

THE PREPARATION OF ANHYDROUS PINACOL.—By HAROLD S. KING,
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ABSTRACT.

Anhydrous pinacol is best prepared from pinacol hydrate by distillation with benzene. The benzene in the distillate is freed from water in an automatic separator and syphoned back into the distilling flask. After the removal of water, the benzene is distilled off, leaving a residue of anhydrous pinacol. The yield is practically theoretical. This method is used for analyzing samples of pinacol hydrate for water content. Fractional distillation of pinacol hydrate without the addition of benzene gives a 75 to 80% yield, 20 to 15% being recoverable as hydrate by chilling the aqueous fraction of the distillate while 4 to 5% remains in solution and is lost. Dehydration in ether solution by means of calcium carbide gives a 90% yield of product possessing an objectionable odour. Treatment with anhydrous copper sulphate results in partial decomposition.

Anhydrous pinacol has been used as an intermediate in the manufacture of a synthetic rubber. Considering the importance of this application, little has been published concerning the preparation of pinacol though many methods of synthesizing its hydrate, which contains six molecules of water, have been devised.

Probably the most satisfactory method for preparing the hydrate is that of Holleman as modified by Adams and Adams¹. A solution of mercuric chloride in a mixture of acetone and benzene is added to magnesium turnings. The magnesium pinacolate formed is decomposed into pinacol by the addition of the calculated quantity of water. After filtering, the pinacol is recovered as hydrate by a further addition of water. Before this second addition of water, fractional distillation of the benzene solution yields an unsatisfactory grade of pinacol. By converting the pinacol first to the crystalline hydrate, a yellow oil containing an unstable mercury derivative remains in benzene solution and is easily removed.

1. Adams and Adams, *Organic Syntheses*, John Wiley and Sons, New York 1925, vol. 5, pp. 87-9.

The water of crystallization is held only loosely since it is partly given off over concentrated sulphuric acid². When distilled, the hydrate decomposes into water and pinacol which may be separated by fractional distillation³. Calvert⁴ states that practically all the water is given off under 115°, ten to fifteen percent of the pinacol distilling with the steam and recoverable as hydrate. Fittig⁵ dehydrated pinacol hydrate in ether solution with anhydrous calcium chloride. After filtering and distilling off the ether on a water bath, pinacol remained as a residue.

In our experiments three methods for the preparation of anhydrous pinacol were investigated. The first involved the use of calcium carbide as a dehydrating agent; the second was Linnemann's fractional distillation of the hydrate; the third was distillation with benzene until all water was removed and subsequent fractionation of the benzene-pinacol mixture. All three yielded anhydrous pinacol, but the yields and purity of product were most satisfactory in the third method.

Dehydration by Calcium Carbide.—Though calcium carbide has been used extensively for the removal of water of crystallization from various substances and for the dehydration of organic liquids⁶, we have found no reference to its use in preparing anhydrous pinacol.

To 118g. of pure pinacol and 108g. of water in a liter flask fitted with a reflux condenser were added 700 cc. of ether and 250g. of coarsely powdered calcium carbide in 25g. portions. The flask was well cooled under the tap and shaken between

2. Fittig, *Ann.*, **110**, 25(1859).
3. Linnemann, *Ann. Suppl.*, **3**, 375(1864).
4. Calvert, *India Rubber and Tire Review*, **26**, No. 9, 54(1926).
5. Fittig, *Ann.*, **114**, 56(1860).
6. In view of the fact that the carbide method has been proposed for the dehydration of ethyl alcohol [Yvon, *Compt. rend.*, **125**, 1181-2 (1897); Lyons and Smith, *Science*, **62**, 224-5 (1925).], it was decided to test this method with n-butyl alcohol. After refluxing for an hour with coarsely powdered calcium carbide, the alcohol was distilled off, refluxed with anhydrous copper sulphate and distilled again. This last distillation must be stopped some time before coming to dryness to prevent the evolution of sulphur dioxide. Evidently alcohol is oxidized by sulphuric acid liberated in the reaction between copper sulphate and acetylene. The yield (B.Pt. 117-118°) was only 80%. Though the product was of good odour, the method is not considered satisfactory.

additions. Much ether was lost during the evolution of acetylene. After standing over night, the flask was heated for an hour on a water bath and the contents filtered. The residue was washed with a liter of dry ether. This extraction was unusually efficient because of the porous nature of the filter cake. The combined filtrates were distilled in a flask fitted with a 3-foot fractionating column, the walls of which were indented to give more surface. The acetylene passed over with the ether. Everything up to 170°C . was collected in fraction A. Fraction B, $170\text{-}174^{\circ}$, was anhydrous pinacol and weighed 106g. Twenty-five cc. of water were added to fraction A and, on cooling in the ice box, 2g. of pinacol hydrate separated out. The residue in the apparatus was washed out with 25 cc. of water and from this solution 10g. of pinacol hydrate were recovered. Thus there was a 90% recovery of the pinacol in anhydrous form, 5% was in the form of hydrate and 5% lost in manipulation. The pinacol, however, had a faint odour resembling cacodyl oxide. It is possible that the carbide contained a trace of an arsenic derivative. A different batch of carbide gave a product with no such odour. It was thought that boiling the ether solution for an hour with anhydrous copper sulphate would remove the odour. It resulted in a further dehydration probably to pinacolone.

