

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 (C₁₂H₁₂O)_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.

URBANA, ILLINOIS

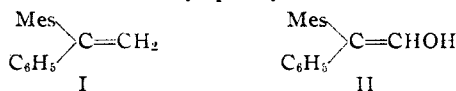
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

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

BY REYNOLD C. FUSON, M. D. ARMSTRONG, WM. E. WALLACE² AND J. WAYNE KNEISLEY³

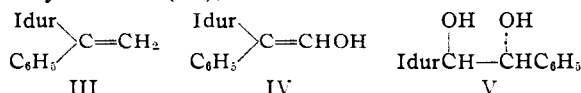
When the olefin 1-mesityl-1-phenylethylene (I) was first examined,⁴ it was found to behave normally in the permanganate and bromine tests for unsaturation. Attempts to ozonize the hydrocarbon, however, brought to light a remarkable peculiarity. The product was the corresponding enol, 2-mesityl-2-phenylvinyl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



Since it was known that ozone reacted with the vinyl alcohol to produce mesitylphenylacetic acid and 2,4,6-trimethylbenzoic acid,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).

The starting point in the synthesis of the glycol

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

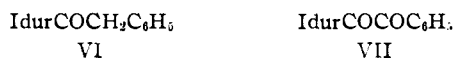
(2) Present address: General Aniline and Film Corporation, Easton, Pennsylvania.

(3) Present address: Hercules Powder Company, Wilmington, Delaware.

(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).

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.



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 specimen¹ showed no lowering.

*Anal.*⁶ Calcd. for C₁₇H₁₈O: 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 C₁₈H₂₀O: 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

(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*, **66**, 739 (1934).

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

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

of acetic anhydride in pyridine. It was crystallized from aqueous ethanol; m. p. 93–93.5°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.71; H, 7.63.

The isodurylphenylacetic acid was recrystallized from high-boiling petroleum ether; m. p. 198–198.5°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.52; H, 7.44.

An authentic specimen of isodurylphenylacetic acid was prepared from mandelic acid and isodurene by a procedure similar to that used by Gyr¹⁰ to synthesize phenyl-*p*-tolylacetic acid. From 80 g. of mandelic acid, 170 g. of isodurene and 210 g. of stannic chloride was obtained a yield of 110 g. (79%) of the desired acid melting at 193–196°. When purified it melted at 198–198.5°.

Isodurylphenylacetic acid was also made from isodurene and α -bromophenylacetic acid by a procedure similar to that of Maxwell and Adams.⁸ Purification was effected by transforming the crude acid to its ethyl ester, fractionally distilling the ester and regenerating the acid by hydrolysis. Ethyl isodurylphenylacetate boiled at 188–189° (6 mm.); n_D^{20} 1.5619. When ligroin was added the ester crystallized; m. p. 57.5–58°.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.17. Found: C, 81.21; H, 8.34.

The ester was easily hydrolyzed to the acid. The latter, after one recrystallization from aqueous ethanol, melted at 196–198°.

Hydrogenation of 2-Isoduryl-2-phenylvinyl Alcohol.—A solution of 1 g. of the vinyl alcohol in ethanol was treated for two hours with hydrogen at 50° and 1000 lb. pressure in the presence of Raney nickel. The residue, left after evaporation of the solvent, crystallized after seven months. The product, presumably 2-isoduryl-2-phenylethanol, was recrystallized from high-boiling petroleum ether; m. p. 72–73°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.14; H, 9.41.

Ozonization of 1-Mesityl-1-(*p*-tolyl)-ethylene.—Five grams of the olefin was treated with ozone in a manner similar to that described for 1-mesityl-1-phenylethylene. The only product which was isolated was mesityl-*p*-tolylacetic acid melting at 211–212°, after recrystallization from high-boiling petroleum ether.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.35; H, 7.65.

Benzyl Isoduryl Ketone.—This ketone was obtained in a 73% yield by the condensation of isodurene with phenylacetyl chloride in the presence of aluminum chloride. After the product was distilled it solidified and was recrystallized from methanol; m. p. 60.5–61°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.70; H, 7.95.

A small amount of pale yellow solid was isolated as a by-product. It was probably the diphenylacetyl derivative of isodurene. It was crystallized from methanol; m. p. 137–137.5°.

Anal. Calcd. for $C_{26}H_{26}O_2$: C, 84.29; H, 7.08. Found: C, 84.25; H, 7.31.

