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E. I. DU PONT DE NEMOURS & Co.]

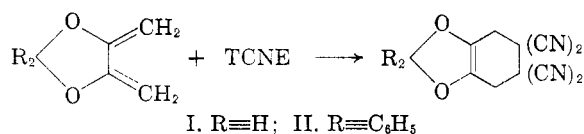
Diels-Alder Reactions of 4,5-Dimethylenedioxolanes

J. B. MILLER

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4,5-Dimethylenedioxolane (I) and 4,5-dimethylene-2,2-diphenyldioxolane (II) failed to react with dienophiles other than tetracyanoethylene. The infrared C=C absorption of dialkoxyolefins occurs below 6 μ and shifts to shorter wave lengths with increasing ring strain and thus is similar to that of fluoroalkenes.

The use of 4,5-dimethylenedioxolanes as dienes in the Diels-Alder reaction apparently has not been previously investigated. However, 1,2-dimethylenecyclopentane,¹ 2,3-dimethylenedioxane,² and 2,3-dimethoxy (and -diethoxy)butadiene³ have all been shown to undergo the Diels-Alder reaction. This implies that the five-membered ring and the oxygen atoms in 4,5-dimethylenedioxolanes should not hinder reaction. This implication is strengthened by the data in Table I which indicates a marked similarity between 1,2-dimethylenecyclopentane and I. However, neither I nor II reacted with dienophiles other than tetracyanoethylene (TCNE).⁴ The spectra of the tetracyanoethylene adducts are consistent with conventional Diels-Alder products.



Thus the near infrared spectra showed no indication of terminal methylene groups, the adduct with I showed no selective ultraviolet absorption, and the nuclear magnetic resonance spectra showed only two types of hydrogen. The 5.73–5.85 μ absorption shown by the tetracyanoethylene adducts is at-

(1) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, and D. T. Longone, *J. Am. Chem. Soc.*, **78**, 6057 (1956).

(2) R. K. Summerbell and G. J. Lestina, *J. Am. Chem. Soc.*, **79**, 3878 (1957).

(3) J. R. Johnson, W. H. Jobling, and G. W. Bodamer, *J. Am. Chem. Soc.*, **63**, 131 (1941).

(4) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

tributed to the olefinic bond by analogy with ketene acetals and fluoroalkenes.

TABLE I
SPECTRA OF SOME BUTADIENE DERIVATIVES

Compound	λ_{\max} m μ	log ϵ (solvent)	μ
Butadiene	217 ^a	4.32 (hexane) ^a	1.64, 5.5, 6.28
2,3-Dimethoxybutadiene	225	4.28 (dioxane)	5.5, 6.30
1,2-Dimethyl- encyclopentane	248 ^b	4.02 (isooctane) ^b	5.66, 6.15 ^b
4,5-Dimethyl- enedioxolane (I)	245	4.06 (dioxane)	1.61, 5.6, 5.95–6.1
4,5-Dimethyl- ene-2,2- diphenyl- dioxolane (II)			1.60, 5.55, 5.95, 6.1

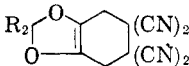
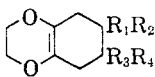
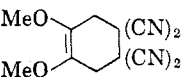
^a A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy*, E. Arnold Ltd., London, 1954, p. 93. ^b Ref. 1.

Olefinic infrared absorption below 6 μ is well-known for fluoroalkenes (Table II).⁵ The reason for this absorption at unusually short wave lengths is not known,⁵ but work in progress indicates the important contribution of a mass effect.⁶ Dr. Crawford has suggested⁶ that the similarity in mass of oxygen and fluorine might be manifested in absorption at unusually short wave lengths for dialkoxyolefins. Thus ketene acetals, R₁R₂C=C-

(5) L. G. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen & Co. Ltd., London, 1958, p. 42.

(6) Private communication from Dr. Bryce Crawford, Feb. 16, 1959.

TABLE II
 INFRARED ABSORPTION SPECTRA OF OLEFINS

Compound	C=C Absorption, μ	Compound	C=C Absorption, μ
Perfluorocyclobutene	5.56 ^a 5.59 ^b		5.73 ^e
Perfluorocyclopentene	5.7 ^c		5.81-5.85 ^f
Perfluorocyclohexene	5.74 ^b		
Perfluorobutene-2	5.77 ^b		5.89
Butene-2	6.06 ^d		
Cyclohexene	6.06 ^d		
Cyclopentene	6.21 ^d		
Cyclobutene	6.37 ^d		

^a J. R. Nielsen, M. Z. El-Sabban, and M. Alpert, *J. Chem. Phys.*, **23**, 324 (1955). ^b R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952). ^c A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.*, **76**, 610 (1954). ^d Ref. 5, p. 387. ^e R = H or C₆H₅. ^f R₁ = R₂ = R₃ = R₄ = CN; R₁ = R₃ = H, R₂ = R₄ = CO₂CH₃; R₁ = R₃ = H, R₂ = R₄ = —CO—O—CO—.

(OR)₂, are reported to absorb at 6.10 μ (R₁ = R₂ = H), 5.97 μ (R₁ = H, R₂ = CH₃), 5.86 μ (R₁ = R₂ = CH₃), and at 6.12 μ (R₁ = C₆H₅, R₂ = H or C₆H₅).⁷ These results appear to confirm the analogy with the fluoroolefins with the important qualification that the dialkoxyolefin must be at least monosubstituted by alkyl groups to exhibit shifts to below 6 μ . The work of McElvain and Starn⁷ also indicates that conjugation acts to nullify, in part, the otherwise expected shift to shorter wave lengths. This is confirmed by examples provided by Yates and Robb.⁸

The effect of oxygen at both ends of an olefinic linkage is of most immediate interest to us in explaining the spectra of the adducts of I and II with tetracyanoethylene. Consistent with the previous remarks concerning ketene acetals, dioxene⁹ absorbed at 6.1 μ and 2,3-diphenyldioxene-2 is reported to absorb at 6.06 μ .¹⁰ It was expected that alkyl substitution, however, would cause a shift to shorter wave lengths and several 2,3-dialkyldioxene-2 derivatives were prepared and were found to absorb in the 5.81–5.85 μ region (Fig. 1 and Table II).

