C(8)	-154.0 ( 4)
C(10)	-C(9)	-C(14)	-C(13)	-43.2 ( 6)
C(10)	-C(9)	-C(14)	-C(15)	80.9 ( 5)
C(14)	-C(9)	-C(10)	-C(11)	47.5 ( 6)
C(9)	-C(10)	-C(11)	-C(12)	-55.1 ( 6)
C(10)	-C(11)	-C(12)	-C(13)	61.7 ( 6)
C(11)	-C(12)	-C(13)	-C(14)	-59.6 ( 6)
C(12)	-C(13)	-C(14)	-C(8)	159.2 ( 4)
C(12)	-C(13)	-C(14)	-C(9)	48.9 ( 6)
C(12)	-C(13)	-C(14)	-C(15)	-77.1 ( 5)

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## References

1. Weigert, F., *Z. Phys. Chem.*, **106**, 313 (1923).
2. Weiss, J. and Fischgold, H., *Z. Physik. Chem.*, **B32**, 135 (1936).
3. Eberson, L., *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Berlin (1987). (b) *Photo-induced Electron Transfer I, Topics in Current Chemistry*, **156**, ed. Mattay, J., Springer-Verlag, Berlin (1990).
4. (a) Mattay, J., *Synthesis*, **233** (1989). (b) Mariano, P. S. and Stavinoha, J. L., *Synthetic Organic Photochemistry*, chapter 3, ed., Horspool, W. M., Plenum Press, London (1984). (c) *Photoinduced Electron Transfer, Part C*, eds., Fox, M. A. and Chanon, M., Elsevier, New York (1988). (d) Mattes, S. L. and Farid, S., *Organic Photochemistry*, **6**, 233, ed., Padwa, A., Marcel Dekker, New York (1983).
5. Dessau R. M., Shih, S. and Heiba E. I., *J. Am. Chem. Soc.* **92**, 412 (1970).
6. Grace, J. A. and Symons, M. C. R. J., *Chem. Soc.*, 958 (1959).
7. Hughs, F., Kirk, R. D., and Patten, F. W., *J. Chem. Phys.*, **40**, 872 (1964).
8. Fry, A. J., *Synthetic Organic Electrochemistry*, Harper and Row, New York (1972).
9. Taube, H., *Electron Transfer REactions of Complex Ions in Solution*, London, Academic Press (1970).
10. *Photoinduced Electron Transfer II, Topics in Current Chemistry* **159**, ed., Mattay, J., Springer-Verlag, Berlin (1990).
11. Woodward, R. B., *J. Am. Chem. Soc.*, **64**, 3058 (1942).
12. (a) Bellville, D. J., Wirth, D. D. and Bauld, N. L., *J. Am. Chem. Soc.*, **103**, 718 (1981). (b) Fukuzumi, S. and Kochi, J. K., *Tetrahedron*, **38**, 1035 (1982).
13. Ashby, E. C. and Bowers, J. R., Jr., *J. Am. Chem. Soc.*, **103**, 2242 (1981).
14. (a) Eberson, L. and Radner, R., *Acta Chem. Scand.*, **B38**, 861 (1984). (b) Sankararaman, S. and Kochi, J. K. J., *J. Chem. Soc. Perkin Trans. 2*, **1** (1991). (c) Ridd, J. H., *J. Chem. Soc. Rev.*, **20**, 149 (1991).
15. Bertz, S. H., Dabbagh, G. and Majsce, A. M., *J. Am. Chem. Soc.*, **113**, 631 (1991).
16. Ashby, E. C., Coleman, D. T. III, Gamasa, M. P., *Tetrahedron Lett.*, **24**, 851 (1983).
17. Umento, K. and Okamura, N., *Bull. Chem. Soc. Jpn.*, **59**, 3047 (1986).
18. (a) Sawyer, D. T. and Roberts, J. L., Jr., *Acc. Chem. Res.*, **21**, 469 (1988). (b) Ballester, M. and Pascual, I., *J. Org. Chem.*, **56**, 841 (1991).

19. Bacaloglu, R., Blasko, A., Bunton, C., Dorwin, E., Ortega, F., and Zucco, C., *J. Am. Chem. Soc.*, **113**, 238 (1991).