Isoduryl Phenyl Diketone.—A mixture of 110 g. of benzyl isoduryl ketone, 300 cc. of dioxane, 51 g. of selenium dioxide and 5 cc. of water was heated under reflux for twelve hours. After removal of the selenium and dioxane, the diketone crystallized from methanol in bright yellow needles; m. p. 65–66°. The yield of product melting at 61–64° was 81%.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.31; H, 6.92.

In one oxidation an isomeric compound was isolated. It separated from ethanol in pale yellow crystals melting at 63–63.5°. It was shown by the mixed melting point method to be different from the parent ketone and from the diketone melting at 65–66°.

(10) Gyr, *Ber.*, **41**, 4321 (1908).

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.50; H, 6.69.

This compound resembles the pseudobenzils.¹¹ It failed to react with acetyl chloride and was not oxidized by Fehling solution. It was, therefore, not a benzoin. It formed an oxime that was different from that described for the diketone melting at 65–66°.

Each of the benzils formed an oxime, but these derivatives were not obtained in entirely pure forms. However, melting points of mixtures showed the two oximes to be unlike. The oxime of the bright yellow benzil (m. p. 65–66°) crystallized from aqueous methanol in fine, white needles; m. p. 87–87.5°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81. Found: C, 77.92; H, 6.31.

The oxime of the pale yellow benzil (m. p. 63–63.5°) crystallized from ethanol in brilliant white cubes; m. p. 129.5–130°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81. Found: C, 77.72; H, 6.44.

The two oximes are presumably *syn* and *anti* forms. They could not be interconverted by seeding. The benzils likewise could not be interconverted by seeding and in this respect differ from the known benzil-pseudobenzil pairs. It may be that the pseudobenzil is stabilized by steric hindrance.

An independent synthesis of the diketone was accomplished by preparing 2,3,4,6-tetramethylbenzoin and oxidizing it with iodine.¹² A solution of 12.2 g. of isoduryl-glyoxal in 50 cc. of dry benzene was added slowly, with stirring, to a mixture of 17.3 g. of anhydrous aluminum chloride and 100 cc. of dry benzene. The time of addition was four hours. Stirring was continued for an additional five and one-half hours, and the mixture poured on a mixture of ice and hydrochloric acid. The benzoin was recrystallized from low-boiling petroleum ether; m. p. 92–93°; yield 71%.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.43; H, 7.48.

The dibenzoate of the corresponding enediol was made by heating the benzoin with benzoyl chloride and pyridine. It was recrystallized from ethanol; m. p. 133–135°.

Anal. Calcd. for $C_{26}H_{24}O_4$: C, 80.62; H, 6.49. Found: C, 80.82; H, 6.58.

One gram of the 2,3,4,6-tetramethylbenzoin was added to a boiling solution of 0.5 g. of sodium in 50 cc. of methanol. An excess of iodine was added and the mixture boiled for a few minutes. The excess iodine was discharged with sodium thiosulfate and the isoduryl phenyl diketone was recrystallized from ethanol. It melted at 65–66°. By the mixed melting point method it was shown that the diketone from the benzoin was identical with the isomer melting at 65–66°, but different from that melting at 63–63.5°.

1-Isoduryl-2-phenylethylene Glycol.—An alcoholic solution of 28 g. of the diketone melting at 65–66° was heated under reflux for one hour with 1 g. of Raney nickel. After removal of the nickel by filtration the solution was hydrogenated over a copper chromite catalyst at 150–175° and 2000 lb. pressure.¹³ The glycol was recrystallized from ethanol; m. p. 131.5–132°; yield 53%.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.97; H, 8.20. Found: C, 80.15; H, 8.24.

2-Isoduryl-2-phenylvinyl Alcohol.—A solution of 110 g. of glacial acetic acid, 22 g. of concentrated hydrochloric acid and 7.5 g. of 1-isoduryl-2-phenylethylene glycol was heated under reflux for three hours and allowed to stand at room temperature for twenty-four hours. The vinyl alcohol separated in long, almost transparent needles; m. p. 121–122°. The yield was 63%. A mixed melting point

(11) Schönberg and Kraemer, *Ber.*, **55B**, 1174 (1922); Schönberg and Malchow, *ibid.*, **55B**, 3746 (1922); Schönberg and Bleyberg, *ibid.*, **55B**, 3753 (1922).

