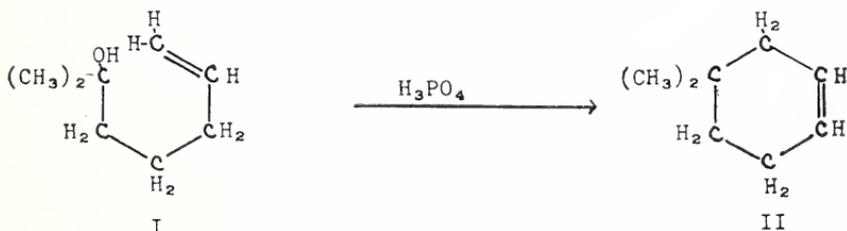


## The Preparation and Dehydration of Some Phenyl-Substituted Ethylenic Carbinols

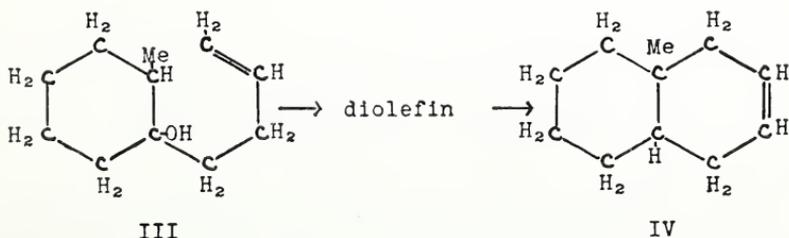
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The dehydration of alcohols is one of the most widely studied fields in organic chemistry. Almost all types of alcohols have been dehydrated, and a large variety of dehydrating agents have been used. Ordinarily the product of dehydration is an olefin, although sometimes an ether is formed, and more rarely a cyclic hydrocarbon. It is with this last type of dehydration that the present paper is concerned.

The conversion of an open-chain alcohol to a cyclic hydrocarbon is usually brought about by acid reagents, especially sulfuric acid and phosphoric acid. As a rule, simple aliphatic saturated alcohols do not yield cyclic products on acid dehydration, they form olefins which may or may not polymerize. With unsaturated aliphatic alcohols the picture is somewhat different. Normal dehydration yields a diolefin, which may polymerize, or may rearrange to a cyclic compound, or direct cyclodehydration may occur. As an example the work of Hibbit and Linstead<sup>1</sup> may be cited. These workers found that 2-methyl-6-hepten-2-ol (I) on treatment with phosphoric acid yielded a cyclohexene derivative, II,



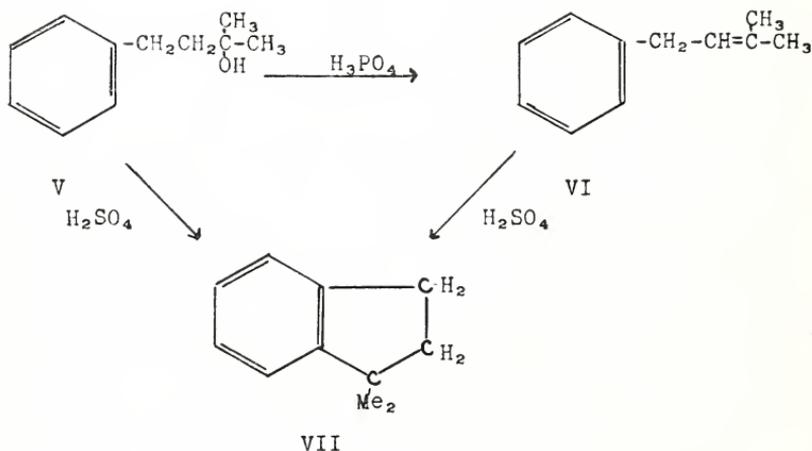
presumably by direct ring closure, but in the case of 1-butenyl-2-methylcyclohexanol (III), the initial dehydration product was an open chain diolefin, which on prolonged heating with the dehydrating agent rear-



<sup>1</sup> Hibbit, D. C., and Linstead, R. P., 1936. J. Chem. Soc., 470.

ranged to a cyclic product, IV. Exactly what structural relations are necessary to obtain ring closure from unsaturated alcohols has not been determined, for Hibbit and Linstead found that many ethylenic alcohols closely related structurally to the two cases cited yielded only diolefins which could not be cyclized. When cyclic products were formed, they always contained five or six carbon atoms in the ring.

