

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & Co., INC., WILMINGTON 98, DEL.]

The Preparation of 1,3-Dioxole and 2,2-Dimethyl-1,3-dioxole

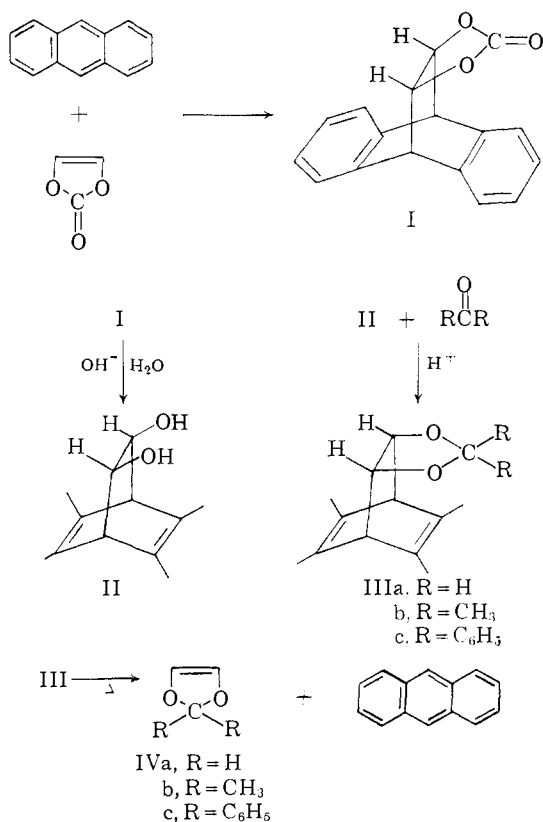
BY N. D. FIELD

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The syntheses of 1,3-dioxole and 2,2-dimethyl-1,3-dioxole were accomplished for the first time by thermally cracking the respective anthracene adducts. These were prepared by hydrolyzing the Diels-Alder adduct of anthracene and vinylene carbonate and treating the resulting diol with the appropriate carbonyl compounds. Both monomers readily polymerized when treated with boron trifluoride. The preparation of the precursor to 2,2-diphenyl-1,3-dioxole is reported.

Although the generic name 1,3-dioxole has been used for many years, there is no report in the literature describing the preparation of either the parent compound in this heterocyclic family or its 2,2-disubstituted derivatives. This paper describes the first syntheses and some properties of these compounds.

The synthetic scheme which led to the desired products is



Following essentially the procedures of Patton,¹ 85 to 95% yields of the diol II were obtained in the first two steps outlined above. While the reactions of II with formaldehyde and with acetone proceeded rapidly under comparatively mild conditions to give IIIa and IIIb, the reaction with benzophenone required more vigorous conditions. This is probably a reflection of the steric effect when R is phenyl. Models demonstrate considerably more crowding in IIIc than in IIIa and IIIb.

The thermal cracking step proceeded without much difficulty in the preparation of 1,3-dioxole

(IVa). As with the 2,2-dimethyl case, however, the heating had to be so adjusted that the adduct cracked, but only the dioxole distilled leaving behind the anthracene and starting material. In runs involving 40 to 50 g. of starting material, this meant about one to two hours of carefully attended heating. The preparation of 2,2-dimethyl-1,3-dioxole (IVb), on the other hand, was somewhat more difficult. It appeared to be more sensitive to impurities in the uncracked material and at times the desired product was obtained contaminated with difficulty removable impurities.

Though 2,2-diphenyl-1,3-dioxole (IVc) could not be prepared using this technique, it is felt that this was because of the comparatively low volatility of the compound. Evidence that the reaction was proceeding was found in the isolation of small amounts of anthracene when IIIc was heated.

Following the cracking step, the dioxoles had to be carefully distilled under nitrogen. Both dioxoles, particularly IVb, were very sensitive to oxidation, rapidly turning green after exposure to air. As distilled, the dioxoles usually showed an extraneous carbonyl peak in the infrared, but overnight contact with sodium hydroxide pellets in a nitrogen atmosphere removed this peak.

The proof of structure of the dioxoles was based on correct elemental analyses, infrared analyses which indicated *cis*-C=C and the absence of carbonyl bands, and nuclear magnetic resonance spectra which showed only two peaks. Chemical evidence was also obtained for the dimethyl compound. In this case, the cracking step could be reversed and the dioxole and anthracene allowed to react to reform IIIb.

