

interest in reference to the failures to obtain 1,2-diols by reduction of "ozonides" prepared in the liquid phase.¹¹ The *trans* nature of the diol would seem to preclude its formation by reduction of an ozonide of the Harries structure, and would seem rather to indicate that the immediate precursor of the diol was cyclohexene oxide.

We express our appreciation for support of this investigation by the Western Oil and Gas Association.

(11) A. Rieche, "Alkylperoxyde und Ozonide," Edwards Brothers, Inc., Ann Arbor, Mich., 1945 (1931), p. 132.

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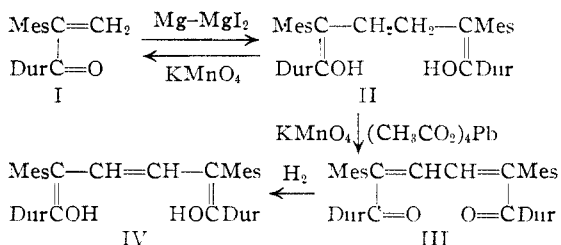
A New Stilbenediol Vinylog

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Duryl α -mesitylvinyl ketone (I) has been found to undergo bimolecular reduction with the binary mixture, Mg + MgI₂,¹ to yield the stable dienol, 1,6-diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol (II). Oxidation of the dienol with lead tetraacetate converted it to the corresponding hexadienedione (III). Treatment with potassium permanganate gave the dione accompanied by the original vinyl ketone (I).

Catalytic hydrogenation of the diketone (III) produced the enediol, 1,6-diduryl-2,5-dimesityl-1,3,5-hexatriene-1,6-diol (IV). Thus it has been



established that duryl α -mesitylvinyl ketone (I) yields a stable vinylog of didurylacetylene glycol.² The new series of compounds, derived from duryl α -mesitylvinyl ketone (I), is very similar to that produced earlier from mesityl α -mesitylvinyl ketone.³

Duryl α -Mesitylvinyl Ketone.—The method was a modification of that of Fuson and Sperati.⁴ A mixture of 3.9 g. of duryl 2,4,6-trimethylbenzyl ketone, 4.0 g. of paraformaldehyde, 2.0 g. of potassium carbonate and 70 ml. of ethanol was stirred under reflux overnight. The reaction was promoted by the addition of 0.20 g. of powdered black ferric oxide. The solution was poured into ice and acidified with dilute (1:10) hydrochloric acid. The white gummy crystals which formed were washed with cold ethanol and recrystallized from ethanol; m.p. 159°, yield 80%. The reported melting point is 159–160°.⁴

1,6-Diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol.—To a mixture of 1.92 g. of magnesium, 40 ml. of dry ether and 80 ml. of dry benzene was added, with stirring, 9.8 g. of iodine.

When the iodine color had disappeared, 12.25 g. of solid duryl α -mesitylvinyl ketone was added within 1 minute. The solution was stirred and heated under reflux for 3 hours, cooled and decomposed with iced hydrochloric acid. The crude product, isolated by usual procedures, weighed 11.6 g., m.p. 189–192°. The pure compound melts at 196°.

*Anal.*⁵ Calcd. for C₄₄H₅₄O₂: C, 85.94; H, 8.52. Found: C, 86.33; H, 8.83.

1,6-Diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol Diacetate.—A solution of 2.0 g. of the diol and 15 ml. of acetic anhydride was heated under reflux for 2 hours and poured into water. The diacetate separated from benzene as colorless crystals; m.p. 209°, yield 2.0 g. It was purified by further crystallization from benzene; m.p. 220–221°.

Anal. Calcd. for C₄₈H₅₈O₄: C, 82.47; H, 8.36. Found: C, 82.67; H, 8.33.

The infrared spectrum⁶ has bands assignable to vinyl ester (1751 cm.⁻¹), mesityl and duryl skeletal ring vibrations (1611 cm.⁻¹) and mesityl hydrogen atoms which are out of the plane of the ring (855 cm.⁻¹).

The Reaction of 1,6-Diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol with Potassium Permanganate.—A solution of 1.9 g. of potassium permanganate in 250 ml. of acetone was added over a period of 0.5 hour, with stirring, to a solution of 5.0 g. of the diol in 160 ml. of acetone. The manganese dioxide was removed by filtration and extracted in a Soxhlet extractor until the extracting solution was no longer yellow. The organic solutions were combined and concentrated to a volume of 150 ml. The excess permanganate was removed by filtration as manganese dioxide, and the clear yellow solution was concentrated to 25 ml. and cooled. The canary-yellow product was washed with methanol, the washings being added to the main filtrate. The crude 1,6-diduryl-2,5-dimesityl-2,4-hexadiene-1,6-dione weighed 2.1 g., m.p. 253–257°. It was recrystallized from benzene; m.p. 265–266°.

