[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

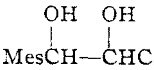
Vinyl Alcohols. XI.[1] 2-Mesityl-2-phenylvinyl Alcohol

BY REYNOLD C. FUSON, NORMAN RABJOHN[2] AND D. J. BYERS[3]

The discovery that 2,2-dimesitylvinyl alcohol could be made readily by dehydration of hydromesitoins[4] suggested a general approach to the synthesis of stabilized vinyl alcohols. The first question to be considered was whether both mesityl radicals were necessary. To obtain an answer to this question 1-mesityl-2-phenyl-ethylene glycol (II) has been prepared and subjected to dehydration. The product to be expected was 2-mesityl-2-phenylvinyl alcohol (III).

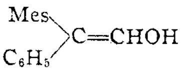
$MesCOCOC_6H_5$

I



$$\mathrm{MesCH(OH)\text{—}CH(OH)C_6H_5}$$

II



$$\mathrm{(Mes)(C_6H_5)C{=}CHOH}$$

III

The desired glycol, as a matter of fact, had been prepared by Weinstock[5] in 1936 by catalytic hydrogenation of 2′,4′,6′-trimethylbenzoin or mesityl phenyl diketone (I). Moreover, Weinstock had treated the glycol with a mixture of sulfuric acid and glacial acetic acid, obtaining a compound which differed from the glycol by the loss of the elements of water. In the present work the dehydration product has been prepared and studied. It resembles 2,2-dimesitylvinyl alcohol in its chemical properties and has, accordingly, been ascribed the structure of the enol, 2-mesityl-2-phenylvinyl alcohol (III). The dehydration is effected most satisfactorily by a mixture of concentrated hydrochloric acid and glacial acetic acid.

An attempt to use a mixture of concentrated sulfuric acid and glacial acetic acid, as indicated by Weinstock, yielded only phenyl 2,4,6-trimethylbenzyl ketone.

The starting point in the synthesis was mesityl phenyl diketone (I), prepared according to the method of Hatt, Pilgrim and Hurran.[6] The directions of Weinstock and Fuson[7] were followed. Catalytic hydrogenation of the benzil afforded a 93% yield of mesitylphenylethylene glycol (II). It is to be noted that but one of the two theoretically possible glycols was isolated.

The new vinyl alcohol is stable not only to heat and to hot acids but to hot methanolic potassium hydroxide as well. Prolonged treatment with oxygen in petroleum ether produced no change; however, after standing two years in air, the alcohol has undergone extensive decomposition.

Treatment in a closed tube with concentrated ammonium hydroxide converted the alcohol to a compound which had the composition of the corresponding divinyl ether.

The alcohol readily yielded an acetate and a benzoate. The alcohol, its acetate and its benzoate absorbed hydrogen in the presence of catalysts.

Oxidation was frequently accompanied by migration of an aryl radical. For example, with ozone the vinyl alcohol was converted to a mixture of mesitylphenylacetic acid and a compound thought to be 2,4,6-trimethylbenzoin. The diarylacetic acid was produced also by ozonization of the acetate. Similarly, oxidation with sodium hypochlorite solution or chromic acid produced mesityl phenyl diketone. Potassium permanganate transformed the vinyl alcohol to a dimeric compound similar to that reported for 2,2-dimesitylvinyl alcohol.[1] The structure of these oxidation products is still in doubt. As with dimesitylvinyl alcohol, the only oxidizing agent to give entirely normal results was alkaline hydrogen peroxide. The product was benzoylmesitylene.

An attempt to ketonize the vinyl alcohol by heating with methanolic hydrogen chloride yielded, not the corresponding aldehyde, but a derivative which has been identified as the methyl ether of the vinyl alcohol.

The infrared absorption spectrum of the new vinyl alcohol, measured in carbon tetrachloride solution, showed peaks at 2.76 and 2.84 μ confirming the presence of a hydroxyl group.

The authors are indebted to Professor W. H. Rodebush and Dr. J. B. Patberg for the measurement and interpretation of the infrared spectrum.

Experimental

1-Mesityl-2-phenylethylene Glycol.—A mixture of 20 g. of mesityl phenyl diketone,[7] 3 g. of copper chromite catalyst and 100 cc. of ethanol was shaken for two hours in a bomb at 150° and 2200 lb. pressure of hydrogen. The catalyst was removed by filtration and the solvent evaporated. The glycol was crystallized from high-boiling petroleum ether; m. p. 144–146°; yield 93.5%.

Anal.[8] Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87. Found: C, 80.11; H, 8.00.