While both n.m.r. spectra showed only the two expected peaks, the area ratios were somewhat off. The 1,3-dioxole (IVa) spectrum showed an area ratio of 1.3 to 1 instead of the theoretical 1 to 1, while the dimethyl derivative IVb showed a ratio of approximately 5 to 1 instead of the theoretical 3 to 1 ratio. Roberts² pointed out that certain compounds have given the correct number of peaks but abnormal area ratios. For example, cyclobutene shows two peaks in the ratio of 2.8 to 1 instead of the theoretical 2 to 1. This appears to be another example of the same phenomenon.

Summerbell and Umhoefer³ pointed out that the unsaturated compounds dioxadiene and 1,4-dioxene boil considerably lower than their saturated counterpart 1,4-dioxane. In addition, the unsatu-

(2) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 32.

(3) R. K. Summerbell and R. R. Umhoefer, *J. Am. Chem. Soc.*, **61**, 3020 (1939).

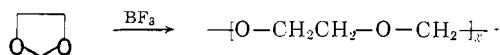
(1) T. I. Patton, U. S. Patent 2,857,434 (1958).

rated compounds, in contrast to 1,4-dioxane, are insoluble in water. These effects were also noted for furan and tetrahydrofuran. Table I summarizes these observations and includes the new data reported here. As can be seen, the physical behavior of the dioxoles closely resembles that of the other oxygen heterocyclics. The large difference in boiling points between ethylene carbonate and vinylene carbonate also has been noted.⁴

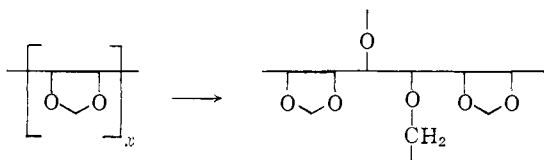
TABLE I

Compound	B. p., °C.	Δ B. p., °C.	Solubility in water
1,4-Dioxane	101	..	Soluble
1,4-Dioxene	94	7	Insoluble
Dioxadiene	75	26	Insoluble
Tetrahydrofuran	65	..	Soluble
Furan	32	33	Insoluble
1,3-Dioxolane	78	..	Soluble
1,3-Dioxole	51.0-52.5	25.5-27	Insoluble
2,2-Dimethyl-1,3-dioxolane	90-91.5	..	Soluble
2,2-Dimethyl-1,3-dioxole	72.5-73.8	16-19	Insoluble

Cationic polymerizations using boron trifluoride as the initiator proceeded readily with both dioxoles at Dry Ice-acetone temperatures. When 1,3-dioxole (IVa) was treated either as bulk monomer or a concentrated solution in methylene chloride, film-like polymer formed almost instantaneously. Infrared analysis confirmed the vinyl-type polymerization in that the C=C bond had disappeared. The polymer was, however, infusible and insoluble in all the conventional solvents tried and appeared to be crosslinked. This result is not unexpected since Gresham⁵ had previously reported that 1,3-dioxolane slowly polymerized in the presence of boron trifluoride to the open-chain polyether.



A relatively small proportion of this mode of polymerization would be sufficient to bring about crosslinking in the poly-(1,3-dioxole).



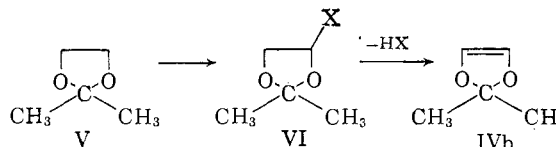
Soluble polymer, accompanied by small amounts of insoluble polymer, resulted from the boron trifluoride treatment of 2,2-dimethyl-1,3-dioxole (IVb). In the best case, polymer with an inherent viscosity in acetone at 30° (In η_{rel} /concn. at 0.5% concentration) of 0.49 was obtained. This polymer was soluble in many solvents including methylene chloride and acetone and appeared to melt on a hot bar at 220-240°. The formation of uncrosslinked polymer in this case may be the result of greater ring stability of a 2,2-disubstituted-1,3-dioxolane as compared to the unsubstituted parent compound.

(4) M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **75**, 1263 (1953).

(5) W. F. Gresham, U. S. Patent 2,394,910 (1946).