20. Kavarnos, G. J., chapter 2 in reference 3b.
21. Rehm, D. and Weller, A., *Isr. J. Chem.*, **8**, 259 (1970).
22. Parker, V. D., *J. Am. Chem. Soc.*, **98**, 98 (1976).
23. Chen, E. C. M. and Wentworth, W. E., *J. Chem. Phys.*, **63**, 3186 (1975).
24. Mattay, J., *Tetrahedron*, **41**, 2405 (1985).
25. Mauzerall, D. C., *Photoinduced Electron Transfer, Part A*, eds., Fox, M. A. and Chanon, M., Elsevier, New York. (1988).
26. Miller, J. R., Beitz, J. V., and Huddleston, R. K., *J. Am. Chem. Soc.*, **106**, 5057 (1984).
27. Fox, M. A., *Adv. Photochem.*, **13**, 237 (1986).
28. (a) Goodson, B. E. and Schuster, G. B., *J. Am. Chem. Soc.*, **106**, 7254 (1984).  
(b) *Tetrahedron Lett.*, **27**, 3123 (1986).
29. Gould, I. R., Ege, D., Moser, J. E., and Farid, S., *J. Am. Chem. Soc.*, **112**, 4290 (1990).
30. Arnold, D. R. and Snow, M. S., *Can. J. Chem.*, **66**, 3012 (1988).
31. Mattes, S. L. and Farid, S., *J. Am. Chem. Soc.*, **108**, 7356 (1986).
32. (a) Fox, M. A., *Chem. Rev.*, **79**, 253 (1979). (b) Tolbert, L. M., *Organic Photochemistry*, ed. Padwa, A., **6**, Marcel Dekker, New York (1983). (c) Fox, M. A., *Adv. Photochem.*, eds. Volman, D. H., Hammond, G. S., and Gollick, K., Wiley, New York (1986).
33. Krogh, E. and Wan, P., *Photoinduced Electron Transfer, Topics in Current Chemistry*, **156**, Springer-Verlag, Heidelberg (1990).
34. Graetzel, M., *Acc. Chem. Res.*, **14**, 376 (1981).
35. Kropp, P. J., *Acc. Chem. Res.*, **17**, 131 (1984).
36. Beecroft, R. A., Davidson, R. S., Goodwin, D., and Pratt, J. E., *Tetrahedron*, **40**, 4487 (1984).
37. (a) Arnold, D. R., Du, X., and Henseleit, K., *Can. J. Chem.*, **69**, 839 (1991).  
(b) Popielarz, R. and Arnold, D. R., *J. Am. Chem. Soc.*, **112**, 3082 (1990).  
(c) Lamont, L. J. and Arnold, D. R., *Can. J. Chem.*, **68**, 390 (1990).
38. Ohashi, M., Furukawa, Y. and Tsujimoto, K., *J. Chem. Soc., Perkin Trans. 1*, 2613 (1980).
39. Bryce-Smith, D., Clarke, M. T., Gilbert, A., Klunklin, G., and Manning, C., *J. Chem. Soc., Chem. Commun.*, 916 (1971).

40. Tsujimoto, K., Miyake, K. and Ohashi, M., *J. Chem. Soc., Chem. Commun.*, 386 (1976).
41. Ohashi, M., Tsujimoto, K., and Kurukawa, Y., *J. Chem. Soc., Perkin Trans. 1*, 1147 (1979).
42. Lan, J. Y. and Schuster, G. B., *Tetrahedron Lett.*, **27**, 4261 (1986).
43. Borg, R. M., Arnold, D. R., and Cameron, T. S., *Can. J. Chem.*, **62**, 1785 (1984).
44. Arnold, D. R. and Du, X., *J. Am. Chem. Soc.*, **111**, 7666 (1989).
45. Cantrell, T. S., *J. Org. Chem.*, **42**, 4238 (1977).
46. (a) McCullough, J. J., Miller, R. C. and Wu, W.-S., *Can. J. Chem.*, **55** 2909 (1977).  
(b) Yang, N. C., Kim, B., Chiang, W., and Hamada, T., *J. Chem. Soc., Chem. Commun.*, 729 (1976).
