[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Epoxyethers. III. Reaction of Desyl Chloride with Base

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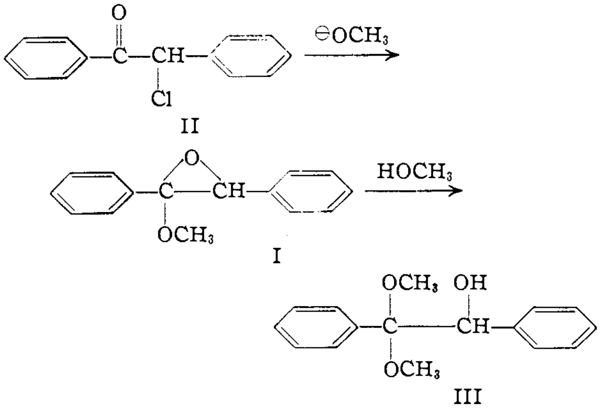
The previously unknown epoxyether, 1,2-diphenyl-1-methoxyethylene oxide (I), has been isolated from the reaction of desyl chloride (II) with alcoholic sodium methoxide. The structure of the epoxyether has been proven and various cleavage reactions studied. The epoxyether was found to rearrange to the methoxy ketone (V) in the presence of magnesium bromide. The structure of the compound reported to be the epoxyacetate (VI) was shown to be the methyl ether acetate of *trans*-stilbenediol.

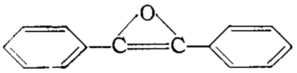
The present paper records the isolation, proof of structure, some chemical reactions and the rearrangement of the epoxyether, 1,2-diphenyl-1-methoxyethylene oxide (I), from desyl chloride (II) and sodium methoxide. The liquid previously assigned the structure of the epoxyether[3] (I) was shown to be mainly benzoin dimethyl ketal (III), the compound assigned the structure of diphenylacetylene oxide[3] (IV) was shown to be the methyl ether of benzoin[1] (V), and the compound assigned the structure of the epoxyacetate[3] (VI) shown to be the monoacetate monomethyl ether of *trans*-stilbenediol (VII).[4]



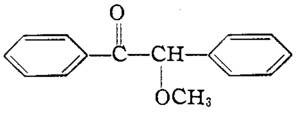
II

I

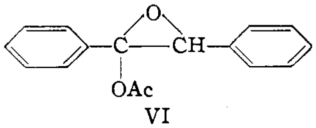
III



IV



V



VI

In 1929 Ward[5] reported the formation of the diethyl ketal of benzoin from the reaction of desyl chloride (II) and alcoholic sodium ethoxide. Since the reaction kinetics indicated a bimolecular reaction and since the hydroxy ketal does not form from the hydroxy ketone under the conditions of the reaction, Ward postulated an epoxyether as an intermediate. A short time later, Madelung and Oberwegner[3] treated desyl chloride (II) with alcoholic sodium methoxide under essentially the same conditions as Ward but claimed the isolation of the epoxyether (I) instead of the hydroxy ketal (III) by distillation at reduced pressure. Further distillation of the reaction product at atmospheric pressure was accompanied by loss of methyl alcohol and a solid, m.p. 52°, was isolated from the pyrolysate. Madelung and Oberwegner claimed this solid to be the oxide of diphenylacetylene (IV). Reaction of I with acetic anhydride was claimed to give the epoxyacetate (VI), m.p. 109°.

The claim of the isolation of IV has been disputed by Roger and McGregor[6] who, following the directions of Madelung and Oberwegner, were able to isolate a compound, m.p. 48–49°, that agreed closely with the description given by the previous workers. However, the analysis indicated the compound was not IV and reaction with *p*-tolylmagnesium bromide did not give the products expected of structure IV but rather a new derivative, m.p. 142–143°. Roger and McGregor recorded analyses but did not identify the two compounds.

In 1933 Richard[7] also reported a study of the reaction of desyl chloride with base. From the reaction of desyl chloride with powdered potassium hydroxide in ether, Richard claimed the isolation of diphenylacetic acid, m.p. 145°, as one of the products of the reaction. However, Fuson and Tull[8] have shown that the acid, m.p. 145°, formed in this reaction is benzilic acid. Roger and McGregor[6] reported the same results using toluene as the solvent.