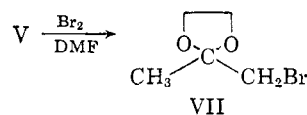
Since dioxoles resemble vinyl ethers, it is apparent that the dioxole double bond would have a large negative character in free radical copolymerizations. This, and the 1,2-disubstituted structure, should make for alternation in free radical copolymerization with maleic anhydride. This was found to be the case. Maleic anhydride and 2,2-dimethyl-1,3-dioxole (IVb) readily copolymerized to give a material which analyzed fairly well for 1:1 copolymer. Interestingly, when a few crystals of maleic anhydride and a few drops of 1,3-dioxole were mixed in bulk, the expected yellow Lewis complex formed instantly, heated up after a few minutes and appeared to polymerize. This is probably another case of spontaneous copolymerization brought about by a very rapid cross initiation rate constant due to extreme differences in the polarities of the double bonds.⁶

Before the reverse Diels-Alder route was successfully utilized, the preparation of 2,2-dimethyl-1,3-dioxole (IVb) was undertaken following the conventional synthetic route of halogenation of 2,2-dimethyl-1,3-dioxolane (V) followed by dehydrohalogenation of VI.



However, none of the usual methods for halogenation which was attempted afforded the desired 2,2-dimethyl-4-halo-1,3-dioxolane (VI). Treatment of V with bromine or N-bromosuccinimide in carbon tetrachloride led to products which were too unstable to isolate, while chlorination in refluxing carbon tetrachloride afforded only starting material and a mixture of chlorinated compounds which could not be separated.

A good yield of 2-methyl-2-bromomethyl-1,3-dioxolane (VII) was obtained, however, when V was treated with bromine in dimethylformamide.



When the bromination was attempted in this solvent using N-bromosuccinimide, a vigorous exothermic reaction occurred at 80° blowing the contents from the flask.

Experimental

Anthracene-Vinylene Carbonate Adduct (I).—This Diels-Alder adduct was prepared according to Patton.¹

Anthracene-Vinylene Glycol Adduct (II).—The hydrolysis of I was carried out essentially according to Patton.¹

Anthracene-1,3-Dioxole Adduct (IIIa).—A mixture of 98 g. (0.41 mole) of II, 30 g. (1.0 base mole) of paraformaldehyde, 250 ml. of dry benzene and 0.5 g. of *p*-toluenesulfonic acid was refluxed using a Dean-Stark water take-off until no further water came over (about 4 hours). The heating was continued until excess formaldehyde was removed by depolymerization and repolymerization in the condenser. The reaction mixture was cooled, filtered and the precipitate

(6) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952, p. 209

crystallized from benzene. The yield of white crystals melting at 239–241° was 77.4 g. (75.4%). A second crop of 7.5 g. was obtained on concentrating the mother liquor. The infrared analysis was compatible with the expected structure.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.4; H, 5.5.

Anthracene-2,2-Dimethyl-1,3-dioxole Adduct (IIIb).—A mixture of 94.1 g. (0.395 mole) of II, 100 ml. of acetone, 100 ml. of methylene chloride and 0.5 g. of *p*-toluenesulfonic acid was refluxed under a 2' × 0.5" glass helices-packed column with a water take-off and methylene chloride return on top. About 5 hours was required for the theoretical amount of water to come off, but the refluxing was allowed to continue for 18 hours. The cooled mixture was poured into 1 liter of water containing 5 g. of sodium carbonate, and extracted with methylene chloride. Drying over sodium sulfate and evaporating to dryness gave 104 g. (95%) of crude product. Crystallization from heptane gave 94.3 g. (86%) of white crystalline product with m.p. 131–137.5°. The infrared spectrum was compatible with the expected structure.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 81.8; H, 6.5.

In a number of subsequent recrystallizations, the melting point ranges could not be narrowed substantially. Anthracene was identified as a contaminant.

Anthracene-2,2-Diphenyl-1,3-dioxole Adduct (IIIc).—A mixture of 100 g. (0.42 mole) of II, 78.5 g. (0.43 mole) of benzophenone, 200 ml. of *p*-xylene and 0.5 g. of *p*-toluenesulfonic acid was refluxed under a Dean-Stark water take-off. The reaction virtually ceased at about 60% conversion after 21 hours, but was pushed to completion by the addition of an additional 1.5 g. of *p*-toluenesulfonic acid and 24 hours more reflux. The mixture was cooled and the heavy crystalline precipitate filtered, washed and dried to give 146 g. (86%). Crystallization from xylene gave 116 g. (69%) of colorless crystals with m.p. 226–228.5°. A second crop of 9.7 g. was obtained by concentration. Infrared analysis was compatible with the expected structure.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 86.5; H, 5.5. Found: C, 86.6; H, 5.7.