Dehydration by Fractional Distillation.—Pinacol hydrate, prepared by mixing 118g. of pure pinacol and 108g. of water in a round-bottomed flask fitted with the three-foot fractionating column previously described, was slowly distilled on an oil bath. Fraction A, distilling from 100° to 170° , weighed 124g. Practically all of this fraction came over below 102° , the rise to 170° being extremely rapid. At 170° a dry condenser was substituted for the one previously used and the fractionating column was wrapped with towels to facilitate the distillation. Fraction B, distilling at $170\text{-}174^{\circ}$, consisted of 93g. of anhydrous pinacol, which was practically odourless. After cooling, the apparatus was washed out with 50 cc. of warm water and the rinsings added to the residue in the distilling flask. Fraction A was chilled in the ice box and

27g. of pinacol hydrate (corresponding to 14g. pinacol) were recovered. From the residue there were likewise recovered 12g. of hydrate corresponding to 6g. of pinacol. Approximate solubility experiments showed that at 3°C. 100g. of water dissolved 3g. and at 6°, 3.5g. of hydrate. In the following calculations we assume that 100g. of water dissolved 3.5g. of hydrate.

Weight Fraction A	= 124g.	Pinacol recovered from A	= 14 g.
Pinacol recovered	= 14g.	Pinacol in B	= 93 g.
Pinacol in solution	= 2g.	Pinacol in residue	= 6 g.
Pinacol in A	= 16g.	Pinacol in solutions	= 2.5g.
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Water recovered	= 108g.	Pinacol recovered	= 115.5g.

Thus we account for all of the water taken and all of the pinacol except 2.5g. The yield of anhydrous pinacol was 79% of theoretical; the pinacol recovered as hydrate was 17% and 4% of the initial pinacol was lost. Another distillation of the solutions did not result in a recovery of any pinacol, so that a certain amount of pinacol is necessarily non-recoverable.

The percentages of pinacol obtained in anhydrous form vary in different experiments from 75 to 80, depending on the speed of distillation, and drop to 70 when the fractionating column is replaced by a simple still-head. Since nearly all of the water came over below 102°, our fractionating column must have been more efficient than that used by Calvert, who states that practically all the water is given off under 115°. Yet in no case was his 90% yield obtained.

Dehydration by Distillation with Benzene.—Pinacol hydrate, obtained from 118g. of pinacol and 108g. of water, together with 200cc. of benzene, was placed in a 3-necked, 1-liter, pyrex flask fitted (a) with the 3-foot, fractionating column leading to a condenser fitted with an adaptor dipping below the surface of the liquid in an automatic separator, (b) with a capillary tube extending to the bottom of the flask for the introduction of air under pressure to prevent bumping, and (c) with a syphon from the automatic separator, through which the distilled benzene, after separation from the accompanying water, returned to the distilling flask. The mixture distilled

at 68° until all the water was removed, when the temperature of distillation rose to 80°. The water fraction of the distillate was collected in a weighed flask and amounted to 108g., a 100% recovery. On cooling this water in the ice box, no pinacol hydrate separated out.

The anhydrous benzene solution of pinacol was poured into a weighed, 1-liter, pyrex flask. The first flask was rinsed out with benzene into the second. The 3-foot fractionating column was attached and the flask heated on a metal bath (Pb 50%, Sn 30% and Bi 20%). Distillation started at 79°. There were collected two fractions, A, boiling at 79-81°, and B, from 81° to 170°. The weight of the anhydrous pinacol remaining in the flask was 113g. or nearly 96% of the initial pinacol. Fraction A, consisting of nearly pure benzene, was shaken with 10 cc. of water, cooled in the ice box and seeded with pinacol hydrate. No crystals appeared. The apparatus was washed out with 50 cc. of water and the rinsings added to fraction B. From this solution 7g. of pinacol hydrate crystallized out. Allowing for 1.6g. of hydrate which remained in solution, this fraction contained 4.5g. of pinacol. Thus we account for all of the initial pinacol with the exception of half a gram. The crystallized hydrate and the aqueous solution were added to the next run and the pinacol recovered.

Though this method of dehydration is slow, it is automatic and requires little attention. The process was used in working up several gallons of dilute pinacol solution without interfering with other experiments. Practically the entire pinacol residue obtained in this way distilled between 170° and 174° to yield a water-white, almost odourless liquid which completely crystallized spontaneously to a nearly transparent solid.

It was thought that toluene might be substituted for benzene, but this was not successful, pinacol distilling over with toluene after the water had been removed.

Analysis of Pinacol Hydrate.—The results of the dehydration of pinacol hydrate by distillation with benzene were so nearly quantitative that the method was adopted for the analysis of pinacol hydrate. This pinacol hydrate was prepared

by the method given by Adams and Adams¹ with minor modifications. One and one-half the quantities of material were used without increasing the size of the apparatus. By adding the water (350 cc. instead of 450 cc.) to the benzene solution of pinacol, obtained in the procedure, while it was still warm, and then cooling to 3° with occasional stirring and shaking, the crystals of hydrate were obtained in the form of a meal which filtered easily. The crystals were filtered by suction, washed with benzene, and exposed in a thin layer to the air of the laboratory for 24 hours. The yield was 553g.

The entire batch of pinacol hydrate was dehydrated by the benzene method already described. From the automatic separator 278g. of water were recovered. The yield of anhydrous pinacol was 273g. Since 1g. of pinacol was recovered from the 81-170° fraction and the rinsings of the apparatus, the total pinacol in the initial hydrate was 274g. The amount of material not accounted for was 1g. 274g. of pinacol corresponds to 525g. of hydrate, making the actual yield of pinacol hydrate obtained from 120g. of magnesium 47% of the theoretical amount. Since the water recovered weighed 278g. and the water combined in 525g. of hydrate is 251g., the excess water in the initial pinacol hydrate was 27g. In other words, the pinacol hydrate, after being sucked as dry as possible at the pump, washed with benzene and dried in the air for 24 hours, still contained 4.9% of uncombined water.