Since epoxyethers have been isolated and characterized previously in this Laboratory,[9] an attempt was made to prepare the epoxyether (I) from desyl chloride. The reaction of dry sodium methoxide in ether failed to yield the epoxyether. However, when an alcoholic solution of sodium methoxide was allowed to react for a short period of time with desyl chloride (II) and the reaction quenched with ice and water, a 33% yield of crystalline epoxyether (I) could be isolated. The compound had the correct carbon, hydrogen and methoxyl analysis and a

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[1] Atomic Energy Predoctoral Fellow, 1950–1952. Presented before the XIIth International Congress of Pure and Applied Chemistry in New York, September, 1951. Abstracted in part from the Doctorate thesis of Milton L. Weiner, Wayne University, April, 1952.

[2] Parke, Davis and Co. Fellow, 1952–1953.

[3] W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 201 (1931).

[4] After the announcement of this work (ref. 1) a paper was published by W. G. Dauben, C. F. Hiskey and M. A. Muhs, THIS JOURNAL, **74**, 2082 (1952), which stated that compounds I and IV of ref. 3 appeared to be the methyl ether of benzoin of different states of purity.

[5] A. M. Ward, *J. Chem. Soc.*, 1541 (1929).

[6] R. Roger and A. McGregor, *ibid.*, 1850 (1934).

[7] G. Richard, *Compt. rend.*, **197**, 1432 (1933).

[8] R. Tull, Ph.D. Thesis, University of Illinois, 1949.

[9] (a) C. L. Stevens, W. Malik and R. Pratt, THIS JOURNAL, **72**, 4758 (1950); (b) C. L. Stevens and E. Farkas, *ibid.*, **74**, 618 (1952).

molecular weight determination indicated the compound was not a dimer. The infrared spectrum indicated the absence of a carbonyl group and the presence of an ether linkage.

The chemical reactions used to characterize the epoxyether (I) were similar to those used previously.[9] Hydrolysis of the epoxyether with water gave benzoin in 96% yield. Benzoic acid and acetic acid reacted rapidly with I to give benzoin benzoate and benzoin acetate in 48 and 57% yield, respectively.

Reaction of I with methyl alcohol gave benzoin dimethyl ketal (III). This ketal could also be prepared in 73% yield directly from desyl chloride and alcoholic sodium methoxide by allowing the mixture to stand at room temperature for one day. Benzoylation of the benzoin dimethyl ketal followed by preferential cleavage of the ketal group with dilute acid gave benzoin benzoate.

This epoxyether was stable when heated and could not be made to rearrange to methyl diphenylacetate[10] by treatment with chemical reagents. During the course of this investigation magnesium bromide was found to cause the rearrangement of the epoxyether (I) to the methyl ether of benzoin (V) in 31% yield.

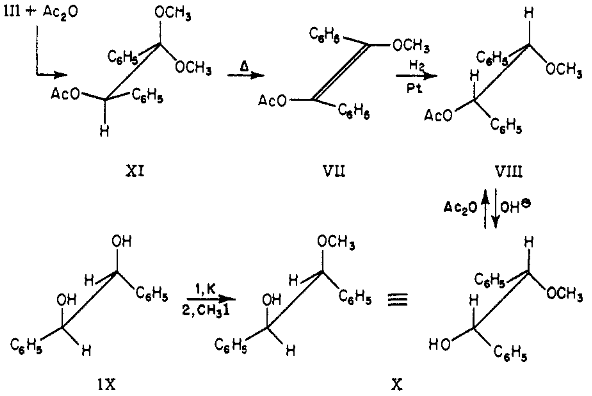
The isolation of the reactive epoxyether and the subsequent reaction with alcohol to form the α-hydroxy ketal (III) confirm the original mechanism postulated by Ward. The work of Roger and McGregor[6] and Madelung and Oberwegner[3] has been repeated and the compounds melting at 48–49°[3,6] and 142–143°[6] have been identified as the methyl ether of benzoin (V) and its *p*-tolyl derivative, respectively. The liquid which Madelung and Oberwegner[3] claim to be the epoxyether (I) was shown in this work to be mainly the hydroxy ketal (III). Pyrolysis of authentic III gave methyl alcohol in agreement with the experimental observations of Madelung and from the pyrolysate the methyl ether of benzoin could be isolated as the oxime.[11]