Bogert and Davidson<sup>2</sup> have made a detailed study of the acid dehydration of phenyl-substituted saturated alcohols. They found that these alcohols on treatment with concentrated sulfuric acid yielded olefin polymers or cyclic hydrocarbons (indanes and tetralins), and they also showed that the olefins were intermediate in the formation of the cyclic hydrocarbons. As an illustration, 4-phenyl-2-methyl-2-butanol (V) when treated with phosphoric acid yielded 4-phenyl-2-methyl-2-butene (VI) but when either the carbinol or the olefin was treated with sulfuric acid, 1,1-dimethylindane (VII) was obtained. These workers found that no



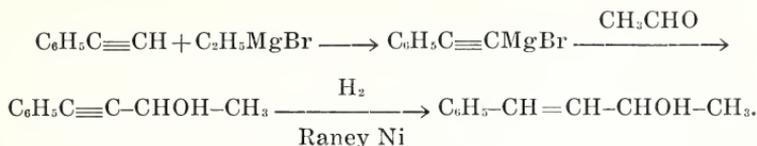
ring closure ever occurred when the hydroxyl group was on the same carbon atom as the phenyl group. The other structural requirements necessary for ring closure have not been definitely determined.

No study has been made heretofore, as far as we are aware, of the dehydration of phenyl-substituted unsaturated alcohols. In this paper we are reporting the preparation of three phenyl-substituted ethylenic alcohols, namely, 1-phenyl-1-hydroxy-2-heptene,  $\text{C}_6\text{H}_5\text{-CHOH-CH=CH-C}_6\text{H}_5$ ; 1-phenyl-3-hydroxy-1-butene,  $\text{C}_6\text{H}_5\text{-CH=CH-CHOH-CH}_3$ ; and the cis and trans forms of 1,3-diphenyl-3-hydroxy-1-propene,  $\text{C}_6\text{H}_5\text{-CH=CH-CHOH-C}_6\text{H}_5$ ; and a study of the dehydration of these alcohols with phosphoric acid.

With the exception of the trans form of 1,3-diphenyl-3-hydroxy-1-propene, these carbinols were made by treating an acetylenic Grignard reagent with a suitable aldehyde, and reducing the acetylenic carbinol

<sup>2</sup> Bogert, M. T., and Davidson, D., 1934. Jour. Am. Chem. Soc., 56:185.

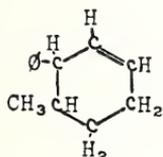
with hydrogen in the presence of Raney nickel to the ethylenic carbinol. This type of reduction has been shown to yield *cis* olefins.<sup>3</sup>



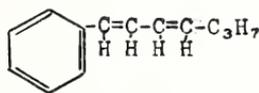
The *trans* form of 1,3-diphenyl-3-hydroxy-1-propene was made from cinnamic aldehyde (in which the double bond has the *trans* configuration) and phenylmagnesium bromide.

Attempts were made to dehydrate these carbinols with sulfuric acid, but only tarry polymers resulted. Phosphoric acid proved to be more satisfactory, although even here large amounts of polymers were formed.