Another analogy of dialkoxyolefins with fluoroalkenes is provided by the effect of ring strain (Table II). As ring strain increases, the wave length of C=C absorption increases for hydrocarbons but decreases for fluorocarbons. Similarly, the dialkoxyolefins (with a fused cyclohexane ring as a common feature) showed a decrease in the wave

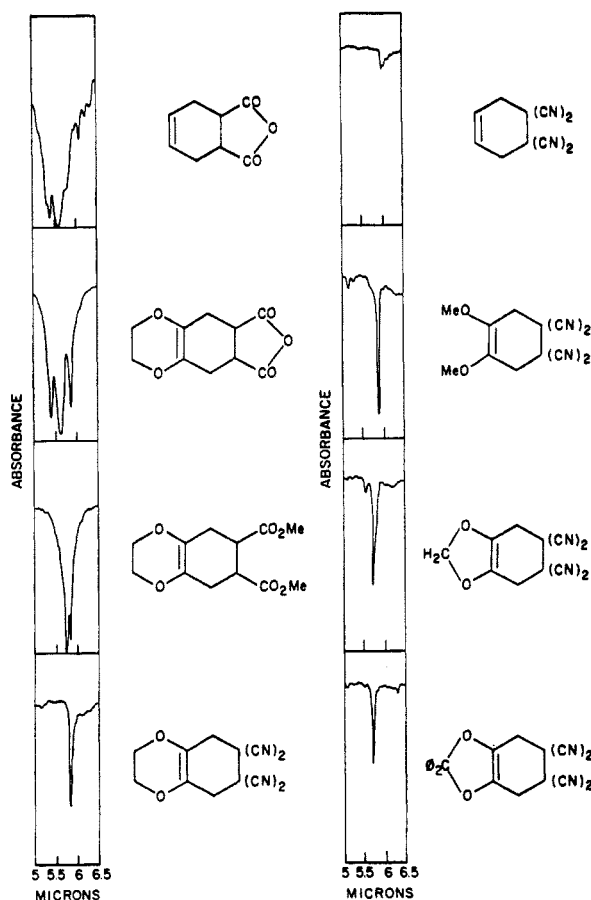


Fig. 1. Infrared spectra of dialkoxy disubstituted olefins

length of C=C absorption in the series open chain > six-membered ring > five-membered ring.

To summarize we suggest that two oxygen atoms attached to a mono- or disubstituted olefin will give rise to C=C absorption below 6.0 μ in the case of monosubstitution and below 5.9 μ in the case of

(7) S. M. McElvain and R. E. Starn, Jr., *J. Am. Chem. Soc.*, **77**, 4571 (1955).

(8) P. Yates and E. W. Robb, *J. Am. Chem. Soc.*, **79**, 5760 (1957).

(9) Prepared according to R. K. Summerbell and R. R. Umhoefer, *J. Am. Chem. Soc.*, **61**, 3016 (1939).

(10) R. K. Summerbell and D. R. Berger, *J. Am. Chem. Soc.*, **81**, 633 (1959).

disubstitution. Ring strain where the double bond is endocyclic will decrease, and conjugation will increase, the wave length of absorption.

The preparation of the 4,5-dimethylenedioxy-lanes (I and II) followed conventional routes and requires only a few comments. The reaction of an epoxide with a ketone to yield a ketal is known,¹¹ but the stereochemistry has apparently not been elucidated. The preparation of the identical compound (VI) by the reaction of III with benzophenone and by the reaction of IV with dichlorodiphenylmethane showed that the epoxide (III) reacts with inversion. Hydrolysis of VI to yield the glycol (IV) further confirmed that inversion had occurred. Use of acetone in place of benzophenone in the sequence III→VI→IV provided a further example of inversion.

The solvolytic stability of III and IX is noteworthy. Thus III was isolated after long standing in a homogeneous aqueous formic acid solution—conditions which might be expected to lead to solvolysis of the epoxide. Dioxolane is completely hydrolyzed in one hour by a 2% sulfuric acid solu-

tion at room temperature¹² but the substituted dioxolane (IX) was recovered after similar treatment for seventeen hours and after refluxing for twenty-one hours with hydrochloric acid ($pH \approx 3$) followed by twenty hours refluxing with concentrated hydrochloric acid. However, dioxolane is soluble in 2% sulfuric acid, whereas IX is insoluble in the above hydrolytic media and IX is hydrolyzed by methanolic hydrogen chloride in which it is soluble.