Finally, the structure was determined of the compound claimed[3] to be epoxyacetate (VI) and claimed to be formed from epoxyether and acetic anhydride in the presence of sulfuric acid catalyst. Authentic epoxyether under these conditions did not give the compound melting at 109°. Pure methyl ether of benzoin gave only the starting material. Only authentic α-hydroxy ketal (III) gave a solid when subjected to the directions of Madelung. The formation of this solid, m.p. 107–108°, further confirms the fact that the liquid fraction stated by Madelung to be epoxyether (I) was α-hydroxy ketal (III).

The solid was shown to be the monoacetate monomethyl ether of stilbenediol by mild acid hydrolysis to benzoin acetate and basic hydrolysis to benzoin methyl ether. Treatment with lithium aluminum hydride also gave benzoin methyl ether. Analytical data, methoxyl analysis, the ultraviolet and infrared spectra and the absorption of one mole of hydrogen support this structure.

The compound was shown to be the *trans*-stilbene derivative by the following reactions. Hydrogenation of the solid gave a methyl ether acetate (VIII) of 1,2-diphenylethylene glycol. The known monomethyl ether of the *erythro*(*meso*)-glycol was prepared and acetylated. Although the melting points and the infrared spectra were similar, the compounds were different as indicated by a depression of the melting point of a mixture. Saponification of the methoxy acetate (VIII) gave a monomethyl ether of 1,2-diphenylethylene glycol that was different from the known monomethyl ether of the *meso*-glycol. The previously unknown monomethyl ether of the *threo*(*dl*)-glycol (IX) was prepared and proved to be identical with the product from the saponification. Further, acetylation of this monomethyl ether gave a methoxy acetate identical with VIII. Since catalytic hydrogenation is known to proceed in a *cis*-manner, the original olefin must have been a *trans*-stilbene derivative.

The stilbene derivative (VII) is considered to have been formed from the α-hydroxy ketal (III) by first acetylation of the hydroxyl group and then pyrolysis of the acetate ketal (XI) with loss of methyl alcohol at the temperature of the refluxing acetic anhydride. This interpretation was confirmed by the fact that authentic ketal acetate (XI) gave the stilbene derivative in refluxing acetic anhydride.



XI VII VIII

IX X

Experimental

Preparation of 1,2-Diphenyl-1-methoxyethylene Oxide (I).—A solution of 0.156 mole of sodium methoxide in dry methanol having a total volume of 500 ml. was heated to reflux and rapidly added to 36 g. (0.156 mole) of desyl chloride dissolved in 210 ml. of dry methanol, which also had been heated to reflux. The mixture was refluxed for two minutes, after which time it was poured onto a large volume of ice and the solid which separated after an hour was removed by filtration from the still cold methanol–water mixture. After the solid had dried, two recrystallizations from low-boiling petroleum ether yielded 11.75 g. (33%) of 1,2-diphenyl-1-methoxyethylene oxide, m.p. 56–58°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.65; H, 6.19; OCH_3, 13.72 mol. wt., 226. Found: C, 79.40; H, 6.29; OCH_3, 13.50 mol. wt., 216.

Hydrolysis of Epoxyether (I).—One gram of epoxyether was dissolved in 15 ml. of acetone and water added until the solution became cloudy. After a drop of hydrochloric acid was added, the solution was heated for one hour. Evaporation of the solvent gave 0.9 g. (96%) of benzoin, m.p. 132–133°.

Reaction of Epoxyether (I) with Benzoic Acid.—A solution of 2.14 g. (9.47 millimoles) of I and 1.22 g. (10.0 millimoles) of benzoic acid in 40 ml. of heptane was allowed to stand for eight hours and then refluxed for three hours.

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[10] J. G. Aston, *et al.*, *ibid.*, **64**, 300 (1942), proposed an epoxyether as an intermediate in the rearrangement of α-haloketones to esters.

[11] Pyrolysis of another α-hydroxy ketal with loss of alcohol has recently been recorded, C. L. Stevens and A. E. Sherr, *J. Org. Chem.*, **17**, 1177 (1952).