1,3-Dioxole (IVa).—An open flame was used to heat 50 g. (0.2 mole) of IIIa in a 100-ml. flask to which was connected a small Claisen head, water-cooled condenser and receiver surrounded by Dry Ice. A slow stream of dry nitrogen was passed over the molten reaction mixture. During about 0.75 hour of careful heating to prevent solid from distilling out, 6.5 g. of yellow-green liquid came over. A pinch of sodium carbonate and a small crystal of di-*t*-butyl-*p*-cresol were added and the mixture was left standing overnight under nitrogen in an ice-box. After decanting, the liquid was distilled through a small spinning band column to give three cuts of light green liquid with n_D^{20} 1.4031–1.4034, totaling 5.0 g. (34.7%), b.p. 51–52.5°. On standing in an ice-box under nitrogen over a sodium hydroxide pellet, the green color disappeared. Infrared analysis showed only a trace of carbonyl on the first cut. The remainder of the spectrum was identical in all three cuts. Major infrared bands were found at 3.16, 3.35, 3.46, 3.57, 6.13, 6.66, 8.5–8.65, 9.2–9.3, 10.11, 10.8–11.05, 11.57 and 14–14.3 μ .

Anal. Calcd. for $C_8H_6O_2$: C, 50.0; H, 5.6. Found: C, 50.1; H, 5.6.

Nuclear magnetic resonance showed only the expected two peaks in the ratio of 1.3 to 1. Theoretical is 1 to 1. In a later preparation, the yield was increased to 7.9 g. (55%).

2,2-Dimethyl-1,3-dioxole (IVb).—In the same equipment described above, 50 g. (0.18 mole) of the anthracene adduct IIIb and a small crystal of di-*t*-butyl-*p*-cresol were heated carefully for 1.75 hours with an open flame and 14.1 g. of light green liquid collected. A pinch of sodium carbonate and a small crystal of di-*t*-butyl-*p*-cresol were added. The decanted liquid was distilled through a small spinning band column to give a forecut containing what appeared to be a small amount of water followed by 8.89 g. (49.4%) of the dioxole, b.p. 72.5–73.8°, n_D^{20} 1.3968. The infrared spectrum was compatible with the expected structure and was identical to that of a previously prepared sample which had been used for the elemental analysis. Major infrared bands

were found at 3.18, 3.34, 3.40, 6.12, 6.86, 7.28, 7.57, 8.1–8.2, 8.6–8.65, 8.75, 9.2, 9.98, 10.41, 11.2, 12.56, 12.96 and 14.25–14.4 μ . The compound was stored at ice-box temperature under nitrogen over a sodium hydroxide pellet. Nuclear magnetic resonance showed only the expected two peaks, but in a ratio varying from 5/1 to 8/1 depending on the conditions of the determination. Theoretical is 3/1.

Anal. Calcd. for $C_8H_8O_2$: C, 60.05; H, 8.05. Found: C, 60.1; H, 7.8.

Diels-Alder Reaction between Anthracene and IVb.—A mixture of 0.41 g. (2.3 mmoles) of anthracene, 0.46 g. of IVb (4.6 mmoles) and 2 ml. of *o*-dichlorobenzene was sealed in a 5-ml. heavy walled glass tube and held for 3 days in refluxing *o*-dichlorobenzene. The mixture was cooled, filtered, and refiltered after the addition of ether. The combined precipitates, identified as anthracene, weighed 0.08 g. The filtrate, after evaporating the ether, was placed on an alumina column and eluted with petroleum ether (30–60°). This yielded an additional 0.11 g. of anthracene. Eluting the column with ether brought down 0.32 g. of IIIb identical by infrared analysis with a sample of IIIb prepared as described above. From these figures 94% of the starting anthracene is accounted for.

Cationic Polymerization of IVa.—Two milliliters of boron trifluoride gas was passed over a solution of 1 ml. of 1,3-dioxole and 2 ml. of methylene chloride, protected from air and moisture by a nitrogen cover and chilled to Dry Ice-acetone temperatures. Polymerization was instantaneous. Following the addition of a mixture of methanol and aqueous ammonia, the film-like polymer was washed with ethanol, petroleum ether and dried; yield 0.5 g. Infrared analysis confirmed the disappearance of the double bond. The polymer was infusible and was insoluble in the conventional solvents tried. X-Ray analysis revealed no crystallinity.