This compound was also made by hydrogenation of mesityl phenyl diketone and of 2′,4′,6′-trimethylbenzoin by the method of Adams and Voorhees.[9]

2-Mesityl-2-phenylvinyl Alcohol.—A solution of 16 g. of 1-mesityl-2-phenylethylene glycol in 200 cc. of glacial acetic acid and 50 cc. of concentrated hydrochloric acid was heated under reflux for one hour, allowed to cool and

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(1) For the preceding paper in this series see Fuson, Southwick and Rowland, THIS JOURNAL, **66**, 1109 (1944).

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(4) Fuson and Rowland, THIS JOURNAL, **65**, 992 (1943).

(5) Weinstock, Ph.D. Thesis, University of Illinois, 1936.

(6) Hatt, Pilgrim and Hurran, *J. Chem. Soc.*, 93 (1936).

(7) Weinstock and Fuson, THIS JOURNAL, **58**, 1233 (1936).

(8) The microanalyses reported in this paper were carried out by Miss Margaret McCarthy, Miss Theta Spoor and Miss Dorothy Schneider.

(9) Adams and Voorhees, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 61.

poured into 1 liter of water. The colorless vinyl alcohol which formed was removed by filtration and crystallized from high-boiling petroleum ether; m. p. 114–115°; yield 83%.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.84; H, 7.88.

An attempt to effect the dehydration of the glycol with a mixture of glacial acetic and sulfuric acids yielded a small amount of a product which proved to be 2,4,6-trimethylbenzyl phenyl ketone.

Three grams of 2-mesityl-2-phenylvinyl alcohol was recovered unchanged after being heated for four and one-half hours at 175° in a sealed tube.

A sealed tube containing 2 g. of 2-mesityl-2-phenylvinyl alcohol in 10 cc. of concentrated ammonium hydroxide was heated at 100° for three hours. The product was a solid which, when crystallized from methanol, melted at 172–174°. A test for nitrogen was negative. The compound had the composition of the divinyl ether.

Anal. Calcd. for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 89.12; H, 7.35.

Oxygen was bubbled for twenty-three hours through a solution of 7 g. of the vinyl alcohol in a mixture of ether and low-boiling petroleum ether. The alcohol was recovered unchanged. It was noticed, however, that the alcohol underwent extensive decomposition when allowed to stand for two years in contact with the air.

The vinyl alcohol was unaffected by heating with a mixture of phosphorus and iodine and likewise by a three-hour treatment with boiling methanolic potassium hydroxide. It gave 0.87 mole of gas in the Grignard machine.[10]

2-Mesityl-2-phenylvinyl Methyl Ether.[11]—To 300 cc. of methanol, which had previously been saturated with dry hydrogen chloride, was added 15 g. of the vinyl alcohol, and the mixture heated under reflux for eleven hours. The solution was allowed to cool and was poured into 3 liters of water. The crude ether was distilled and induced to crystallize by trituration with a mixture of methanol and solid carbon dioxide. It was recrystallized from methanol; b. p. 144–145° (0.1 mm.); n^{20}D 1.5895; m. p. 44–45°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.66; H, 8.04.

A mixture of 0.5 g. of the methyl ether, 10 cc. of dioxane and 1 g. of selenium dioxide was heated under reflux for six hours. The product, a yellow solid melting at 133–136°, was shown by the mixed melting point method to be mesityl phenyl diketone.

Ethyl 2-Mesityl-2-phenylvinyl Ether.—Treatment of the vinyl alcohol with ethanolic hydrogen chloride yielded the ethyl ether, which was an oil boiling at 169–170° (2 mm.); n^{20}D 1.5804.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 86.00; H, 8.17.

2-Mesityl-2-phenylvinyl Acetate.—The acetate was prepared in 85% yield by allowing the vinyl alcohol to stand overnight with a mixture of acetic anhydride and pyridine. It was crystallized from ethanol; m. p. 91–92°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.54; H, 7.41.

2-Mesityl-2-phenylvinyl Benzoate.—A mixture of 0.5 g. of 2-mesityl-2-phenylvinyl alcohol, 7 cc. of pyridine, 2.5 cc. of benzoyl chloride and enough chloroform to produce homogeneity was heated to boiling and allowed to stand for eight hours. The reddish-brown solution was poured into water and extracted with 50 cc. of benzene. The benzene solution was washed twice with dilute aqueous sodium bicarbonate, acidified and washed three times with dilute hydrochloric acid. Evaporation of the solvent left a pale yellow oil which was induced to crystallize by rubbing with cold methanol. Crystallized from ethanol, the colorless product weighed 0.6 g. and melted at 111–115°. The pure benzoate melted at 117–117.5°.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.44; H, 6.75.

Hydrogenation of the Vinyl Alcohol.—A solution of 6 g. of mesitylphenylvinyl alcohol in 100 cc. of ethanol was hydrogenated over Raney nickel at 150° and 1700 pounds pressure. The product boiled at 170–173° (4 mm.).