On cooling the reaction mixture, benzoin benzoate precipitated. Recrystallization from heptane yielded 1.45 g. (48%), m.p. 124–125°, mixed m.p. with benzoic acid, 102–110°.

Preparation of Benzoin Benzoate.—A mixture composed of 3.2 g. (0.015 mole) of benzoin and 2.1 g. (0.015 mole) of benzoyl chloride was fused and maintained at a bath temperature of 140° until evolution of hydrogen chloride ceased and then heated at the same temperature for 20 minutes longer. After standing for two days, the resultant oil had solidified. Recrystallization from heptane yielded 2.7 g. (57%) of benzoin benzoate,[12] m.p. 123.5–125°, mixed melting point with the compound from the epoxyether, 124–125°.

Reaction of Epoxyether (I) with Acetic Acid.—To a solution of 0.51 g. (2.25 millimoles) of I in 10 ml. of glacial acetic acid and 0.5 ml. of acetic anhydride, a trace of sulfuric acid was added. The solution was then warmed on the steam-bath for 30 minutes and was poured onto ice. A white solid was filtered which yielded, after recrystallization from methylcyclohexane, 0.33 g. (57%) of benzoin acetate, m.p. 81–82°.

A mixed melting point with benzoin acetate made by the method of Francis and Keane[13] was not depressed, m.p. 81–82°.

Preparation of Benzoin Dimethyl Ketal (III) from Desyl Chloride (II).—A solution of 10.3 g. (44.6 millimoles) of desyl chloride in 70 ml. of dry methanol was added to 28 ml. of a methanolic solution containing 49.1 millimoles of sodium methoxide at such a rate that addition was complete in 30 seconds. After allowing the mixture to stand for 24 hours, the precipitated sodium chloride was filtered, the filtrate was concentrated on the steam-cone as far as practicable, and the remainder of the methanol was removed under reduced pressure. Distillation of the residue yielded 8.45 g. (73%) of the colorless benzoin dimethyl ketal (III) as a viscous oil, b.p. 136–139° (0.7 mm.); n^{25}D 1.5617.

Preparation of Benzoin Dimethyl Ketal (III) from the Epoxyether (I).—To a solution of 2.50 g. (0.011 mole) of I in 30 ml. of dry methanol was added 5 ml. of a methanolic solution containing 2.6 millimoles of sodium methoxide. After 15 hours, the solution was concentrated and distilled under reduced pressure to give 1.13 g. (40%) of benzoin dimethyl ketal (III), b.p. 127–128° (0.25 mm.); n^{25}D 1.5620.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.42; H, 6.98. Found: C, 74.49; H, 7.05.

Reaction of the Benzoin Dimethyl Ketal with Benzoyl Chloride.—Into a solution of 9.15 g. (0.0355 mole) of III in 30 ml. of dry pyridine was added 5.48 g. (0.039 mole) of benzoyl chloride. The resulting solution was heated on the steam-cone for five hours and was then extracted with a mixture of 200 ml. of water and 100 ml. of ether. The ethereal layer was washed with two 50-ml. portions of water, dried over sodium sulfate, and the ether was evaporated on the steam-cone. Distillation of the residue yielded 6.0 g. (47%) of the benzoate of benzoin dimethyl ketal[14] as an extremely viscous yellow oil, b.p. 196–200° (0.7 mm.).

Anal. Calcd. for $C_{23}H_{22}O_4$: C, 76.24; H, 6.08. Found: C, 76.58; H, 6.04.

A solution of 0.75 g. of the ketal benzoate in a mixture of 1.8 ml. of concentrated hydrochloric acid and 11.2 ml. of 95% ethanol was heated on the steam-cone for 30 minutes. After being allowed to stand overnight at 0°, 0.45 g. (67%) of benzoin benzoate separated, m.p. 122–124°. A mixed m.p. with an authentic sample of benzoin benzoate was not depressed.