47. Maroulis, A. J. and Arnold, D. R., *J. Chem. Soc., Chem. Commun.*, 351 (1979).
48. Arnold, D. R., Wong, P. C., Maroulis, A. J., and Cameron, T. S., *Pure Appl. Chem.*, **52**, 2609 (1980).
49. Nicholas, A. M. de P. and Arnold, D. R., *Can. J. Chem.*, **60**, 2165 (1982).
50. Arnold, D. R. and Maroulis A. J., *J. Am. Chem. Soc.*, **98**, 5932 (1976).
51. Neunteufel, R. A. and Arnold, D. R., *J. Am. Chem. Soc.*, **95**, 4080 (1978).
52. Maroulis, A. J., Shigemitsu, Y. and Arnold, D. R., *J. Am. Chem. Soc.*, **100**, 535 (1978).
53. Hixson, S. S., *J. Am. Chem. Soc.*, **94**, 2505 (1972).
54. Majima, T., Pac, C., Nakasone, A., and Sakurai, H., *J. Am. Chem. Soc.*, **103**, 4499 (1981).
55. Lewis, F. D. and DeVoe, R. J., *Tetrahedron*, **38**, 1069 (1982).
56. Mattes, S. L. and Farid, S., *J. Am. Chem. Soc.*, **108**, 7356 (1986).
57. Mattes, S. L. and Farid, S., *J. Am. Chem. Soc.*, **104**, 1454 (1982).
58. Fischer, H., *J. Am. Chem. Soc.* **108**, 3925 (1986).
59. (a) Mizuno, K., Pac, C., and Sakurai, H., *J. Am. Chem. Soc.*, **96**, 2993 (1974).  
(b) Pac, C. and Sakurai, H., *Chem Letts.*, 10667 (1976).
60. Okamoto, A., Snow, M. S., and Arnold, D. R., *Tetrahedron*, **42**, 6175 (1986).
61. Dinnocenzo, J. P., Todd, W. P., Simpson, T. R., and Gould, I. R., *J. Am. Chem. Soc.*, **112**, 2462 (1990).
62. Rao, V. R. and Hixson, S. S., *J. Am. Chem. Soc.*, **79**, 6458 (1979).



63. Mizuno, K., Ogawa, J., and Otsuji, Y., *Chem. Letts.*, 741 (1981).
64. Pac, C., Nakasone, A., and Sakurai, H., *J. Am. Chem. Soc.*, **99**, 5806 (1977).
65. Arnold, D. R., Bolton, J. R., and Pederson, J. A., *J. Am. Chem. Soc.*, **94**, 2872 (1972).
66. Wagner, P. J. and Siebert, E. J., *J. Am. Chem. Soc.*, **103**, 7329 (1981).
67. *Gaussian 90*, Frisch, M. J., Head-Gordon, M., Trucks, G. W., Foresman, J. B., Schlegel, H. B., Raghavachari, K., Robb, M. A., Binkley, J. S., Gonzalez, C., DeFrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Topiol, S., and Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1990.
68. Mulliken, R. S., *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).
69. (a) Hehre, W. J., Radom, L., Schleyer, P.v.R., and Pople, J. A., *Ab initio Molecular Orbital Theory*, Wiley, New York (1986). (b) Collins J. B. and Streitwieser, A., *J. Comput. Chem.*, **1**, 81 (1980); (c) Luthi, H. P., Ammeter, J. H., Almlöf, J., and Faegri, K., *J. Chem. Phys.*, **77**, 2002 (1982).
70. (a) Jones, R. A. Y., *Annual Reviews of NMR Spectroscopy*, Vol 2, ed., Mooney, E. F., Academic Press, London (1969). (b) Ronayne, J. and Williams, D. H., *ibid*, Vol 2.
71. Williams, D. H. and Bacca, N. S., *Tetrahedron*, **21**, 2021 (1965).
72. Forrest, T. P. and Sukumar, S., *Can. J. Chem.*, **55**, 3686 (1977).
73. Arnold, D. R., Hinman, R. L., and Glick, A. H., *Tetrahedron Lett.*, 1425 (1964).
74. Sandstrom, J., *Dynamic NMR Spectroscopy*, Academic Press, London (1982).
75. *Encyclopedia of Electrochemistry of the Elements*, p.58, eds., Bard, A. J. and Lund, H. Vol.XII, Marcel Dekker, N. Y. (1978).
76. House, H. O., *Modern Synthetic Reactions*, 2nd. edition, p.72, W. A. Benjamin Inc., Menlo Park (1972).
77. Ashby, E. C., *Pure Appl. Chem.*, **52**, 545 (1980), and references therein.
78. (a) Lund, T. and Lund, H., *Acta Chem. Scand.*, **B41**, 93 (1987). (b) Fuhlendorff, R., Occhialini, R., Pedersen, S. U., and Lund, H., *ibid.*, **43**, 803 (1989).