EXPERIMENTAL

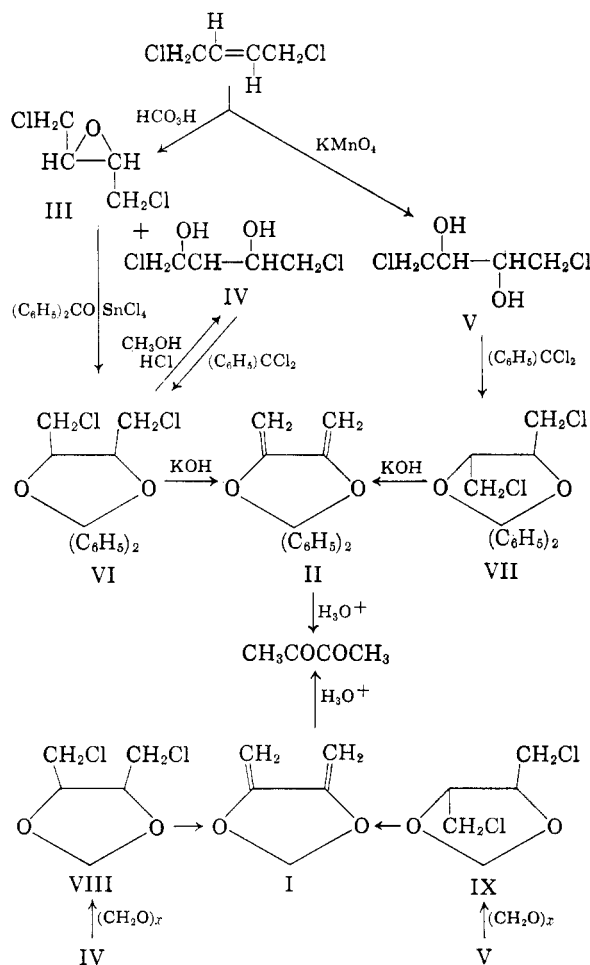
DL-Bis(chloromethyl)oxirane (III) and *meso*-1,4-dichlorobutanediol (IV). The following method is a modification of Owen's procedure¹³ for the preparation of IV in 49% yield.

A mixture of 600 ml. of 98% formic acid and 140 ml. of 30% hydrogen peroxide was prepared and maintained at room temperature for 2 hr. It was then cooled to 5° over a period of 1 hr. To this mixture was added dropwise 125 g. (1 mole) of *trans*-1,4-dichlorobutene-2¹⁴ over 3.25 hr. The initially homogeneous reaction mixture became cloudy when somewhat less than one-half of the dichloro compound had been added and remained cloudy even when addition was stopped for 30 min. When addition was complete the reaction mixture was allowed to warm spontaneously to 29° over 45 min. The mixture was then held at -5° for 20 hr. and then at +5° for 12 hr. When allowed to warm spontaneously, the temperature rose to 36° and the mixture became homogeneous. It was then allowed to stand at auto-temperatures for an additional 27 hr. The solvent was removed under reduced pressure to yield a mixture of liquid and crystals. Steam distillation gave a liquid which was separated from the water, dissolved in ether, dried with sodium sulfate, and filtered. Removal of the solvent under reduced pressure gave 29 g. (21%) of *DL*-bis(chloromethyl)oxirane whose infrared spectrum showed no hydroxyl or olefinic bands. Redistillation gave a pure sample, b.p. 78–79° (13 mm.), n_D^{20} 1.474(5) (reported¹⁵ b.p. 66–68° [5 mm.], n_D^{20} 1.4743).

The pot liquor on standing deposited 13.2 g. of crude *meso*-1,4-dichlorobutanediol, m.p. 129–132° (reported^{13,16} m.p. 127°). The mother liquor was neutralized with a mixed cation-anion exchange resin (IR MB-1) and the solvent removed under reduced pressure to yield an additional 7.9 g. of glycol, m.p. 124.5–127° (total yield 13%).

DL-1,4-Dichlorobutanediol (V). Following the procedure of Owen¹³ 80 g. (0.64 mole) of *trans*-1,4-dichlorobutene-2 was dissolved in 1200 ml. of ethanol and cooled to -15°. To this rapidly stirred solution was added dropwise a solution of 80 g. (0.51 mole) of potassium permanganate and 60 g. (0.50 mole) of magnesium sulfate in 1650 ml. of water. Addition required approximately 3 hr. during which time the temperature was maintained at -30 to -15°. After warming to room temperature, the manganese dioxide was removed by centrifuging. The supernatant liquid was extracted with four 200-ml. portions of ether. The ethereal extracts were dried with sodium sulfate and the solvent was removed under reduced pressure to yield 52 g. of crude glycol, m.p. 75°.

To the manganese dioxide was added a saturated sodium bisulfite solution until a gray slurry was obtained. The slurry



(11) M. T. Bogert and R. O. Roblin, Jr., *J. Am. Chem. Soc.*, **55**, 3741 (1933); T. Bersin and G. Willfang, *Ber.*, **70**, 2167 (1937); G. Willfang, *Ber.*, **74**, 145 (1941).

(12) H. Hibbert and J. A. Timm, *J. Am. Chem. Soc.*, **46**, 1283 (1924).

(13) L. N. Owen, *J. Chem. Soc.*, 241 (1949).

(14) Polychemicals Dept., E. I. du Pont de Nemours & Co.

(15) P. S. Starcher, D. L. MacPeck, B. Phillips, British Patent 794,209, U. S. Patent 2,861,084.

(16) W. Reppe *et al.*, *Ann.*, **596**, 141 (1955), R. M. Evans and L. N. Owen, *J. Chem. Soc.*, 239 (1949).

was thinned with water and extracted with three 200-ml. portions of ether. These ethereal extracts when treated as above yielded 5 g. of crude glycol, m.p. 75°, total yield 56%.

In the course of six preparations the reported^{13,17,18} melting point, 62–63°, was observed in the first three preparations, whereas the last three gave products melting at 75°.

Once having obtained the higher melting form all attempts to convert it to the lower melting polymorph by recrystallization were unsuccessful. A sample of the higher melting polymorph when vacuum distilled gave a crystalline distillate which melted at 61.3–62.9° when broken into small particles and at 74.9–76.8° after being finely ground. This interconversion on grinding prevented characterizing the polymorphs by means of x-ray diffraction. The identity of the higher melting polymorph was confirmed by preparing the diacetate, m.p. 75.2–76.6° (reported¹³ m.p. 76° for the diacetate of the lower melting form), mixed melting point with starting material 55–71°.