The infrared spectrum has absorption bands assignable to a conjugated ketone grouping (1656 cm.⁻¹) and mesityl hydrogen atoms out of the plane of the ring (857 cm.⁻¹).

Anal. Calcd. for C₄₄H₅₀O₂: C, 86.51; H, 8.25. Found: C, 86.28; H, 8.21.

The mother liquor was evaporated to dryness and subjected to fractional crystallization from methanol. In this manner there was isolated an additional 0.2 g. of the yellow dione (m.p. 263–264°) and 1.2 g. of a colorless compound (m.p. 159°) identified by a mixed melting point as duryl α -mesitylvinyl ketone.

Reaction of 1,6-Diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol with Lead Tetraacetate.—To a hot solution of 5.0 g. of the diol in 100 ml. of benzene was added, with stirring, 10.5 g. of lead tetraacetate. The mixture was stirred under reflux for 14 hours. The yield of 1,6-diduryl-2,5-dimesityl-2,4-hexadiene-1,6-dione (m.p. 265–266°) was 2.3 g. From the mother liquor was isolated 0.4 g. of duryl α -mesitylvinyl ketone, m.p. 159°.

1,6-Diduryl-2,5-dimesityl-1,3,5-hexatriene-1,6-diol (A).—A solution of 0.2 g. of the diketone in 150 ml. of benzene was shaken with a platinum oxide catalyst and hydrogen at atmospheric pressure until the yellow color had disappeared. The catalyst was removed by filtration and the solution was concentrated to a small volume and cooled. The resulting colorless diol melted at 236–237°. When the pure compound was exposed to the atmosphere it assumed a brownish color, and after one week the melting point had dropped to 231–232°.

The infrared spectrum has bands attributable to hydroxyl (3476 cm.⁻¹), mesityl and duryl skeletal ring vibrations (1611 cm.⁻¹), C–O–H (1142 cm.⁻¹), mesityl hydrogen out of the plane of the ring (850 cm.⁻¹) and double bond hydrogen (869.5 and 1007 cm.⁻¹). Absorption at 1282 cm.⁻¹ indicates the possible presence of an epoxy structure, which might account for the manner in which the compound decomposes when exposed to air.

Anal. Calcd. for C₄₄H₅₂O₂: C, 86.22; H, 8.55. Found: C, 86.38; H, 8.46.

(B).—To a solution of 0.5 g. of the diketone in 75 ml. of hot glacial acetic acid was added 3.0 g. of zinc dust. The

(1) M. Gomberg and W. E. Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

(2) R. C. Fuson and S. C. Kelton, Jr., *ibid.*, **63**, 1500 (1941).

(3) R. C. Fuson, D. J. Byers and A. I. Rachlin, *ibid.*, **64**, 2891 (1942).

(4) R. C. Fuson and C. A. Sperati, *ibid.*, **63**, 2648 (1941).

(5) Microanalyses by Miss Emily Davis, Mrs. Katherine Pih and Mrs. Jeanne Fortney.

(6) The infrared spectra were observed and interpreted by Miss Elizabeth Petersen.

mixture was heated on a steam-bath for 1 hour and filtered while hot. Cooling of the filtrate caused the separation of 0.4 g. of a brownish crystalline solid which melted, after being washed with water, at 224–229°. Recrystallized from ethanol, the product was colorless and melted at 236–237° alone or when mixed with a sample of the material obtained by method A.

1,6-Diduryl-2,5-dimesityl-1,3,5-hexatriene-1,6-diol Diacetate.—A solution of 0.5 g. of the diol in 25 ml. of acetic anhydride was heated under reflux for 90 minutes. Cooling caused the separation of 0.49 g. of white needles, m.p. 252–255°. The diacetate was purified by recrystallization from glacial acetic acid; m.p. 275°.

Anal. Calcd. for $C_{48}H_{56}O_4$: C, 82.71; H, 8.09. Found: C, 82.41; H, 8.26.

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The Polarographic Behavior of Methyl Vinyl Ketone and Methyl Vinyl Sulfone¹

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Most α,β -unsaturated carbonyl compounds exhibit, on polarographic reduction, two waves which have been considered to be due to the reduction of the enol form of the compound (pH dependent) followed by the reduction of the double bond (pH independent).² If the corresponding α,β -unsaturated sulfone exhibited similar polarographic behavior, the reduction could plausibly be expected to proceed through a similar mechanism involving the enol form if it is assumed that this is the current picture of the reduction of α,β -unsaturated carbonyl compounds. In order for the sulfone to form the enol, the sulfur octet would have to enlarge to hold ten electrons. This expansion of the sulfur octet has been the subject³ of much controversy. Thus, it seemed of interest to examine the polarographic behavior of an α,β -unsaturated sulfone and the corresponding α,β -unsaturated ketone.