79. Ashby, E. C., *Pure Appl. Chem.*, **52**, 545 (1980).
80. Holm, T., *Acta Chem. Scand.*, **B37**, 567 (1983).
81. Blicke, F. F. and Powers, L. D., *J. Am. Chem. Soc.*, **51**, 3378 (1929).
82. Holm, T. and Crossland, I., *Acta Chem. Scand.*, **A25**, 59 (1971).
83. Ashby, E. C. and Bowers Jr., J. S., *J. Am. Chem. Soc.*, **99**, 8504 (1977).

84. Ashby, E. C. and Wiesemann, T. L., *J. Am. Chem. Soc.*, **100**, 189 (1978).
85. Ashby, E. C. and Goel, A. B., *J. Am. Chem. Soc.*, **103**, 4983 (1981).
86. Kristensen, L. H. and Lund, H., *Acta Chem. Scand.*, **B33**, 735 (1979).
87. reference 3d, p.133.
88. (a) Fraenkel, G., Chow, A., and Winchester., W. R., *J. Am. Chem. Soc.*, **112**, 6190 (1990). (b) Al-Aseer, M. A. and Smith., S. G., *J. Org. Chem.*, **49**, 2608 (1984).
89. Birch, A. J. and Subba Rao, G., *Adv. Org. Chem.*, **8**, 1 (1972).
90. Birch, A. J. and Nasipuri, D., *Tetrahedron*, **6**, 148 (1959).
91. (a) Masnovi, J., *J. Am. Chem. Soc.*, **111**, 9081 (1989). (b) Simic, M. and Hoffman, M. Z., *J. Phys. Chem.*, **76**, 1398 (1972).
92. Andrieux, C. P., Gallardo, I., and Saveant, J. -M., *J. Am. Chem. Soc.*, **111**, 1620 (1989).
93. (a) Garst, J. F., Barbas, J. T., and Barton II, F. E., *J. Am. Chem. Soc.*, **90**, 7159 (1968). (b) Sargent, G. D. and Lux, G. A., *J. Am. Chem. Soc.*, **90**, 7162 (1968).
94. Pointeau, R., *Ann. Chim. (Paris)*, **7**, 669 (1962).
95. For a review see Foster, R., *Molecular Complexes Vol.2*, chpt.3, **p.107**, ed. Foster, R., Elek Science, London (1974).
96. Foster, R. and Fyfe, C. A., *J. Chem. Soc., Faraday Trans.*, **61**, 1626 (1965).
97. Epley, T. D. and Drago, R. S., *J. Am. Chem. Soc.*, **89**, 5770 (1967).
98. Mulliken, R. S. and Person, W. B., *Molecular Complexes*, chpt.7, **p.81**, Wiley-Interscience, New York (1969).
99. Benesi, H. A. and Hildebrand, J. H., *J. Am. Chem. Soc.*, **71**, 2703 (1949).
100. LaBudde, R. A. and Tamres, M., *J. Phys. Chem.*, **54**, 4009 (1970).
101. Cantrell, T. S., *J. Org. Chem.*, **42**, 4238 (1977).
102. Saito, I., Kanehira, K., Shimozono, K., and Matsuura, T., *Tetrahedron Lett.*, **21**, 2737 (1980).
103. (a) Saito, I., Shimozono, K., and Matsuura, T., *J. Am. Chem. Soc.*, **102**, 3948 (1980). (b) Saito, I., Shimozono, K., and Matsuura, T., *J. Org. Chem.*, **47**, 4356 (1982).
104. Ohashi, M., Aoyagi, N., Miyama, T., Kyushin, S., and Yamada, S., *J. Chem. Soc., Perkin Trans. 1*, 189 (1990).

105. Becker, R. S., *Theory and Interpretation of Fluorescence and Phosphorescence*, **chpt.11**, Wiley, New York (1969).
106. Yamasaki, N., Inoue, Y., Yokoyama, T., Tai, A., Ishida, A., and Takamuku, S., *J. Am. Chem. Soc.*, **113**, 1933 (1991).