(12) This synthesis was carried out by Dr. W. E. Holland.

(13) The hydrogenation was carried out by Dr. J. C. Robinson, Jr.

determination showed the alcohol to be identical with that obtained by the action of ozone on 1-isoduryl-1-phenylethylene.

Summary

The direct oxidation of two olefins to the corresponding vinyl alcohols has been achieved. The action of ozone on 1-mesityl-1-phenylethylene

and 1-isoduryl-1-phenylethylene has been found to convert them to 2-mesityl-2-phenylvinyl alcohol and 2-isoduryl-2-phenylvinyl alcohol, respectively. The latter, a new vinyl alcohol, has been prepared also by the dehydration of 1-isoduryl-2-phenylethylene glycol.

URBANA, ILLINOIS

RECEIVED MAY 6, 1944

[CONTRIBUTION OF THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Synthesis of Polyenes. IV

BY M. S. KHARASCH, W. NUDENBERG AND E. K. FIELDS

The preparations of hexatriene, dimethylhexatriene and an isomer of stilbestrol dimethyl ether by the action of sodamide (or potassium amide) in liquid ammonia on allyl chloride, methylallyl chloride and anethole hydrobromide, respectively, have been described.¹ The over-all reaction involves the elimination of two molecules of halogen acid, as indicated by the equation



It has been shown,^{1b,1c} however, that the reaction probably proceeds in two steps



In the present paper, this method of diene (or polyene) synthesis is applied to a variety of organic halides with the object of ascertaining the scope and mechanism of the reaction.

Discussion

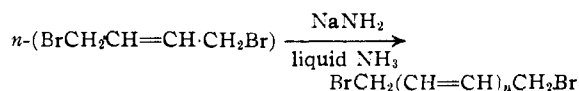
On the basis of the work described in this and previous papers, the following generalization appears to be justified. Alkali amides, in liquid ammonia, react with organic halides of the type RCH_2X to yield substances like the products given in equations (A) and (B) only if the radical R is strongly electronegative. That is, R must be α,β -unsaturated (*e. g.*, vinyl), or aromatic (*e. g.*, phenyl), or an acyl (R_1CO) group, in which R_1 is an aromatic radical. Some of the results obtained are summarized in Table I.

Some comments on the reactions cited are in order. Dibenzoyl ethylenes can be prepared in the manner indicated only from those phenacyl halides which do not contain substituents (*e. g.*, the nitro group), which react with sodamide in liquid ammonia. When the attempt was made to condense *m*-nitrophenacyl chloride by the use of sodamide, the product was a dark viscous liquid from which no pure compound could be isolated. Furthermore, compounds such as chloroacetone

(1) (a) Kharasch and Sternfeld, *THIS JOURNAL*, **61**, 2318 (1939); (b) Kharasch, Nudenberg and Sternfeld, *ibid.*, **62**, 2035 (1940); (c) Kharasch and Kleiman, *ibid.*, **65**, 11 (1943).

which react rapidly with liquid ammonia are not suitable for the condensation in question.

The polymer (m. p. above 350°) formed by the action of sodamide in liquid ammonia on 1,4-dibromobutene-2 has not been identified. However, the condensate is of considerable interest. Its molecular weight (calculated from its bromine content of 11.3%) is 1416. If the reaction proceeds as follows



then the molecule should have 47 conjugated double bonds. Very probably, the highly insoluble product contains a number of distinct polymers. If such is the fact, the calculated number of double bonds refers to an average.

Cinnamyl chloride, when treated with sodamide in liquid ammonia, gave 10% of diphenylhexatriene. No other product was isolated. The nature of the other products formed depended upon the quantity of sodamide used. When the usual 10% excess of sodamide was employed, the product was a chlorinated resin which may be similar to the condensate of hexatriene and allyl chloride.^{1a} When a large excess of sodamide (7 moles per mole of cinnamyl chloride) was used, the product was a hydrocarbon containing three diphenylhexatriene units per molecule.

The usefulness of the sodamide reaction in the preparation of unsymmetrical phenylated dienes has been demonstrated by the preparation of 1-phenyl-3-methylbutadiene from benzyl chloride and β -methylallyl chloride, as well as by the formation of 1-phenylbutadiene from benzyl chloride and allyl chloride. The other expected products (stilbene and 2,5-dimethylhexatriene in the first instance, and stilbene and hexatriene in the