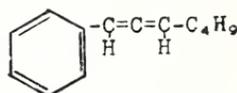
The dehydration of 1-phenyl-1-hydroxy-2-heptene could occur in any of several ways, to yield a cyclic compound (VIII), or a diolefin, in which the double bonds could be conjugated (IX), cumulated (X), or isolated



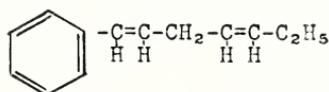
VIII



IX



X

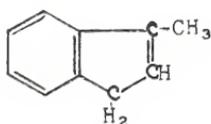


XI

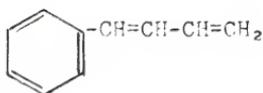
(XI). The product obtained had a molecular weight in agreement with any of these possibilities, and was unsaturated. A parachor determination gave a value of 457. The parachor calculated for a cyclic compound of formula VIII is 441, while the calculated parachor for any of the diolefins is 458. This result would seem to eliminate the cyclic structure VIII from consideration. Quantitative microhydrogenation showed the presence of two aliphatic double bonds, thus providing additional evidence that the product did not have structure VIII. The hydrocarbon reacted readily with maleic anhydride to give a well-defined crystalline product. Since in general maleic anhydride reacts only with conjugated diolefins, the aggregate of the data establishes formula IX, 1-phenyl-1,3-heptadiene, as that of the dehydration product. The molecular refraction (61.4) is in agreement with this structure, since it shows a high optical exaltation (calculated, 56.0).

<sup>3</sup> Campbell, K. N., and Eby, L. T. 1940. *Jour. Am. Chem. Soc.*, **62**, December.

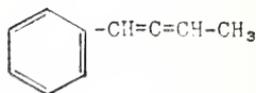
Dehydration of 1-phenyl-3-hydroxy-1-butene,  $C_6H_5CH=CH-CHOH-CH_3$ , could yield a cyclic compound, methylindene (XII), a conjugated diolefin, phenyl-1,3-butadiene (XIII) or a cumulated diene (XIV), although this latter is unlikely. The molecular weight was in agreement with any of these possibilities. The parachor was found to be 326, while the value calculated for methylindene (XII) is 326.4, and for either diene, (XIII or XIV) is 331. The substance on quantitative micro-



XII



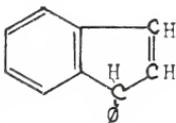
XIII



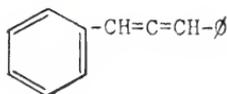
XIV

hydrogenation showed the presence of but one double bond. These data establish the fact that dehydration of this carbinol yields a cyclic substance, a methylindene, XII.

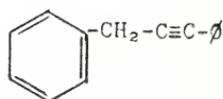
The *cis* and *trans* forms of 1,3-diphenyl-3-hydroxy-1-propene,  $C_6H_5-CH=CH-CHOH-C_6H_5$ , yielded the same unsaturated hydrocarbon. This could have any of the following structures: phenylindene (XV), diphenylpropadiene (XVI) or phenylbenzylacetylene (XVII). The parachor was



XV



XVI



XVII

found to be 478, while the value calculated for phenylindene is 461, and for the open-chain compounds is 475. Quantitative micro-hydrogenation showed absorption of four atoms of hydrogen, thus eliminating phenylindene (XV) from consideration. The evidence is not sufficient to distinguish between the allene XVI and the acetylene XVII.

### Experimental Part

**Preparation of 1-Phenyl-1-hydroxy-2-heptene.**—*n*-Butylethynylmagnesium bromide was prepared by treating ethylmagnesium bromide (from 21.5 g. of magnesium, 109 g. of ethyl bromide and 400 cc. of ether) with 59.6 g. of *n*-butylacetylene in an equal volume of dry ether. The reaction flask was then packed in an ice-salt bath, and a solution of 74 g. of redistilled benzaldehyde in 75 cc. of dry ether was added drop-wise during the course of two hours. The mixture was allowed to warm up to room temperature, and was then hydrolyzed with ice and ammonium chloride. The organic layer and ether extracts were dried over magnesium sulfate, and the residue left after evaporation of the ether was

distilled under reduced pressure to yield 81 g. (62%) of 1-phenyl-1-hydroxy-2-heptyne, b.p.  $152^{\circ}/8$  mm.,  $n_D^{20}$ : 1.5268,  $d_4^{20}$ : 0.9950,  $MR_D$  obs. 58.20,  $MR_D$  calc'd., 58.0.