Rearrangement of Epoxyether (I) by Magnesium Bromide.—A solution of 5.15 g. (0.0227 mole) of epoxyether (I) in 20 ml. of dry ether was added as rapidly as possible to a stirred solution of 4.0 g. (0.0217 mole) of dry magnesium bromide in 20 ml. of dry ether with immediate exothermic salt formation. The mixture was stirred and refluxed for 20 hours and was then hydrolyzed with a saturated solution of ammonium chloride. The ethereal layer was washed with water, dried over sodium sulfate, and the ether was removed by gentle evaporation. A few ml. of heptane was added and 4.0 g. of a yellow solid precipitated. One recrystallization from a mixture of benzene and low boiling petroleum ether gave 1.95 g. of a solid, m.p. 45–48°. Recrystallization from 70% ethanol gave 1.60 g. (31%) of a white solid, m.p. 48–49°. A mixed m.p. with an authentic sample of benzoin methyl ether was not depressed.

Pyrolysis of Benzoin Dimethyl Ketal.—Pure dimethyl ketal of benzoin (10.0 g.) was distilled at 35 mm. pressure and 7.0 g. collected boiling at 217–224°. During the distillation, 0.9 g. of methyl alcohol collected in a cold trap. Since the high boiling material did not crystallize immediately, an oxime was prepared in 8% over-all yield which proved to be identical by mixed melting point determination with the oxime of benzoin methyl ether. The methyl alcohol was identified by preparation of an α-naphthylurethan and comparison with an authentic sample.

Benzoin methyl ether, then, corresponds to the material obtained in ref. 3 and ref. 6 in the attempted preparation of IV. This conclusion was further confirmed by the reaction of benzoin methyl ether with *p*-tolylmagnesium bromide to give a derivative, m.p. 142–143°, as indicated in ref. 6.

Reaction of Benzoin Dimethyl Ketal with Acetic Anhydride in the Presence of Sulfuric Acid.—To 10 g. of III (0.0387 mole) was added 40 g. (0.392 mole) of acetic anhydride and one drop of concentrated sulfuric acid. A light yellow color was developed when the acid was added. The solution was then refluxed five minutes and neutralized with a little potassium acetate. Then the mixture was subjected to vacuum distillation, b.p. 185–195° (2 mm.). Crystals slowly formed in the distillate and after recrystallization from ethanol or methylcyclohexane had m.p. 107–108°, 2.0 g. (20%).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; OCH_3, 11.57. Found: C, 76.37; H, 6.31; OCH_3, 11.54.

Benzoin Dimethyl Ketal Acetate (XI).—Into a solution of 9.6 g. (0.0372 mole) of III in 30 ml. of dry pyridine was added 11.1 g. of acetic anhydride. The resulting solution was heated on a steam-bath four hours and then poured onto ice. The crystals that formed were recrystallized from ethanol, m.p. 75–76°, and amounted to 8.45 g. (89%). A mixed melting point with benzoin acetate was depressed, m.p. 63–64°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71; OCH_3, 20.67. Found: C, 72.34; H, 6.93; OCH_3, 20.32.

The pure ketal acetate (XI, 5 g.) was dissolved in 20 g. of acetic anhydride and one drop of sulfuric acid added. After heating to the reflux temperature for 5 minutes the mixture was neutralized with potassium acetate. The solvent was evaporated and the product distilled, b.p. 164–166° (0.1 mm.). The distillate crystallized and was washed with ethanol and amounted to 1.6 g. (35%), m.p. 106–107°. A mixed melting point with VII was not depressed.

Degradation Reactions of the Methyl Ether Acetate of *trans*-Stilbenediol (VII). (a) Basic Hydrolysis.—To a solution of 0.3 g. of VII in 10 ml. of 95% alcohol was added 6 ml. of 0.5 *N* sodium hydroxide. The solution was refluxed for three hours after which 3 ml. of water was added. After cooling the solution, 0.14 g. (55%) of benzoin methyl ether was isolated, m.p. 48–49°.

(b) **Acid Hydrolysis.**—To a solution of 0.34 g. of VII in 10 ml. of 95% alcohol was added 6 ml. of 0.5 *N* hydrochloric acid. After the solution was refluxed for one hour, 2 ml. of water was added. After cooling the solution, white crystals separated, m.p. 80–83°. A mixed melting point with benzoin acetate was not depressed, m.p. 82–83°. The yield was 10%.