The crude glycol contained a trace of impurity which was believed to be a manganese compound [see preparation of DL-4,5-bis(chloromethyl)-2,2-diphenyldioxolane]. This impurity was not removed by recrystallization from benzene-petroleum ether but was removed by distillation. The impurity had no effect on the melting point and was not detected by x-ray fluorescence.

Attempts to use zinc permanganate in place of the potassium permanganate-magnesium sulfate system gave 0–23% yields of product.

meso-4,5-Bis(chloromethyl)-2,2-diphenyldioxolane (VI). a) From DL-bis(chloromethyl)oxirane (III). To a solution of 5 ml. of stannic chloride in 100 ml. of carbon tetrachloride was added dropwise a solution of 39.5 g. (0.28 mole) of DL-bis(chloromethyl)oxirane (III) and 58.2 g. (0.32 mole) of benzophenone in 60 ml. of carbon tetrachloride. The reaction mixture became bright yellow and at the end of 55 min. became slightly cloudy. Addition was complete in 70 min. after which the reaction was stirred for an additional hour. Sixty milliliters of 17% potassium hydroxide was added with shaking. The residue was removed by filtration and thoroughly washed with water until no longer basic to litmus to yield 58.9 g. of the dioxolane, m.p. 135–141°.

The water was removed from the filtrate and the organic phase was dried with sodium sulfate. Removal of the solvent under reduced pressure gave an oily crystalline solid. The solid was washed thoroughly with carbon tetrachloride to yield an additional 11.85 g. of the dioxolane, m.p. 135–137°, total yield 78%.

The wash liquor was distilled and after the carbon tetrachloride forerun the following fractions were obtained: 1) b.p. 82–161°, 4.69 g.; 2) b.p. 161–169°, 17.16 g., crystallized on seeding with benzophenone, m.p. 46°; 3) pot residue, 3.42 g. of VI, m.p. 132–134.4° (from cyclohexane and ethanol).

An analytical sample of the dioxolane was prepared by recrystallizing three times from cyclohexane and once from carbon tetrachloride to give a product melting at 139–140.2°, m.w. 291 in benzene, calcd. 323. The sample was then recrystallized from alcohol to give a product having m.p. 139.4–140.4°, m.w. 291 in benzene, ϵ_{\max} 459 at 258 $m\mu$ (C_2H_5OH).

Anal. Calcd. for $C_{17}H_{16}O_2Cl_2$: C, 63.17; H, 4.99; Cl, 21.94; m.w. 323. Found: C, 63.08; H, 5.08; Cl, 21.84; m.w. 287 (Rast).

b) From *meso*-1,4-dichlorobutanediol (IV). A mixture of 150 ml. of xylene, 7.95 g. (0.05 mole) of *meso*-1,4-dichlorobutanediol, and 11.85 g. (0.05 mole) of dichlorodiphenylmethane was refluxed for 19 hr. Sodium bicarbonate (5.5 g.) was added and the mixture was stirred for 1 hr. Water (100 ml.) was then added and the mixture was stirred for

1 hr. The mixture was then filtered and the residue washed with 50 ml. of ether. The organic layer was separated from the filtrate and washed twice with 50-ml. portions of water. The organic layer was then dried with sodium sulfate to yield a clear, slightly yellow solution. Removal of the solvent under reduced pressure gave slightly yellow crystals which were recrystallized from cyclohexane to yield 6.26 g. of product, m.p. 137.2–139.8°. The mother liquor yielded an additional 9.28 g. of product (total yield 40%).

An attempt to prepare this compound from the corresponding diol (IV) and benzophenone in refluxing benzene using *p*-toluenesulfonic acid as a catalyst gave after 16 hr. essentially no water, a 79% recovery of benzophenone and a 90% recovery of the diol.

c) *Methanolysis*. Methanolysis was effected by suspending 2.96 g. (0.0094 mole) of *meso*-4,5-bis(chloromethyl)-2,2-diphenyldioxolane in 150 ml. of methanol saturated with hydrogen chloride. After standing for 2 days, the solvent was removed under reduced pressure to yield a pasty solid. The solid was slurried with ether, filtered, and washed extensively with ether to yield 0.18 g. of *meso*-1,4-dichlorobutanediol, m.p. 129–130°, mixed melting point with authentic *meso*-glycol 129–130°, yield 12%.

The ether wash was neutralized with 5% sodium bicarbonate solution, dried with sodium sulfate, and the solvent removed under reduced pressure to yield a crystalline solid. The solid was washed by decantation with hot water, dissolved in ether, and the ethereal solution dried with sodium sulfate. Removal of the solvent under reduced pressure gave a slightly yellow oil which instantly crystallized on seeding with benzophenone to yield 0.86 g. of benzophenone, m.p. 40–45°, yield 50%.

DL-4,5-Bis(chloromethyl)-2,2-diphenyldioxolane (VII). A mixture of 12.72 g. (0.08 mole) of crude DL-1,4-dichlorobutanediol (m.p. 63.5–66.1°), 15.3 ml. (18.96 g., 0.08 mole) of dichlorodiphenylmethane, and 400 ml. of xylene was refluxed for 19 hr. During the initial warm up period the solution turned yellow and then deep blue. The color then changed to green and after about 3 hr. was greenish-yellow. At the end of the reflux period the solution was bright yellow. (On another occasion, using glycol melting at 55–60°, only a yellow color was observed throughout the reaction.) The solution was filtered to yield a trace of a gray powdery residue. The residue when spotted with 0.1N sodium hydroxide turned brown. After drying it was spotted with benzidine which gave a blue color indicating the probable presence of a manganese compound in the glycol starting material.