107. (a) Inoue, Y., Kunitomi, Y., Takamuku, S., and Sakurai, H., *J. Chem. Soc., Chem. Commun.*, 1024 (1978). (b) Inoue, Y., Takamuku, S., Kunitomi, Y., and Sakurai, H., *J. Chem. Soc., Perkin Trans 2*, 1672 (1980). (c) Goto, S., Takamuku, S., Sakurai, H., Inoue, Y., and Hakushi, T., *ibid.*, 1678 (1980).
108. Lamola, A. A., *Energy Transfer and Organic Photochemistry*, Interscience, New York (1969).
109. (a) Arnold, D. R. and Wong, P. C., *J. Am. Chem. Soc.*, **101**, 1894 (1979). (b) *Can. J. Chem.*, **58**, 918 (1980). (c) *ibid.*, **59**, 982 (1981).
110. Hammond, G. S. and Cole, R. S., *J. Am. Chem. Soc.*, **37**, 3256 (1965).
111. Inoue, Y., Yokoyama, T., Yamasaki, N., and Tai, A., *J. Am. Chem. Soc.*, **111**, 6480 (1989).
112. Bryce-Smith, D., *Pure Appl. Chem.*, **34**, 193 (1973).
113. Turro, N. J., *Modern Molecular Photochemistry*, **p.455**, Benjamin/Cummings, Menlo Park (1978).
114. Gould, I. R., Mueller, L. J., and Farid, S., *Z. Phys. Chem.*, submitted (1991).
115. Mulliken, R. S., *J. Am. Chem. Soc.*, **72**, 610 (1950).
116. Gould, I. R., Young, R. H., and Farid, S., *Photochemical Processes in Organised Molecular Systems*, Elsevier, Amsterdam, in press.
117. Marcus, R. A., *J. Chem. Phys.*, **24**, 966 (1956).
118. Weller, A., *Z. Phys. Chem., (Wiesbaden)*, **130**, 129 (1982).
119. (a) Mattes, S. and Farid, S., *J. Chem. Soc., Chem. Commun.*, 126 (1980). (b) *J. Am. Chem. Soc.*, **105**, 1386 (1983). (c) *J. Am. Chem. Soc.*, **108**, 7356 (1986).
120. Loufty, R. O. and Loufty, R. O., *Can. J. Chem.*, **54**, 1454 (1976).
121. Wagner, P. J., *Creation and Detection of the Excited State*, Part A, **Vol.1**, p.201, ed., Lamola, A. A., Marcel Dekker, New York (1971).
122. Still, I. W. J., *Organic Sulfur Chemistry, Studies in Organic Chemistry 19*, **chpt. 11**, p. 596, eds. Bernardi, F., Csizmadia, I. G., and Mangini, A., Elsevier, Amsterdam (1985).
123. Exner, O. and Vetesnik, P., *Collect. Czech. Chem. Commun.*, **43**, 2763 (1978).

124. (a) Horner, L. and Neumann, H., *Chem. Ber.*, **98**, 1715 (1965). (b) Simonet, J. and Jeminet, G., *Bull. Soc. Chim. Fr.*, 2754 (1971). (c) Chambers, J. Q., *Encyclopedia of Electrochemistry of the Elements*, Vol.XII, chpt. 3, eds. Bard, A. J. and Lund, H., Marcel Dekker, New York (1978).
125. Lamm, B., *Tetrahedron Lett.*, 1469 (1972).
126. Manousek, O., Exner, O., and Zuman, P., *Collect. Czech. Chem. Commun.*, **33**, 3988 (1968).
127. Carsky, P. and Zuman, P., *Collect. Czech. Chem. Commun.*, **34**, 497 (1969).
128. Houser, K. J., Bartak, D. E., and Hawley, M. D., *J. Am. Chem. Soc.*, **95**, 6033 (1973).
129. Rieger, P. H., Bernal, I., Reinmuth, W. H., and Fraenkel, G. K., *J. Am. Chem. Soc.*, **85**, 683 (1963).
130. Buick, A. R., Kemp, T. J., Neal, G. T., and Stone, T. J., *J. Chem. Soc.(A)*, 666 (1969).
131. Coleman, J. P., Naser, U. D., Gilde, H. G., Utley, J. H. P., Weedon, B. C. L., and Ebersson, L., *J. Chem. Soc., Perkin Trans. 2*, 1903 (1973).