One gram (wet weight) of Raney nickel catalyst was added to a solution of 39 g. (0.21 moles) of the acetylenic carbinol in 100 cc. of absolute methanol, and the mixture was shaken with hydrogen at an initial pressure of 4 atmospheres until 0.21 moles had been absorbed. The methanol was removed from the filtered reaction product by distillation, and the residue dried over magnesium sulfate and distilled under reduced pressure. A 63% yield of ethylenic carbinol was obtained, b.p.  $150^{\circ}/7$  mm.,  $n_D^{20}$ : 1.5142,  $d_4^{20}$ : 0.9514,  $MR_D$  obs. 59.67,  $MR_D$  calc'd., 59.7.

**Dehydration of 1-Phenyl-1-hydroxy-2-heptene.**—A mixture of 50 cc. of 85% syrupy phosphoric acid and 11 g. of the carbinol was heated on the steam bath for thirty minutes, and was then steam-distilled under reduced pressure. The organic layer so obtained was dried and redistilled to yield 7.8 g. (75%) of a viscous yellow liquid, b.p.  $122^{\circ}/8$  mm.,  $n_D^{20}$ : 1.5643,  $d_4^{20}$ : 0.9122,  $MR_D$  obs. 61.4. This product decolorized bromine in carbon tetrachloride and was oxidized by aqueous alkaline potassium permanganate in the cold. It gave negative tests for phosphorus, carbonyl and hydroxyl groups.

Mol. Wt. (cryoscopic in benzene). Found, 179.0, calc'd for  $C_{13}H_{16}$ , 172. Parachor. Surface tension (maximum bubble-pressure method),<sup>4</sup> 34.84 dynes/cm. P, found, 475.4 P, calc'd for 1-phenyl-1,3-heptadiene, 458.1, P, calc'd for phenylmethylcyclohexene, 441.

**Quantitative Hydrogenation.**—1.3537 g. (0.007 moles) required 0.014 moles of hydrogen for saturation, using Raney nickel as catalyst and methyl alcohol as solvent.

**Reaction with Maleic Anhydride.**—One gram of the compound was heated with 1.5 g. of maleic anhydride for ten minutes. The product on recrystallization from high-boiling ligroin and benzene was obtained as white crystals, m.p.  $62^{\circ}$ . Mol. Wt., found, 266, calc'd for  $C_{17}H_{14}O_3$ , 266. Saponification equivalent, found, 146, calc'd for  $C_{17}H_{14}O_3$ , 142.

**Preparation of 1-Phenyl-3-hydroxy-1-butene.**—Phenylethynylmagnesium bromide was prepared from 0.8 moles of ethylmagnesium bromide and 71.5 g. of phenylacetylene. The reaction flask was immersed in a salt-ice bath and a solution of 26.4 g. of acetaldehyde in three volumes of dry ether was added very slowly. The mixture was worked up in the usual way, and gave a 63% yield of 1-phenyl-3-hydroxy-1-butyne, b.p.  $128^{\circ}/$  mm.,  $n_D^{20}$ : 1.5662,  $d_4^{20}$ : 1.0664,  $MR_D$  obs. 45.4,  $MR_D$  calc'd. 45.0. A solution of 28.9 g. (0.198 moles) of the acetylenic carbinol in 50 cc. of methanol containing 1 g. of Raney nickel required three minutes to absorb 0.198 moles of hydrogen. The 1-phenyl-3-hydroxy-1-butene, obtained in 50-60% yields, had the following properties: b.p.  $118^{\circ}/12$  mm.,  $n_D^{20}$ : 1.5388,  $d_4^{20}$ : 1.0050,  $MR_D$  obs. 46.1,  $MR_D$  calc'd. 45.8.

<sup>4</sup> Sugden, S., 1930. "The Parachor and Valency," First Edition, p. 121.

**Dehydration of 1-phenyl-3-hydroxy-1-butene.**—Thirty-five grams of the carbinol was treated as described above, with 100 cc. of phosphoric acid. Considerable tar was formed, and only a 10% yield of hydrocarbon was isolated. The product had the following properties: b.p. 94°/10 mm.,  $n_D^{20}$ : 1.5956,  $d_4^{20}$ : 1.0422.  $MR_D$  obs. 42.3,  $MR_D$  calc'd for methylindene, 42.1.