Anal. Calcd. for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 83.21; H, 10.19.

When the clear, viscous oil was heated with *p*-nitrobenzoyl chloride at 100° for ten minutes it formed a *p*-nitrobenzoate. The ester crystallized from ethanol; m. p. 124–125°.

Anal. Calcd. for $C_{24}H_{29}NO_4$: C, 72.88; H, 7.39. Found: C, 72.83; H, 7.45.

Oxidation (A) with Ozone.—A solution of 4 g. of the vinyl alcohol in 60 cc. of chloroform was treated with 1% ozone for three and one-half hours. The chloroform solution was then heated for one hour with 60 cc. of water. Two products were isolated. One was an acid melting at 171–172°, which was shown by the method of mixed melting points to be mesitylphenylacetic acid.[12] The yield was 0.5 g.

The other product, a neutral compound, was purified by recrystallization from an ethanol–water mixture, low-boiling petroleum ether and high-boiling petroleum ether; m. p. 104–105°; yield 2 g. This is the melting point of 2,4,6-trimethylbenzoin.[13]

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.98; H, 7.36.

When the benzoin was dried at 80° in an Abderhalden dryer it developed a yellow color, caused by oxidation to the benzil.

Ozonization of the acetate of the vinyl alcohol yielded mesitylphenylacetic acid.

(B) With Potassium Permanganate.—To a solution of 3 g. of the vinyl alcohol in 50 cc. of acetone was added slowly a solution of 1 g. of potassium permanganate in 100 cc. of acetone. Decolorization of the permanganate took place rapidly. The product, isolated by the usual method, was colorless. It was recrystallized from the ethanol; m. p. 152–153°, with decomposition; yield 3 g.

Anal. Calcd. for $C_{34}H_{34}O_2$: C, 86.03; H, 7.22. Found: C, 85.88; H, 7.17.

The oxidation product was unaffected by extended exposure to hydrogen in the presence of a platinum oxide catalyst. Heating with acetic anhydride converted it to an oil which failed to crystallize.

(C) With Sodium Hypochlorite Solution.—A solution of 2 g. of the vinyl alcohol in 50 cc. of methanol was mixed with a sodium hypochlorite solution prepared from 9 g. of sodium hydroxide, 6 g. of chlorine and 50 cc. of water. A vigorous reaction took place and the reaction mixture developed a yellow color. The crude product (2 g.) was a light yellow substance. Fractional crystallization of this material yielded 0.05 g. of pure mesityl phenyl diketone.

(D) With Alkaline Hydrogen Peroxide.—A mixture of 5 g. of the vinyl alcohol, 200 cc. of methanol, 10 cc. of 20% sodium hydroxide solution and 25 cc. of 30% hydrogen peroxide was allowed to stand at room temperature for eighteen hours. From the reaction mixture were obtained by suitable procedures 0.3 g. of mesitoic acid and 3.3 g. of benzoylmesitylene. The latter, when treated at 0° with fuming nitric acid, formed a trinitro derivative (m. p. 201–203°) which proved to be identical with that prepared from a known specimen of benzoylmesitylene.[14]

(E) With Chromic Acid.—A solution of 2 g. of the vinyl alcohol, 150 cc. of glacial acetic acid, 20 cc. of water and 5 g. of chromic acid was allowed to stand at room temperature for sixteen hours. The reaction mixture was diluted with water and extracted with ether. Only a very slight amount of acidic material was isolated by extraction of the ether solution with alkali. The chief product was a yellow

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[10] Kohler and Richtmyer, This Journal, **52**, 3736 (1930).

[11] This experiment was carried out by Mr. Robert E. Jones.

[12] Maxwell and Adams, This Journal, **52**, 2959 (1930).

[13] Fuson, Weinstock and Ullyot, *ibid.*, **57**, 1803 (1935).

[14] Fuson and Armstrong, *ibid.*, **63**, 2650 (1941).

oil which has not been identified. However, small amounts of two solids were obtained from it. These were crystallized from ethanol. One (m. p. 135–136°) was bright yellow and proved to be mesityl phenyl diketone. The other was colorless and melted at 204–205°, with decomposition.

Anal. Calcd. for $(C_{12}H_{12}O)_x$: C, 83.68; H, 7.03. Found: C, 83.50; H, 7.10.

Summary

2-Mesityl-2-phenylvinyl alcohol has been produced by the dehydration of 1-mesityl-2-phenylethylene glycol. Its properties are similar to those described previously for 2,2-dimesitylvinyl alcohol.