132. Pauling, L., *The Nature of the Chemical Bond*, p.314, Cornell Univ. Press, Ithaca, (1960).
133. Kornblum, N., *Angew. Chem. Int. Ed. Engl.*, **14**, 734 (1975).
134. Stark, M. and Arnold, D. R., *J. Chem. Soc., Chem. Commun.*, 434 (1982).
135. Fry, A. J., *Synthetic Organic Electrochemistry*, 2nd ed., p.136, Wiley, New York (1988).
136. (a) Ross, S.D., Finkelstein, M., and Petersen, S., *J. Am. Chem. Soc.*, **82**, 1582 (1960). (b) *J. Am. Chem. Soc.*, **92**, 6003 (1970).
137. Mayell, J. S. and Bard, A. J., *J. Am. Chem. Soc.*, **85**, 421 (1963).
138. Horner, L. and Roder, H., *Chem. Ber.*, **101**, 4179 (1968).
139. (a) Sertel, M., Yildiz, A. H., Gambert, R., and Baumgartel, H., *Electrochim. Acta*, **31**, 1287 (1986). (b) *ibid.*, **33**, 169 (1988).
140. Ingold, K. U., Johnston, L. J., Lusztyk, J., and Scaiano, J. C., *Chem. Phys. Lett.*, **110**, 433 (1984).
141. Büchi, G., Inman, C. G., and Lipinsky, E. S., *J. Am. Chem. Soc.*, **76**, 4327 (1954).
142. (a) Carless, H. A. J., *Photochemistry in Organic Syntheses*, chpt. 6, ed., Coyle, J. D., Special Publication No. 57, The Royal Society of Chemistry, London (1986). (b) Arnold, D. R., *Adv. Photochem.*, **6**, 301 (1968). (c) Jones II, G., *Org. Photochem.*, **5**, 1, ed., Padwa, A., Marcel Dekker, New York (1981).
143. Turro, N. J., *Pure Appl. Chem.*, **27**, 267 (1972).

144. Freilich, S. C. and Peters, K. S., *J. Am. Chem. Soc.*, **107**, 3819 (1985).
145. Caldwell, R. A., Sovocool, G. W., and Gajewski, R. P., *J. Am. Chem. Soc.*, **95**, 2549 (1973).
146. Wagner, P. J., *Topics in Current Chemistry*, **66**, 1 (1976).
147. Pac, C., Mizuno, K., Tosa, T., and Sakurai, H., *J. Chem. Soc., Perkin 1*, 561 (1974).
148. Zeldes, H. and Livingston, R., *J. Phys. Chem.*, **45**, 1946 (1966).
149. Harwood, L. H., *Aldrichimica Acta*, **18**, 25 (1985).
150. Nicholson, R. S. and Shain, I., *Anal. Chem.*, **36**, 706 (1964); **37**, 178 (1965).
151. Haines, A. H. and Shandiz, M. S., *J. Chem. Soc., Perkin Trans.*, **1**, 1671 (1981).
152. Russell, G. A. and Ros, F., *J. Am. Chem. Soc.*, **107**, 2506 (1985).
153. Pearson, D. E., *J. Am. Chem. Soc.*, **72**, 4169 (1950).
154. Bordwell, F. G. and Kern, R. J., *J. Am. Chem. Soc.* **77**, 1141 (1955).
155. Fuller, A. T., Tonkin, I. M., and Walker, J., *J. Chem. Soc.*, 633 (1945).
156. Tadros, W. and Sakla, A. B., *J. Chem. Soc.*, 1116 (1953).
157. Cameron T. S. and Cordes, R. E., *Acta Crystallogr.*, **B35**, 749 (1979).
158. Walker, N. and Stuart, D., *Acta Crystallogr.*, **A39**, 158 (1983).
159. *International Tables for X-ray Crystallography, Vol IV*, Kynoch Press, Birmingham, U.K. (1974).
160. SHELXS-86, G.M. Sheldrick in 'Crystallographic Computing 3', eds., Sheldrick, G. M., Kruger, C., and Goddard, R., Oxford University Press, 1985, 175-189.
161. Sheldrick, G. M., SHELX-76. Program for Crystal Structure Determination. University of Cambridge, Cambridge, U.K. (1976).
162. Davies, E. K., the CHEMGRAF Suite, Chemical Crystallography Laboratory, Oxford, U.K. (1983).