Cationic Polymerization of IVb.—Boron trifluoride gas, in 1-ml. increments, was passed over a mixture of 1 ml. of IVb and 1 ml. of methylene chloride protected from air and moisture by a nitrogen cover and chilled to Dry Ice-acetone temperature. After the addition of a total of 3 ml. of gas, the mixture suddenly polymerized. About 5 ml. of methylene chloride was added and gaseous ammonia admitted to neutralize the boron trifluoride. On warming to room temperature, a few gel particles present remained undissolved. After the addition of 10 ml. of acetone, the mixture was centrifuged and the clear solution separated from the insoluble material. The soluble polymer was isolated by precipitation into water, washing and drying; yield 0.61 g. The polymer melted on a hot bar at 220–240° and had an inherent viscosity in acetone at 30° of 0.49. Clear brittle films could be cast from this solvent.

Copolymerization of IVb and Maleic Anhydride.—To a solution of 1 g. of maleic anhydride in 5 ml. of benzene was added 0.8 ml. of IVb. An immediate yellow color developed. After a few minutes, 10 mg. of azobisisobutyronitrile was added and the solution rapidly brought to reflux. The solution quickly turned hazy and within 10 minutes gel-like material had wrapped around the stirrer. After 0.75 hour, the mixture was cooled, taken up in acetone and precipitated with water. The precipitated polymer was washed a number of times and dried in a vacuum oven; yield 1.65 g. The polymer was soluble in acetone from which clear but brittle films could be cast. The inherent viscosity at 30° in this solvent was 0.38. The analysis corresponds to a 1 to 1 copolymer containing about 2.5 to 3% water.

Anal. Calcd. for a 1 to 1 copolymer: C, 54.4; H, 5.1. Found: C, 53.1; H, 5.6.

2-Methyl-2-bromomethyl-1,3-dioxolane (VII).—To a solution of 50.0 g. (0.5 mole) of 2,2-dimethyl-1,3-dioxolane (V) in 200 ml. of dimethylformamide held at 90–97° by external cooling, was added dropwise 80 g. (0.5 mole) of bromine over a 20-minute period. Each drop of bromine was rapidly consumed under these conditions. The solution was cooled to room temperature and poured into 1 liter of ice-water containing 53 g. (0.5 mole) of sodium carbonate. Following an ether extraction, the ether layer was washed with a 5% sodium carbonate solution, dried over sodium sulfate and distilled to give 51.4 g. (58%) of colorless liquid, b.p. 73–74° at 18 mm. (lit.⁷ 76–78° at 16 mm.), n_D^{20} 1.4719.

(7) M. Kuhn, *J. prakt. Chem.*, **156**, 103 (1940).

Infrared analysis was compatible with the dioxolane structure but showed no *gem*-dimethyl splitting. The compound gave a negative silver nitrate test for active halogen.

Anal. Calcd. for $C_{10}H_{18}O_2Br$: C, 33.2; H, 5.0; O, 17.7. Found: C, 33.1; H, 5.1; O, 17.8.

The author is grateful to Mr. C. Mathews for determining the n.m.r. spectra and Mr. M. K. Brandt for the determination of the infrared spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Transannular Interactions. III. Synthesis and Assignment of Configurations in the *cis*- and *trans*-5-Cyclodecen-1-yl System¹

BY HARLAN L. GOERING, WILLIAM D. CLOSSON² AND ALFRED C. OLSON³

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trans-5-Cyclodecenol (II, X = OH) was isolated from a mixture of *cis*- and *trans*-5-cyclodecenol (85% *trans* isomer) which was prepared in two steps from 6-ketocyclodecyl *p*-toluenesulfonate (VI). *cis*-5-Cyclodecenol (I, X = OH) was obtained from a mixture of the isomeric alcohols (70% *cis* isomer) prepared by the thermal decomposition of trimethyl-(6-hydroxycyclodecyl)-ammonium hydroxide (III). Structural assignments are based on hydrogenation to cyclodecanol and determination of the position and configuration of the double bond. The isomeric 5-cyclodecenones (VII and VIII) can be prepared by oxidation of the corresponding alcohols.

