

THE GRIGNARD SYNTHESIS: THE ACTION OF PHENYL MAGNESIUM BROMIDE ON CAMPHOR.\*—BY H. JERMAIN M. CREIGHTON, Dalhousie University, Halifax, N. S.

(Read April 9th, 1906.)

As is well known, the organo-metallic compounds have long been used in a great many organic syntheses, as for instance, in the synthesis of the hydrocarbons and the ketones, to take two examples at random. In all these reactions the yields have always been small, and most of the methods complicated, roundabout and unsatisfactory.

By means of the so-called "Grignard reaction" these difficulties have been done away with, the syntheses of a great many compounds effected, and many new compounds prepared.

Compounds of the hydrocarbons with magnesium have long been known, but it was not until recently (1900) that Grignard investigated their action toward different organic compounds.

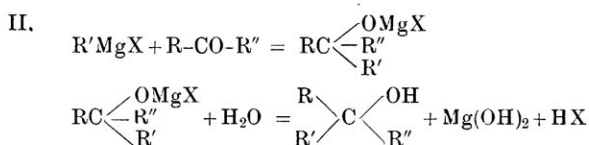
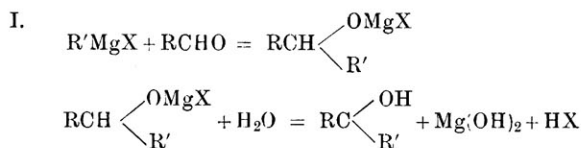
Grignard found that when methyl iodide was allowed to react with many organic compounds in the presence of magnesium, a vigorous reaction took place and a new compound was formed. When the air was not excluded the mixture took fire. He saw from the variety of ways in which the reaction could be employed that magnesium was likely to make the compounds of zinc and sodium with organic radicles of secondary importance in organic syntheses. Moreover, the reaction should be expected to be more complete with magnesium than with zinc, because magnesium is much more electro positive.

It has been found when an organo-magnesium halide is allowed to act on an aldehyde, or ketone, and the reaction pro-

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\* Contributions from the Science Laboratories of Dalhousie University (Chemistry).

duct decomposed with water, that secondary and tertiary alcohols are formed respectively, the reactions taking place in accordance with these equations:—



In these reactions the double linking of the oxygen of the aldehyde or ketone is broken, and one of the free bonds of the oxygen unites with hydrogen to form hydroxyl, while the free carbon bond takes up a hydrocarbon residue.

Japan camphor  $\text{C}_{10}\text{H}_{16}\text{O}$  contains the ketone group  $\text{C}=\text{O}$ ; under the influence of an organo-magnesium compound, it should therefore form a tertiary alcohol. Zelinsky,<sup>1</sup> who has done a great deal of work on the preparation of cyclic alcohols, found that when camphor is treated with magnesium methyl iodide, and the reaction product decomposed with water, there is obtained a tertiary alcohol whose composition is expressed by the formula  $\text{C}_{11}\text{H}_{20}\text{O}$ .<sup>2</sup>

No work having been done on the action of organo-magnesium halides of the aromatic series on ketones, it was decided to investigate the action of magnesiumphenylbromide on Japan camphor.

#### *Experimental.*

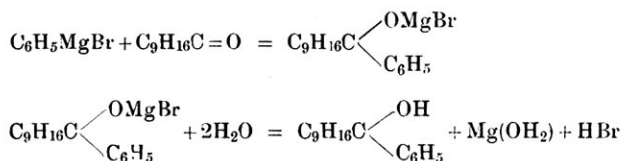
32 g. of phenyl bromide dissolved in  $1\frac{1}{2}$  times its weight of ether, was allowed to drop slowly on the calculated amount,

<sup>1</sup> Ber. d. deut. chem. Ges., 1901, 34, 2877.

<sup>2</sup> Ibid.

4.8 g., of cleaned magnesium ribbon contained in a round bottomed flask, to which was fitted a reflux condenser. It is most essential that the magnesium ribbon be perfectly free from oxide. When about  $\frac{1}{3}$  of the halide had been added, the flask became warm and a vigorous reaction set in, making it necessary to cool the flask with running water, lest too great heat should cause decomposition.

The calculated amount (17 g.) of camphor, the camphor and halide reacting molecule for molecule, was dissolved in  $1\frac{1}{2}$  times its weight of ether and allowed to drop slowly into the magnesium halide. This compound was contained in a round-bottomed flask fitted with a return condenser. The mixture was kept at  $60^{\circ}\text{C}$ . The contents of the flask were allowed to stand over night, the reaction being a gradual one. Next morning the mixture was poured on crushed ice, containing a small excess of dilute hydrochloric acid to dissolve the precipitated  $\text{Mg}(\text{OH})_2$ , and the new product separated out as an oily yellow liquid. These equations illustrate the reactions taking place:—



The oil was separated from the rest of the mixture and shaken up five times with sodium acid sulphite to remove any ketone that had not been acted upon. It was then washed with water to remove the sodium acid sulphite and dehydrated over calcium chloride.

The oil was then heated in a distilling flask, and at  $205\text{--}210^{\circ}\text{C}$ . a vapour was given off, which on cooling, solidified in the condenser to a white mass. This proved to be camphor. The flask was allowed to cool and the contents heated in vacuo, a pale yellow oil distilling over at  $150^{\circ}\text{C}$ .

The yield was nearly ten grams, about twenty-five per cent. of the theoretical yield. As has been mentioned above, the action between the ketone and halide is a gradual one; the small yield and the large quantity of uncombined camphor are probably due to the mixture not having been allowed to stand sufficiently long.

This new alcohol is a pale yellow oil, with a balsam-like taste. It is miscible with alcohol, ether and chloroform. Its specific gravity is 0.977.

The boiling point of this oil is 143°-145°C. at 14 mm. pressure and 258°-260° at 760mm.

#### *Molecular Weight.*

Its molecular weight was determined by the Victor Meyer method.

I.	The vapour 0.0600g of substance displaced 6.6 cc. air at 715mm.	
		and 19°C giving Mol. Wt. 231.9
II.	“ “ 0.0620 “ “ displaced 6.8 cc. air at 715mm.	
		and 19°C giving Mol. Wt. 232.6
		Mean Molecular Weight, 232.1
		Calculated for C <sub>16</sub> H <sub>22</sub> O, 230.17

#### *Analysis.*

Two analyses of the oil were made, but owing to an accident one was a failure, and there was not enough oil to make a third.

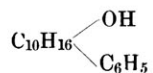
0.2510 g of substance	: 0.7722 CO <sub>2</sub>	0.2883 H <sub>2</sub> O
giving	83.89% C	9.28% H
calculated for C <sub>16</sub> H <sub>22</sub> O	83.42% C	9.63% H

#### *Specific Rotation.*

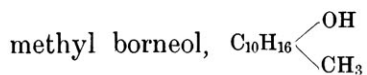
The specific rotation was determined, but owing to the thickness and colour of the liquid only a small quantity could be used. Consequently the deflection of the plane of polarisation was very small, less than one degree, and the percentage error probably as great as 5%.

The specific rotation  $(a)_D$  in alcohol solution was found to be  $7^\circ.55'$ .

The foregoing results show that the compound obtained by the action of magnesiumphenylbromide on Japan camphor is a tertiary alcohol, whose composition is expressed by the formula,



This is analogous to the tertiary alcohol,



prepared by Zelinsky, and should therefore be called phenyl borneol.

DALHOUSIE UNIVERSITY, HALIFAX,  
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