Mol. Wt. (cryoscopic). Found, 132.0, calc'd. for  $C_{10}H_{10}$ , 130.

Parachor. Surface tension, 47.1 dynes/cm. P, obs. 326.0 P, calc'd. for methylindene, 326.4, P, calc'd. for phenylbutadiene, 331.1.

Quantitative hydrogenation. 0.0079 moles of compound absorbed 0.0079 moles of hydrogen.

**Preparation of trans 1,3-Diphenyl-3-hydroxy-1-propene.**—A solution of 110 g. (0.9 moles) of redistilled cinnamaldehyde in two volumes of dry ether was added during the course of five hours to one mole of phenylmagnesium bromide, cooled in an ice-salt bath. The product, isolated in the usual way, was obtained as a white solid (yield, 63%), which melted at 55° after four recrystallizations from ligroin-carbon tetrachloride.

Mol. Wt. (cryoscopic). Found, 200. Calc'd. for  $C_{15}H_{14}O$ , 210.

**Preparation of cis 1,3-Diphenyl-3-hydroxy-1-propene.**—Phenylethynylmagnesium bromide, made from 66 g. of phenylacetylene and 0.7 moles of ethylmagnesium bromide, was cooled in an ice-salt bath and treated with a solution of 52 g. of redistilled benzaldehyde in 50 cc. of dry ether. The acetylenic carbinol was obtained as a very viscous liquid, b.p. 180°/5 mm.,  $n_D^{20}$  1.5842. A solution of 30 g. (0.13 moles) of undistilled acetylenic carbinol in 50 cc. of methyl alcohol containing 1 g. of Raney nickel was treated with hydrogen until 0.13 moles had been absorbed. The cis 1,3-diphenyl-3-hydroxy-1-propene so obtained had the following properties: b.p. 158-160°/4 mm.,  $n_D^{20}$ : 1.5821,  $d_4^{20}$ : 1.0638.,  $MR_D$  obs. 60.8,  $MR_D$  calc'd., 63.3.

**Dehydration of 1,3-Diphenyl-3-hydroxy-1-propene.**—The cis and trans carbinols on treatment with syrupy phosphoric acid in the usual way apparently yielded the same unsaturated hydrocarbon, together with considerable tar. The physical properties are as follows:

Product from cis carbinol, b.p. 130-133°/4 mm.,  $n_D^{20}$ : 1.6045,  $d_4^{20}$ : 1.0252,  $MR_D$  obs. 64.4,  $MR_D$  calc'd. for phenylindene, 61.6.  $MR_D$  calc'd. for phenylbenzylacetylene or diphenylpropadiene, 63.3. Mol. Wt. (cryoscopic), found, 194, calc'd. for  $C_{15}H_{12}$ , 192.

Product from trans carbinol, b.p. 145-150°/8 mm.,  $n_D^{20}$ : 1.6045,  $d_4^{20}$ : 1.0248,  $MR_D$  obs. 64.4. Mol. Wt. (cryoscopic), found, 196.

Johnson and co-workers<sup>5</sup> report the following for phenylbenzylacetylene: b.p. 128-129°/2 mm.,  $n_D^{20}$ : 1.5946,  $d_4^{20}$ : 1.0273.

<sup>5</sup> Johnson, J. R., Jacobs, T. L., and Schwartz, A. M., 1938. Jour. Am. Chem. Soc., 60:1885.

Quantitative hydrogenation: 1.0025 g. (0.0075 moles) required 0.015 moles of hydrogen for saturation.

Parachor. Surface tension, 41.98 dynes/cm. P, obs. 478, P, calculated for phenylindene, 461.3 P, calculated for diphenylpropadiene or phenylbenzyl acetylene, 475.

### Summary

Three new phenyl-substituted ethylenic alcohols have been prepared, and their dehydration with phosphoric acid studied. Formulas have been proposed for the dehydration products.