over potassium carbonate. The ether was evaporated to leave a residue of 6.1 g. of a base-insoluble, white, crystalline solid of m.p. 50°.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.54; H, 8.95.

This substance is assigned the structure of menthofurfuryl alcohol on the basis of its method of preparation and analysis. Exposure of it to the atmosphere, even momentarily, caused discoloration and rapid liquefaction and tar formation. Hence, the ultraviolet absorption of the material, $\lambda^{\text{alc.}}_{\text{max}}$ 228 mμ (3.96), 294 mμ (2.31) cannot be regarded as indicative of its structure.

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Anomalies in the Vapor Phase Ozonolysis of Cyclohexene

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Ozonolysis of cyclohexene in the liquid phase has been shown[1] to produce adipic acid and the corresponding half and dialdehydes. The renewed interest in the ozonolysis reaction[2] prompts this preliminary report of a study of the vapor phase ozonolysis of cyclohexene which has been found to produce the abnormal products formic acid and *trans*-1,2-cyclohexandiol in small yield in addition to adipic acid as the major product.

A. Materials and Method.—The cyclohexene (Phillips Petroleum) was redistilled 99 mole per cent. material of infrared absorption[3] identical with that reported.[4]

For the preparation of cyclohexene ozonide a stream of dry nitrogen flowing at a rate of 50 ml. per minute was passed through a thermostated hydrocarbon bubbler to carry cyclohexene vapor into a reaction tube at 0.16 millimole per minute. Ozone entered the reaction tube at the rate of 0.10 millimole per minute in a dry, ozonized oxygen stream flowing at the rate of 150 ml. per minute. At the confluence of the streams an aerosol was produced as a heavy smoke. As the reaction proceeded, a viscous, colorless condensate appeared on the walls of the reactor tube and slowly ran down into a trap provided for its collection.

The ultraviolet absorption spectrum of the ozonide showed only general absorption of low intensity in the 220–310 mμ region. Absorption in the carbonyl region (270–300 mμ) was specifically absent in samples taken with precaution to avoid moisture but appeared in samples exposed to laboratory air or treated with water.

The infrared absorption of the ozonide showed strong bands at 2.95, 3.40 and 5.82 μ which are attributed to OH, CH and C=O[5] vibrations, respectively. The 6–13 μ region showed only general absorption with a suggestion of discrete bands at 8.5 and 9.1 μ.

As the ozonide stood, crystals of adipic acid were slowly deposited. The yield of adipic acid never exceeded 50% in a number of experiments, the remainder of the material being an intractable, alkali-soluble, viscous oil.

Titration of the ozonide with sodium hydroxide against phenolphthalein gave neutral equivalents of 269, 261 and 243. A Zerewitinoff determination in cineole as solvent showed 0.75 active H per $C_6H_{10}O_3$ unit. Iodometry showed an active oxygen content of 1.8%. Analysis of the ozonide gave: C, 52.0, 52.2, 52.4; H, 7.9, 8.5, 8.9. Calcd. for $C_6H_{10}O_3$: C, 55.4; H, 7.7.

B. Isolation of Formic Acid.—Cyclohexene ozonide (10.6 g.) was distilled into two traps in series, one at 0° and the second at −78°. The pressure was slowly lowered to 2 mm. as the pot temperature was raised to 90°. The contents of the traps were found to be aqueous formic acid solutions. Identity was established by infrared absorption and by the hydroxamic acid–ferric ion color reaction. The quantity of formic acid was determined by titration and corresponded to 10% of the theoretical based upon one mole per mole of $C_6H_{10}O_3$ (0.37 g.).

C. Isolation of *trans*-1,2-Cyclohexandiol.—Cyclohexene ozonide (8.7 g.) was decomposed by heating under reflux with water (40 ml.) for 2.5 hours. The hydrolysate was brought to *p*H 9 by the addition of standard sodium hydroxide corresponding to 0.8 carboxyl group per $C_6H_{10}O_3$; and, the alkaline solution was continuously extracted with ether for 10 hours. Evaporation of solvent left 1.3 g. of yellowish oil which was distilled to give 0.47 g., b.p. 70–110° at 14 mm. which was presumably largely cyclopentenealdehyde-1 since it showed $\lambda^{\text{alc}}_{\text{max}}$ 235 mμ, and formed a semicarbazone[1] of m.p. 208–209°; and, 0.2 g. b.p. 110–170° at 1 mm. which solidified on being cooled. Three crystallizations of the solid from benzene plus hexane gave 0.1 g. of white plates of m.p. 100–102.5°.