Removal of the solvent from the filtrate under reduced pressure yielded a bright yellow crystalline slurry which was filtered and washed twice with xylene to yield 19.6 g. of white crystals, m.p. 129.5–132.0°. The filtrate when worked up yielded an additional 3.4 g. (total yield 88%) of brown colored crystals, m.p. 128–129.5°. One recrystallization from cyclohexane, two recrystallizations from carbon tetrachloride, and one recrystallization from ethanol gave an analytical sample, m.p. 138–140°, mixed m.p. with the *meso* isomer 125–130°, ϵ_{\max} 479 at 258 $m\mu$ (C_2H_5OH).

Anal. Calcd. for $C_{17}H_{16}O_2Cl_2$: C, 63.17; H, 4.99; Cl, 21.94. Found: C, 63.42, 63.45; H, 5.08, 4.99; Cl, 21.51, 21.79.

The *meso* and DL isomers are not readily distinguished by melting point but are easily distinguished by their infrared spectra. The *meso* isomer (VI) has bands at 12.0 and 12.4 μ which are not present in the spectrum of the DL isomer (VII). The preference for using infrared spectra rather than physical properties to distinguish between *meso* and DL isomers was also encountered in the case of the 4,5-bis(chloromethyl)dioxolanes (VIII and IX).

4,5-Dimethylene-2,2-diphenyldioxolane (II). (a) *Preparation*. To 150 ml. of 2N ethanolic potassium hydroxide solution was added 9.75 g. (0.03 mole) of DL(or *meso*)-4,5-bis(chloromethyl)-2,2-diphenyldioxolane (VI or VII). The solution was refluxed for 4.5 hr. under nitrogen. Dry Ice was then added with shaking followed by 250 ml. of carbon tetrachloride. The solution was filtered and the residue washed

(17) G. W. Kilmer, M. D. Armstrong, G. B. Brown, and V. du Vigneaud, *J. Biol. Chem.*, **145**, 495 (1942).

(18) M. R. Radcliffe and W. G. Mayes, U. S. Patent 2,445,733.

with an additional 50 ml. of carbon tetrachloride. Additional Dry Ice was added to the filtrate and the gelatinous precipitate was again filtered. The solvent was again removed from the filtrate under reduced pressure and the amorphous material obtained was dissolved in 100 ml. of carbon tetrachloride. The solvent was again removed under reduced pressure and the residue dissolved in 100 ml. of carbon tetrachloride. Filtration of the solution gave a clear, yellow filtrate. A sample of this filtrate was not basic to wet litmus paper. Removal of the solvent under reduced pressure gave a viscous orange oil which crystallized. This was dissolved in carbon tetrachloride and the solution passed through an F20 alumina¹⁹ column (12 × 2 cm.) and eluted with carbon tetrachloride until the effluent no longer gave a positive bromine test for unsaturation. The effluent had a slightly yellow color and the column contained an immobile colored zone 0–0.5 cm. from the top. The solvent was removed from the effluent under reduced pressure to yield a very slightly yellow, heavy oil which on scratching immediately crystallized with the evolution of considerable heat. The crystals melted at 54–62°, weight 2.53 g., yield 33%.

Further attempts to purify this material by recrystallization and distillation were not successful and an analytical sample was not obtained.

The infrared spectrum of this material showed absorption at 5.5 μ ($=\text{CH}_2$) and a doublet at 6.0 μ . The near infrared absorption spectrum of this compound showed absorption at 1.6 μ characteristic of a terminal methylene group.

A sample of this material was suspended in water containing sulfuric acid and distilled until the distillate was no longer yellow. Addition of hydroxylamine hydrochloride and sodium acetate to the distillate followed by a solution of nickel chloride gave a scarlet red precipitate characteristic of nickel dimethylglyoxime.

(b) *Reaction with tetracyanoethylene*. To a solution of 1.02 g. (0.008 mole) of tetracyanoethylene in 20 ml. of tetrahydrofuran was added 2 g. (0.008 mole) of 4,5-dimethylene-2,2-diphenyldioxolane (II). This experiment was run in triplicate using 1) commercial tetrahydrofuran containing hydroquinone, 2) tetrahydrofuran free of hydroquinone but containing peroxides, and 3) tetrahydrofuran freshly purified and containing neither peroxides nor hydroquinone.

The commercial tetrahydrofuran gave a dark blue solution with tetracyanoethylene which changed to a dark green on adding the diene and then faded to a light green after 2 hr. After 18 hr. there was no further color change. On removing the solvent under reduced pressure a dark green oil was obtained which on trituration with ethanol yielded crystals. These were slurried with ethanol, filtered, and then recrystallized from ethanol to yield 1.56 g. of product, yield 60%, m.p. 164–166°. The tetrahydrofuran free of hydroquinone but containing peroxides gave a greenish yellow solution with tetracyanoethylene which changed to an orange-yellow color on adding the diene. After 2 hr. the solution was light yellow and after 18 hr. dark orange. This solution when worked up as described above yielded 0.15 g. of product, yield 5.8%, m.p. 165–167°. The freshly purified tetrahydrofuran gave a greenish-yellow color with tetracyanoethylene which changed to an orange-yellow color on adding the diene. After 2 hr. the color was dark yellow and no further change occurred on standing for 18 hr. Work up of this solution as described above yielded 1.91 g. of product, yield 74%, m.p. 165–166.6°.

This material after two additional recrystallizations from ethanol and drying overnight at 100° under vacuum over phosphorus pentoxide melted at 175–177°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{14}\text{N}_4\text{O}_2$: C, 73.00; H, 3.73; N, 14.81; m.w. 378. Found: C, 72.79; H, 3.53; N, 15.04; m.w. 347 (Rast), 368 (in benzene).

The product (4,4,5,5-tetracyano-1,2-diphenylmethylenedioxycyclohexene-1) did not decolorize bromine in carbon tetrachloride but did decolorize potassium permanganate

in acetone. The spectrum of this product showed no terminal methylene group in the 1.6 μ region and had strong sharp absorption at 5.7 μ . The nuclear magnetic resonance spectrum²⁰ in deuterochloroform was composed of an aromatic hydrogen peak at +99 c.p.s. of relative intensity 2.5 and a ring methylene hydrogen peak at –65 c.p.s. of intensity 1.