(c) **Reduction with Lithium Aluminum Hydride.**—To a solution of 0.5 g. (1.8 millimoles) of VII in 25 ml. of ether was added 0.26 g. (6.8 millimoles) of lithium aluminum hydride in 20 ml. of ether. The addition time was 40 minutes after which the reaction was stirred for 4.5 hours. The excess anhydride was destroyed with 10 ml. of acetone. After 25 ml. of 2.5 *N* sulfuric acid was added, the ether layer was washed and evaporated. The residue was crystallized from alcohol to give 0.24 g. (58%) of benzoin methyl ether.

Hydrogenation of Acetate Methyl Ether of *trans*-Stilbenediol (VII).—The theoretical amount of hydrogen (465 ml.) was absorbed in one hour by 5 g. of the acetate methyl ether of stilbenediol dissolved in 300 ml. of methylcyclohexane in the presence of 0.85 g. of palladium on charcoal (5%) at room temperature and atmospheric pressure. The reaction mixture was then filtered and the filtrate evaporated under reduced pressure to about 10–15 ml. on a steam-bath.

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(12) E. P. Kohler and J. L. E. Erickson, THIS JOURNAL, **53**, 2301 (1931).

(13) A. G. Francis and C. A. Keane, *J. Chem. Soc.*, 344 (1911).

(14) NOTE ADDED IN PROOF:—After 2 years this compound crystallized. m.p. 70–71°. Found: C, 76.10; H, 6.15.

After the solution had cooled, 2.65 g. (53%) of the methyl ether acetate of *threo*-1,2-diphenylethylene glycol (VIII), m.p. 64–65°, was obtained.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.10; H, 6.55.

Hydrolysis of the Methyl Ether Acetate of *threo*-1,2-Diphenylethylene Glycol (VIII).—A solution of 0.5 g. of VIII and 20 ml. of 10% alcoholic sodium hydroxide was refluxed two hours on a steam-bath. The reaction mixture was cooled, diluted with 200 ml. of water and the solution extracted with ether. The ether layer was dried with sodium sulfate and evaporated to dryness. The residue was recrystallized from petroleum (b.p. 30–60°) and yielded 0.35 g. (83%) of the methyl ether of *threo*-1,2-diphenylethylene glycol (X), m.p. 53–54°.

Preparation of the Methyl Ether of *threo*-1,2-Diphenylethylene Glycol (X).—The method of Curtin[15] was used with the following modifications. Potassium sand was made from 0.36 g. (9.31 milliatoms) of potassium metal in 50 ml. of dry benzene in a nitrogen atmosphere. A solution of 2 g. (9.31 millimoles) of *threo*-1,2-diphenylethylene glycol[16] in 50 ml. of dry benzene was added. Hydrogen was evolved rapidly for the first 30 minutes and the reaction mixture was stirred four hours longer in a nitrogen atmosphere, after which time 20 ml. of methyl iodide was rapidly added. The mixture was stirred, refluxed for three hours and allowed to stand overnight. The solvent was then evaporated and the residue treated with 100 ml. of water and the aqueous suspension steam distilled. The steam distillate was extracted with ether, dried with sodium sulfate and evaporated to dryness. The oily residue was dissolved in petroleum ether (30–60°) from which crystallized 1 g. (47%) of X, m.p. 53–54°. A mixed m.p. with the product from saponification of VIII was undepressed.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 78.68; H, 7.03.

Acetylation of the Methyl Ether of *threo*-1,2-Diphenylethylene Glycol (X).—To 0.2 g. of monomethyl ether (X) from the above preparation in 10 ml. of dry pyridine was added 10 ml. of acetic anhydride. The solution was allowed to stand at room temperature for two days and poured onto ice. Ammonium hydroxide was added to destroy the excess acetic anhydride and the reaction mixture extracted with ether. The ether extract was dried with sodium sulfate, evaporated to dryness, and recrystallized from 95% ethanol to yield 0.2 g. (85%) of VIII, m.p. 64–65°. A mixed m.p. with the product obtained from the hydrogenation of VII was undepressed.