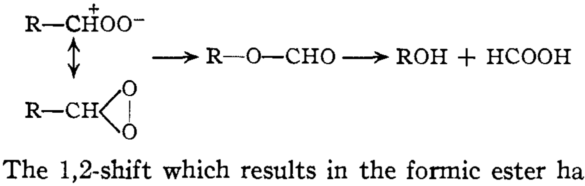
Anal. Found: C, 61.9; H, 10.4. Calcd. for $C_6H_{12}O_2$: C, 62.1; H, 10.4.

The infrared absorption of this material was identical with that of an authentic sample[6] of *trans*-1,2-cyclohexandiol, and no depression was observed in a mixed melting point determination.

Discussion

These results support the earlier observation[7] that the reaction of ozone with olefins in the vapor phase produces "ozonides" having different properties than those produced in condensed systems. Thus, the absence of ketone or aldehyde absorption in the ultraviolet is to be contrasted with the frequent appearance of these groups in liquid phase ozonolyses.[5] Further, in a direct comparison of the infrared absorption of the liquid phase product, prepared according to Harries,[1] and the vapor phase product, although both showed a strong band at 5.82 μ, the band at 2.92 μ was absent in the liquid phase product. In addition there was no correspondence in the 6–13μ region.

A possible source of formic acid in the distillate from the vapor phase reaction product is suggested by application of the mechanism proposed by Criegee[8] as



The 1,2-shift which results in the formic ester has further analogy in the formation of lactones from ketones on treatment with peracids.[9] Alternatively, an ozone-catalyzed free radical oxidation of cyclohexene at the position allylic to the double bond may occur with the production of 2-cyclohexenol. Normal ozonolysis of the cyclohexenol would lead to formic acid.[10]

The isolation of *trans*-1,2-cyclohexandiol is of

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[1] C. Harries and R. Seitz, *Ann.*, **410**, 24 (1915).

[2] B. Witkop and J. B. Patrick, THIS JOURNAL, **74**, 3855, 3861 (1952); references 5 and 8.

[3] Spectra were determined with a Perkin–Elmer model 12-c spectrophotometer in the region 2.5 to 12 μ using rock salt optics.

[4] A.P.I. Index.

[5] E. Briner, *et al.*, have found a band at 5.8 μ in the spectra of a large number of ozonized solutions of hydrocarbons, including cyclohexene; *Helv. Chim. Acta*, **35**, 340, 345, 353 (1952).

[6] J. B. Senderens and J. Aboulenc, *Comp. rend.*, **173**, 1367 (1921).

[7] E. Briner, *Helv. Chim. Acta*, **12**, 154, 529 (1929); E. Briner and S. de Nimitz, *ibid.*, **21**, 748 (1938).

[8] R. Criegee, 120th Meeting of the American Chemical Society, New York, N. Y., Sept. 7, 1951, Abstracts 22M.

[9] W. E. Doering and L. Speers, THIS JOURNAL, **72**, 5515 (1950).

[10] J. E. Leffler, *Chem. Rev.*, **45**, 400 (1949). This alternative was suggested by one of the Referees.

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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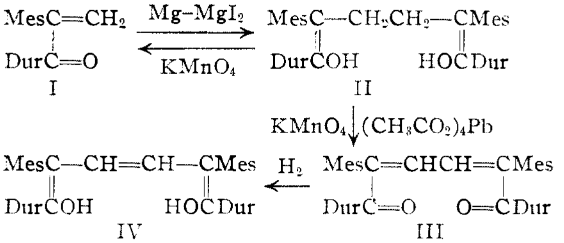
Duryl α-mesitylvinyl ketone (I) has been found to undergo bimolecular reduction with the binary mixture, $Mg + MgI_2$,[1] to yield the stable dienol, 1,6-diduryl-2,5-dimesityl-1,5-hexadiene-1,6-diol (II). Oxidation of the dienol with lead tetraacetate converted it to the corresponding hexadienedione (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 $C_{44}H_{54}O_2$: 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 $C_{48}H_{58}O_4$: C, 82.47; H, 8.36. Found: C, 82.67; H, 8.33.

The infrared spectrum[6] 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 $C_{44}H_{50}O_2$: 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 $C_{44}H_{52}O_2$: 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

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[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**, 2643 (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.