(c) *Attempted reaction of II with other dienophiles*. 4,5-Dimethylene-2,2-diphenyldioxolane (II) failed to yield products on attempted reaction with (a) ethylene (600 atm.) in alcoholic potassium hydroxide at 100° for 18 hr., (b) maleic anhydride in refluxing benzene for 2 hr., (c) phenylazomaleianil in benzene for 24 hr., (d) benzoquinone in benzene for 96 hr., (e) fumaronitrile in tetrahydrofuran for 48 hr., and (f) dimethyl acetylenedicarboxylate in refluxing carbon tetrachloride for 16 hr.

meso-4,5-Bis(chloromethyl)dioxolane (VIII). An intimate mixture of 119.3 g. (0.75 mole) of *meso*-1,4-dichlorobutanediol and 24 g. (0.80 mole) of paraformaldehyde was heated until a homogeneous melt was obtained. The mixture was then allowed to cool until solids began to form. An additional 1 g. of paraformaldehyde and 15 ml. of stannic chloride was then added. The mixture was heated on a steam bath for 20 hr. After cooling to room temperature, 350 ml. of 17% potassium hydroxide solution was added with cooling. A two-phase liquid resulted. The organic phase was separated and the water was extracted with three 50-ml. portions of ether. The ether extracts and the organic phase were combined, dried with sodium sulfate, filtered, and then dried with potassium carbonate. Removal of the solvent under reduced pressure gave a liquid which was vacuum distilled. A 16.71 g. forerun, b.p. 38–94° (13 mm.), was obtained whose vapor phase chromatogram indicated 8 components. A second fraction (72.92 g.) was obtained with b.p. 94–101° (13 mm.), n_D^{25} 1.482(8)–1.484(2), whose vapor phase chromatogram showed only one component. A brown oily pot residue remained (5.8 g.). A second distillation of the homogeneous fraction gave an analytical sample, b.p. 216–219.5° (762 mm.), n_D^{25} 1.484(7). The infrared spectrum is discussed in the following section.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{Cl}_2\text{O}_2$: C, 35.12; H, 4.72; Cl, 41.47; m.w. 171. Found: C, 35.29; H, 4.75; Cl, 41.32; m.w. 168 (Rast).

DL-4,5-Bis(chloromethyl)dioxolane (IX). (a) *Preparation*. A mixture of 34.3 g. (0.216 mole) of DL-1,4-dichlorobutanediol and 6.6 g. (0.22 mole) of paraformaldehyde was heated until partially melted. To this was added 4 ml. of stannic chloride and the mixture was heated on a steam bath for 17 hr. The reaction mixture was diluted with 100 ml. of ether and 70 ml. of 17% potassium hydroxide solution was added. This mixture was initially quite viscous but thinned on shaking. The ether layer was separated and the aqueous phase was extracted with two 50-ml. portions of ether. The combined ether extracts were dried with sodium sulfate, filtered, and the solvent removed under reduced pressure. The residual liquid was distilled and after a small forerun, b.p. 40–84° (8 mm.), there was obtained 30 g. (yield 82%) of DL-4,5-bis(chloromethyl)dioxolane, b.p. 84–89° (8 mm.), n_D^{25} 1.477(0). Vapor phase chromatography indicated this material to be homogeneous. A second distillation gave an analytical sample, b.p. 85.5–86.0° (10 mm.), 212–214° (760 mm.), n_D^{25} 1.478(5) [reported¹⁸ b.p. 102° (17 mm.)].

Anal. Calcd. for $\text{C}_6\text{H}_8\text{O}_2\text{Cl}_2$: C, 35.12; H, 4.72; Cl, 41.47; m.w. 171. Found: C, 35.25; H, 4.74; Cl, 41.47; m.w. 171 (in exaltone).

(20) We are indebted to Mr. C. B. Matthews, who determined and interpreted the NMR spectra by means of a high resolution NMR spectrometer and associated electromagnet manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of water. Negative frequency displacements indicate resonance occurring at higher field relative to the reference

(19) Aluminum Co. of America, East St. Louis, Ill.

The physical properties of *meso*- and DL-4,5-bis(chloromethyl)dioxolane are very similar and the two compounds are not readily distinguished by boiling point or refractive index. Vapor phase chromatography of the pure compounds over didodecyl phthalate on Celite at 190° indicated a slightly greater retention time for the *meso* compound. This difference did not permit, however, a separation of a mixture of the two compounds. The compounds are most readily distinguished by their infrared spectra which although similar do possess distinct differences. The most intense peak in the 7–8 μ region is at 7.7 μ for the DL isomer and at 7.96 μ for the *meso* isomer; in the 12–13 μ region the DL compound has one peak at 12.19 μ and the *meso* isomer has peaks at 12.30 and 12.60 μ ; in the 14–15 μ region the DL compound shows no peaks and the *meso* isomer has sharp absorption at 14.59 μ .

(b) *Methanolysis*. Two milliliters of DL-4,5-bis(chloromethyl)dioxolane was dissolved in 35 ml. of methanol saturated with hydrogen chloride. After 16.5 hr. the solvent was removed under reduced pressure to yield a colorless, heavy oil smelling strongly of hydrogen chloride. Seeding with DL-1,4-dichlorobutanediol caused immediate crystallization. The crystals were washed with ether and yielded 1.18 g. of DL-1,4-dichlorobutanediol, m.p. 77–78°, mixed melting point with an authentic sample, 77.0–77.5°.