The two compounds selected for investigation were methyl vinyl sulfone and methyl vinyl ketone. Only the ketone has been reported as being polarographically reducible.⁴ Only one wave was observed at -1.43 v. *vs.* S.C.E. in 0.1 *M* potassium chloride solution.

Experimental

Apparatus.—All polarograms were recorded with a Sargent Polarograph Model XXI. The linearity of the potential dial was checked by means of a Leeds and Northrup Potentiometer. Half-wave potentials were read directly from the chart and were calculated to be accurate within 15 millivolts. Corning marine barometer tubing was used for the capillary which had a value of 1.51 mg./^{2/3} sec.^{1/6} for the capillary constant at open circuit in 0.5 *M* potassium chloride at 25°. The water-jacketed, H-type cell⁵ with

attached saturated calomel electrode, was maintained at $25 \pm 0.2^\circ$ by circulating water through the jacket from an external constant temperature bath. The pH of all solutions were measured with a Beckman Model G pH Meter.

Materials.—The methyl vinyl ketone was obtained from E. I. du Pont de Nemours and Co. as 85% azeotrope with water having about 0.5% acetic acid and 0.1% hydroquinone present. Since neither of these compounds is reduced at the dropping mercury electrode, the ketone solution was used without further purification. The methyl vinyl sulfone was prepared by the method of Price⁶ and after careful purification had the following physical constants; b.p. 110° (18 mm.) (literature value⁶ b.p. 115 – 117° (19 mm.)) and n_D^{20} 1.4262. Appropriate quantities of the organic compounds were dissolved in 95% ethanol and an aliquot diluted with aqueous buffer to give a final solution 0.5 *mM* in reducible species and 10% in ethanol. The buffer was 0.1 *M* with respect to buffering constituents (acetic, boric and phosphoric acids with various amounts of 1 *M* sodium hydroxide in order to cover the pH range 2 to 12) and 0.5 *M* with respect to potassium chloride in order that a high ionic strength (0.62 *M*) might be maintained.⁷ Tank nitrogen, purified by passage through gas bubblers (one, containing concentrated sulfuric acid; a second, an alkaline solution of pyrogallol; and a third, a sample of cell solution) was bubbled through the solution in the polarographic cell for five minutes before polarographing. Polarograms were recorded over the potential range 0 to -2 volts *vs.* S.C.E. at a suitable sensitivity. The half-wave potentials were determined by the usual graphical method.

Results and Discussion

The half-wave potential *vs.* pH curves for both ketone and sulfone are shown in Fig. 1. It is seen that methyl vinyl ketone exhibits the polarographic behavior expected of an α,β -unsaturated carbonyl compound, *i.e.*, two waves, one pH dependent and one pH independent. Methyl vinyl sulfone, on the other hand, exhibits only one wave which is pH independent indicating that the double bond is the only group present that is polarographically reducible in the potential range available. This lack of reduction of the sulfone group may be explained by the inability of the sulfone group to form an appreciable concentration of conjugate acid (see following paragraph).

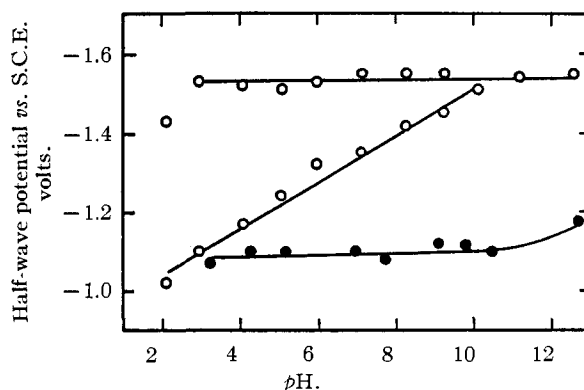


Fig. 1.—Half-wave potential *vs.* pH curves for methyl vinyl sulfone (closed circles) and methyl vinyl ketone (open circles).

Thus, another possible mechanism of the reduction of the α,β -unsaturated carbonyl group could involve, rather than the reduction of the enol form, the reduction of the conjugate acid of the keto form I which would be expected to be pH dependent.

(6) C. C. Price and J. Zomlefer, *THIS JOURNAL*, **72**, 14 (1950).

(1) Abstracted from the thesis of C. W. Johnson, submitted in partial fulfillment of the requirements of the degree Master of Science in Chemistry, June, 1952.

(2) S. Wawzonek, *Anal. Chem.*, **21**, 62 (1949).

(3) For an excellent discussion of this question see H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951). In particular it is demonstrated that due to the geometry of the orbitals in linear α,β -unsaturated sulfone systems less expansion or less interaction of the electrons of the double bond and of the sulfone group is probable than in the cyclic α,β -unsaturated sulfone systems that are present in substituted thiophene-1-dioxides.

(4) E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem., Anal. Ed.*, **16**, 469 (1944).

(5) J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

(7) P. J. Elving, J. C. Komyathy, R. E. VanAlta, C. S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).