Preparation of the Methyl Ether Acetate of *erythro*-1,2-Diphenylethylene Glycol.—Benzoin methyl ethyl was reduced with lithium aluminum hydride[17] to give the monomethyl ether of the *meso*-glycol,[18] m.p. 101–102°, in 95% yield. To 6.0 g. of this monomethyl ether in 30 ml. of dry pyridine was added 10 g. of acetic anhydride and the solution heated for 5 hours on the steam-bath. After the resulting solution was poured onto ice, the solid was recrystallized from alcohol to give a quantitative yield of the *erythro*-acetate methyl ether, m.p. 59–60°. A mixed melting point with the product from hydrogenation of VII was depressed, m.p. 48–53°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; OCH_3, 11.48. Found: C, 75.25; H, 6.81; OCH_3, 11.54.

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(15) D. Y. Curtin, E. E. Harris and E. K. Meislich, THIS JOURNAL, **74**, 2901 (1952).

(16) Prepared according to the method of S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946).

(17) *Cf.* the procedure of W. G. Dauben, R. A. Micheli and J. F. Eastham, *ibid.*, **74**, 3852 (1952).

(18) J. C. Irvine and J. Weir, *J. Chem. Soc.*, 1384 (1907).

DETROIT 1, MICH.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Action of Oxidizing Agents on Salts of Nitroalkanes. I. Oxidative Dimerization[1,2,3]

BY HAROLD SHECHTER AND RALPH B. KAPLAN

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Oxidation of *s*-alkanenitronates with either cationic or anionic oxidants results, in general, in simultaneous formation of *vic*-*t*-dinitroalkanes and ketones. Oxidants which effect these reactions are: persulfates, ferricyanides, hydrogen peroxide, bromates, silver nitrate and ammoniacal cupric chloride; reaction occurs most rapidly and highest yields of *vic*-dinitroalkanes are obtained with persulfates. Oxidation of alkaline solutions of 2-nitropropane with potassium permanganate yields acetone. Nitroethane, a primary nitroalkane, upon oxidation with persulfates gives 3,4,5-trimethylisoxazole. The action of cationic or anionic oxidants on a *s*-alkanenitronate is believed to involve transfer of one electron to the oxidant; the resulting nitroalkyl radicals may then dimerize to *vic*-dinitroalkane or be converted into ketone and nitric oxide (or its oxidized products).

Electrolysis of salts of primary and secondary nitro compounds results in formation of *vicinal* dinitroalkanes[4]; Pearson and Evans[4e] report that anodic oxidation of aqueous sodium 2-propanenitronate also yields acetone (65%) and nitric oxide along with 2,3-dimethyl-2,3-dinitrobutane (15%). With the chemical oxidants: nitrogen dioxide,[5a] air[5b] or hydrogen peroxide,[5b] sodium 2-propanenitronate is converted to 2,3-dimethyl-2,3-dinitrobutane in low yield.

In order to obtain additional information concerning the nature and yields of products from oxidation–reduction reactions of this type, an investigation has been made of the actions of various chemical oxidants on salts of primary and secondary nitroalkanes. The mononitro compounds investigated are 2-nitropropane, 2-nitrobutane, nitrocyclohexane and nitroethane; the oxidizing agents are: sodium or ammonium persulfates, hydrogen peroxide, potassium ferricyanide, ferric chloride, silver nitrate, sodium bromate, ammoniacal cupric chloride and potassium permanganate.

(1) A portion of this research was abstracted from a thesis submitted by Ralph B. Kaplan to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, 1950.

(2) Financial support for much of this research was provided by the Office of Naval Research.

(3) The term oxidative dimerization is used to describe processes involving transfer of one electron from an anion that result in pairing of the resulting oxidized intermediates.

(4) (a) N. J. Zelinsky, *J. Russ. Phys. Chem. Soc.*, **26**, 610 (1894); (b) C. Ulpiani and O. Gasparini, *Gazz. chim. ital.*, **32**, II, 242 (1902); (c) C. D. Nenitzescu, *Ber.*, **62**, 2669 (1929); (d) C. D. Nenitzescu and D. A. Isacescu, *ibid.*, **63**, 2484 (1930); (e) R. Pearson and W. V. Evans, *Trans. Electrochem. Soc.*, **84**, 173 (1943); (f) C. T. Bahner, U. S. Patent 2.485,803, October 25, 1949.

(5) (a) C. G. Goebel, Ph.D. Thesis, Purdue University, 1944; (b) C. S. Coe, E. C. Attané and T. F. Doumani, U. S. Patent 2,465,974, March 29, 1949.