4,5-Dimethylenedioxolane (I). (a) *Preparation*. A solution of 24 g. (0.6 mole) of sodium hydroxide in 27 ml. of water was added to 200 ml. of 2-(2-ethoxyethoxy)ethanol. To this was added 33.1 g. (0.193 mole) of *meso* (or DL)-4,5-bis(chloromethyl)dioxolane. The mixture was heated and vigorous boiling commenced when the pot reached 113°. Heating was continued until the pot temperature reached 144°, at which point the head temperature was 121°. The two phase distillate was collected over potassium carbonate in an ice-cooled receiver. Fifty milliliters of ether was added and the ether layer was separated from the yellow water phase. The water was extracted with an additional 50 ml. of ether and the combined ether extracts were dried with potassium carbonate to yield a colorless solution. The solution was then decanted and dried with sodium hydroxide which gave a milky solution. The solution was again decanted and lithium aluminum hydride was added. When reaction subsided the mixture was rapidly filtered and then distilled from fresh lithium aluminum hydride. After the ether forerun a fraction, b.p. 75–106.5°, was obtained followed by 4.97 g. of product, b.p. 106.5° (reported²⁰ b.p. 115–116°), n_D 1.472(6)–1.473(8). Vapor phase chromatography of the product indicated three trace impurities and dissection and weighing of the chromatogram indicated a purity of approximately 99%. The product gave a negative Beilstein halogen test and was more dense than water.

The ultraviolet spectrum of this compound in dioxane gave $\log \epsilon_{\max}$ 4.06 at 245 m μ , in excellent agreement with the value reported for 1,2-dimethylenecyclopentane, $\log \epsilon_{\max}$ 4.02 at 248 m μ .¹ The near infrared spectrum showed strong, sharp absorption at 1.61 μ ($=CH_2$) and the infrared spectrum showed absorption at 5.6, 11.12, and 11.25 μ ($R_1R_2C=CH_2$) and at 5.95–6.1 μ (a poorly resolved doublet).

The compound when freshly prepared was colorless and had a sweet odor. After exposure to the air for 5–10 min. the liquid turned yellow and smelled strongly of formaldehyde and after exposure overnight it was converted to a yellow glass. Stopped samples turned yellow but remained liquid over several weeks. The instability of the compound prevented obtaining a satisfactory analysis.

Unsuccessful attempts were made to dehydrohalogenate the starting material using sodium hydride to avoid the formation of water.

(b) *Hydrolysis*. 4,5-Dimethylenedioxolane (0.27 g.) was mixed with 10 ml. of water containing two drops of concd. hydrochloric acid. Shaking for 5 min. gave a yellow solution with a characteristic biacetyl odor and a white amorphous solid. The solution was filtered and treated with hydroxylamine hydrochloride and sodium acetate on a steam bath

for several minutes. A nickel chloride solution was added and gave a red precipitate whose infrared spectrum was identical with that of an authentic sample of nickel dimethylglyoxime.²¹

(c) *Reaction with tetracyanoethylene*. To the dark blue solution prepared from 3.96 g. (0.031 mole) of tetracyanoethylene and 35 ml. of commercial tetrahydrofuran (hydroquinone inhibited) was added 3 g. (0.031 mole) of 4,5-dimethylenedioxolane. The reaction mixture became hot and within 1 min. assumed an olive-green color. The mixture was allowed to stand at room temperature for 19 hr. during which time no further change was noted. The solvent was removed under reduced pressure at room temperature to yield an initially dark blue crystalline solid which became light blue on more complete removal of the solvent. The solid was slurried with ethanol, filtered, and washed thoroughly with ethanol to yield a green filtrate which was discarded and a very slightly green crystalline solid, weight 5.9 g., yield 86%.

An analytical sample was prepared by recrystallizing from ethanol-1,2-dimethoxyethane, vacuum sublimation, and two recrystallizations from benzene to yield a white crystalline solid, m.p. 237.2–237.7° dec. (discolored at 220°).

Anal. Calcd. for $C_{11}H_8N_4O_2$: C, 58.40; H, 2.67; N, 24.77; m.w. 226. Found: C, 58.95, 59.06; H, 2.95, 3.09; N, 24.60, 24.87.

An additional recrystallization from benzene gave a solid which was dried under oil pump vacuum over phosphorus pentoxide for 2 days, m.p. 238.5–239.5 dec. Found: C, 58.75; H, 2.61; N, 25.04; m.w. 241, 226 (in acetone).

This compound (4,4,5,5-tetracyano-1,2-methylenedioxy-cyclohexene-1) showed infrared absorption at 5.7 μ , no terminal methylene group in the near infrared, a simple cut-off in the ultraviolet similar to that found for dihydropyran, and in particular no absorption at 280 m μ (no R_2CO). The NMR spectrum¹⁸ in hexadeuteroacetone was composed of a ring methylene hydrogen peak at –67 c.p.s. of relative intensity 2 and a formal methylene hydrogen peak at +18 c.p.s. of intensity 1.

(d) *Attempted reaction of I with other dienophiles*. 4,5-Dimethylenedioxolane (I) failed to yield products on attempted reaction with 1) maleic anhydride in benzene for 19 hr., 2) dichloromaleic anhydride in benzene for 16 hr., 3) dimethyl acetylenedicarboxylate in benzene for 19 hr., and 4) acrolein (no solvent) for 16 hr.

4,4,5,5-Tetracyano-1,2-dimethoxycyclohexene-1. To a solution of 3.99 g. (0.0311 mole) of tetracyanoethylene in 50 ml. of commercial tetrahydrofuran was added 3.55 g. (0.0311 mole) of 2,3-dimethoxybutadiene.³ The solution became quite hot and the initial blue color changed to an olive green within 1 min. and to a light green within 5 min. After standing overnight the solvent was removed under reduced pressure at room temperature to yield 7.38 g. of a blue solid, yield 98%. Two recrystallizations from benzene followed by three recrystallizations from ethanol yielded an analytical sample, m.p. 95.2–96.5°.