The isomeric 5-cyclodecenols (I and II, X = OH) were of interest in connection with an investigation of transannular participation by the double bond in the *cis*- and *trans*-5-cyclodecen-1-yl systems (I and II). This paper describes the preparation, proof of structure and some reactions of the isomeric alcohols (I and II, X = OH). The kinetics and products of solvolysis (aqueous acetone) of the isomeric *p*-nitrobenzoate derivatives are described in the following paper.⁴



Binary mixtures of the isomeric 5-cyclodecenols were prepared from 6-hydroxycyclodecanone (IV)^{1b} by three routes. Conversion of IV to the quaternary base III followed by thermal decomposition of the latter gave mixture A. The thermal decomposition of III was first investigated by Cope and co-workers.⁵ However, configurations were not assigned—the product was first believed to be the *trans* isomer⁵—and neither isomer was obtained in pure form. In the preceding paper in this series^{1b} it was shown that the product (mixture A) is a mixture in which the *cis* isomer predominates. Recently it has been found that the composition of this mixture is 70% *cis* I and 30% *trans* isomer II (X = OH).⁶

In the earlier work^{1b} it was shown that pure *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (I, X = OTs) can be made directly from mixture A (the *trans* isomer is so reactive that it is completely destroyed prior to isolation). It was also shown^{1b} that pure *cis*-5-cyclodecenol can be isolated from the mixture

by repeated recrystallization of the *p*-chlorobenzoate derivative followed by saponification. This method, however, is not very satisfactory because a large number of recrystallizations are required to obtain pure material.

In the present work it was found that pure *cis*-alcohol I (X = OH) can be isolated in excellent yields from mixtures of the isomeric alcohols by conversion to the *p*-nitrobenzoate derivative, selective solvolysis of the *trans*-*p*-nitrobenzoate (II, X = O₂CC₆H₄NO₂) in aqueous acetone, and saponification of the unreacted *cis*-*p*-nitrobenzoate.⁷ As shown in the next paper,⁴ in 90% aqueous acetone at 120° the *trans*-*p*-nitrobenzoate is 300 times more reactive than the *cis* isomer. By this method pure *cis*-alcohol was obtained in good yields from binary mixtures of alcohols containing as little as 15% of the *cis* isomer.

The purity of the isomeric alcohols was determined by infrared analysis. Intercontamination can be detected readily by this method because the *cis* isomer has a characteristic strong band at 14.2 μ (disubstituted *cis* double bond⁸) and the *trans* isomer has a characteristic strong band at 10.18 μ (disubstituted *trans* double bond⁸).

Deamination of 6-aminocyclodecanol (V)⁹ (probably a mixture of diastereoisomers) gave 5-cyclodecenol in poor yield. This product evidently consisted primarily of the *cis*-alcohol I (X = OH) because homogeneous derivatives of the *cis*-alcohol were obtained from it in high yield.

A binary mixture of the isomeric 5-cyclodecenols consisting of 85% of the *trans* isomer and 15% of the *cis* isomer (mixture B) was prepared in two steps from 6-ketocyclodecyl *p*-toluenesulfonate (VI). It has been shown¹⁰ that when VI is heated in diethylaniline a mixture of about 10% bicyclo-[3.2.0]decan-2-one (IX) and 90% 5-cyclodecenone

(1) (a) The first paper in this series is H. L. Goering, A. C. Olson and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 5371 (1956); (b) The second paper in this series is H. L. Goering, H. H. Espy and W. D. Closson, *ibid.*, **81**, 329 (1959).

(2) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

(3) Minnesota Mining and Mfg. Fellow 1952–1953.

(4) H. L. Goering and W. D. Closson, *J. Am. Chem. Soc.*, **83**, 3511 (1961).

(5) A. C. Cope, R. J. Cotter and G. G. Roller, *ibid.*, **77**, 3594 (1955).

(6) A. C. Cope, private communication.

(7) Attempts to separate binary mixtures of I and II (X = OH) by fractionation with an efficient column were unsuccessful. Fractional crystallization of the *p*-nitrobenzoate derivative also failed to give complete separation of the isomers.

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapt. 3.

(9) A. C. Cope, R. J. Cotter and G. G. Roller, *J. Am. Chem. Soc.*, **77**, 3590 (1955).

(10) A. C. Cope and G. Holzman, *ibid.*, **72**, 3062 (1950).