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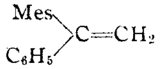
Vinyl Alcohols. XII.[1] The Oxidation of 1,1-Diarylethylenes

BY REYNOLD C. FUSON, M. D. ARMSTRONG, WM. E. WALLACE[2] AND J. WAYNE KNEISLEY[3]

When the olefin 1-mesityl-1-phenylethylene (I) was first examined,[4] it was found to behave normally in the permanganate and bromine tests for unsaturation. Attempts to ozonize the hydrocarbon, however, brought to light a remarkable peculiarity. The product was the corresponding enol, 2-mesityl-2-phenylvinyl alcohol (II), accompanied by small amounts of mesitylphenylacetic acid and mesityl phenyl diketone.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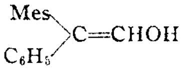
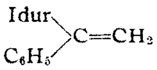
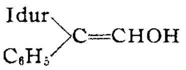

II

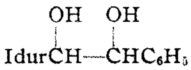
Since it was known that ozone reacted with the vinyl alcohol to produce mesitylphenylacetic acid and 2,4,6-trimethylbenzoin,[1] it seemed very probable that the olefin was converted initially to the vinyl alcohol, which yielded the acid and diketone by subsequent oxidation. The oxidation of an ethylenic hydrocarbon to the corresponding vinyl alcohol is a new type of reaction and provides an entirely new synthesis of these enols.

The oxidation of 1,1-dialkylethylenes to the corresponding dialkylacetic acids, which has also been observed by others,[5] may also involve the formation of an enol as an intermediate.

The new method of producing vinyl alcohols has been used successfully with 1-isoduryl-1-phenylethylene (III) also. When this olefin was treated with ozone a new alcohol, 2-isoduryl-2-phenylvinyl alcohol (IV), was formed. The structure of this alcohol was confirmed by an independent synthesis. The alcohol was produced by dehydration of 1-isoduryl-2-phenylethylene glycol (V).


III


IV


$\text{IdurCH(OH)—CH(OH)C}_6\text{H}_5$
V

The starting point in the synthesis of the glycol was benzyl isoduryl ketone (VI). Oxidation of this ketone with selenium dioxide produced a high yield of the corresponding diketone (VII). The latter underwent hydrogenation to form the glycol.

$\text{IdurCOCH}_2\text{C}_6\text{H}_5$
VI

$\text{IdurCOCOC}_6\text{H}_5$
VII

Experimental

Ozonization of 1-Mesityl-1-phenylethylene.—Eight grams of the olefin was dissolved in 25 cc. of glacial acetic acid, and 5% ozonized oxygen was passed through the solution for twenty-three minutes. (This corresponded to the introduction of three times the theoretical amount of ozone.) The solution was poured into 100 cc. of water and the resulting emulsion was heated under reflux for thirty minutes. The mixture was cooled and extracted with ether; the ether layer was washed with a 10% sodium hydroxide solution and with water. The solution was dried and the ether evaporated. The dark brown oil which remained was induced to crystallize partially. The 2-mesityl-2-phenylvinyl alcohol thus obtained was purified by recrystallization from high-boiling petroleum ether. It was colorless and melted at 114–115° (cor.). A mixed melting point with an authentic specimen[1] showed no lowering.

Anal.[6] Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.10; H, 7.77.

From the residual oil was isolated a small amount of yellow crystals melting at 132–134°. They proved to be mesityl phenyl diketone.[7] A third product, melting at 170–171°, was isolated by extracting the oil with alkali. It was shown to be mesitylphenylacetic acid.[8]

The sample of 1-mesityl-1-phenylethylene made from benzoylmesitylene and that prepared from acetophenone were treated separately with ozone. In each instance the ozonization products were those just described.

Ozonization of 1-Isoduryl-1-phenylethylene.—The olefin was treated with ozone in acetic acid. The products were 2-isoduryl-2-phenylvinyl alcohol and isodurylphenylacetic acid. The vinyl alcohol was crystallized from methanol; m. p. 121.5–122°; yield 20%.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.62; H, 7.67.

Both the vinyl alcohol and the acetic acid were identified by the method of mixed melting points. The vinyl alcohol gave one mole of methane in the Grignard machine.[9]

The **acetate** of the vinyl alcohol was prepared by the use

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(1) For the preceding paper of this series see Fuson, Rabjohn and Byers, THIS JOURNAL, **66**, 1272 (1944).

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(4) Fuson, Armstrong, Wallace and Kneisley, THIS JOURNAL, **66**, 681 (1944).

(5) Farmer and Pitkethly, *J. Chem. Soc.*, 290 (1938); Whitmore and Surmatis, THIS JOURNAL, **63**, 2200 (1941).

(6) The microanalyses reported in this paper were carried out by Miss Margaret McCarthy, Miss Theta Spoor, Miss Mary S. Kreger and Mr. L. G. Fauble.

(7) Gray and Fuson, THIS JOURNAL, **56**, 739 (1934).

(8) Maxwell and Adams, *ibid.*, **52**, 2959 (1930).

(9) Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930).