Anal. Calcd. for $C_{15}H_{10}N_4O_2$: C, 59.50; H, 4.16; N, 23.14; m.w. 242. Found: C, 59.68, 59.50; H, 4.11, 4.05; N, 23.22, 23.08; m.w. 253 (Rast).

The infrared spectrum of this compound showed strong, sharp absorption at 5.89 μ . The NMR spectrum¹⁹ in deuteriochloroform was composed of a methyl hydrogen peak at –44 c.p.s. of relative intensity 1.5 and a methylene hydrogen peak at –67 c.p.s. of intensity 1.

2,2,3,3-Tetracyano-5,8-dioxaoctalin. To a solution of 12.8 g. (0.10 mole) of tetracyanoethylene in 60 ml. of purified tetrahydrofuran cooled to 10° was added in small portions 13.75 g. (0.123 mole) of 2,3-dimethylene-dioxane,² diluted with a equal volume of tetrahydrofuran. A very vigorous exothermic reaction ensued, the solution boiled, and a dark red color was produced which instantly faded after each

(21) Kindly provided by Dr. L. G. Donaruma of this laboratory.

addition. When addition was complete the solution was light yellow and darkened as the solution cooled to room temperature. After standing for 1 hr. the solvent was removed under reduced pressure to yield a yellow solid. One recrystallization from 1,2-dichloroethane gave 17.56 g. of product, yield 73%, m.p. 196.2–198.4° (sealed tube). An additional recrystallization from 1,2-dichloroethane followed by vacuum sublimation gave an analytical sample, m.p. 198.2–199.4° (sealed tube).

Anal. Calcd. for $C_{12}H_8N_4O_2$: C, 60.00; H, 3.36; N, 23.33; m.w. 240. Found: C, 60.16, 60.15; H, 3.53, 3.57; N, 23.48, 23.52; m.w. 251, 248 (Rast).

This compound showed strong, sharp absorption at 5.82 μ .

Dimethyl 5,8-dioxaoctalin-cis-2,3-dicarboxylate. A solution of 3.4 g. (0.0162 mole) of 5,8-dioxaoctalin-cis-2,3-dicarboxylic anhydride² in 100 ml. of methanol was allowed to stand at room temperature for 4 hr. followed by refluxing for 17 hr. To this solution was added an ethereal solution of diazomethane until a permanent yellow color was obtained and the solution was no longer acidic to moist litmus paper. Removal of the solvent under reduced pressure gave a slightly yellow oil. Freezing this oil in a stoppered flask in Dry Ice and allowing to warm spontaneously to room temperature initiated crystallization to give a product, m.p. 77–81°. Recrystallization from boiling methanol-ether (1:1 by volume) gave 3.03 g. of product, yield 73%, m.p. 83°, mixed m.p. 61–65° with a sample of starting material, m.p. 84–85°. Three additional recrystallizations from methanol-ether followed by drying overnight at room temperature over phosphorus pentoxide gave an analytical sample, m.p. 82.0–83.0°.

Anal. Calcd. for $C_{12}H_{16}O_6$: C, 56.25; H, 6.30; sap. eq. 128. Found: C, 56.16, 56.34; H, 6.40, 6.41; sap. eq. 135, 127.

The anhydride starting material showed infrared absorption at 5.4 and 5.61 ($-\text{CO}-\text{O}-\text{CO}-$) and 5.86 μ . The dimethyl ester showed absorption at 5.72 ($-\text{CO}_2\text{CH}_3$) and 5.82 μ .

meso-4,5-Bis(chloromethyl)-2,2-dimethyldioxolane. (a) *Preparation.* To a stirred solution of 5 ml. of stannic chloride in 100 ml. of carbon tetrachloride was added dropwise a solution of 24 ml. of acetone and 39.5 g. of DL-2,3-bis(chloromethyl)oxirane in 75 ml. of carbon tetrachloride. Addition was carried out over 2 hr. and the mixture was then stirred an additional 17 hr. A solution of 20 g. of 85% potassium hydroxide in 80 ml. of water was added with shaking. The organic phase was separated, washed free of base with water, and dried with sodium sulfate. The carbon tetrachloride was removed under vacuum with a hot water bath and the residual bright yellow liquid was distilled through a 15 cm. Vigreux column. The distillate weighed 33.56 g., b.p. 75–92° (10 mm.), n_D^{25} 1.466(2)–1.468(8). A second distillation gave 3 fractions: (a) b.p. 48–88° (8 mm.), n_D^{25} 1.468(2), 8.79 g.; (b) b.p. 88–90° (8 mm.), n_D^{25} 1.468(5), 7.60 g.; (c) b.p. 90–91° (8 mm.), n_D^{25} 1.468(0), 14.25 g. Vapor phase chromatography indicated all fractions contained epoxide starting material, an unidentified component, and the major component (as-

sumed to be product). The chromatograms when dissected and weighed indicated the following approximate percentage compositions: fraction (a), 64.3% product, 33.1% epoxide, 2.5% unknown; fraction (b), 87.8% product, 9.8% epoxide, 2.3% unknown; fraction (c), 97.3% product, 1.0% epoxide, 1.7% unknown. Fraction (c) was analyzed.

Anal. Calcd. for $C_7H_{12}O_2Cl_2$: C, 42.22; H, 6.08; Cl, 35.62 m.w. 199. Found: C, 42.21; H, 6.07; Cl, 35.89; m.w. 194, 209 (in exaltone).

(b) *Methanolysis.* Two milliliters of *meso*-4,5-bis(chloromethyl)-2,2-dimethyldioxolane (fraction C above) was dissolved in 35 ml. of methanol saturated with hydrogen chloride. At the end of 66 hr. the solution was black. The solvent was removed under reduced pressure to yield an amber colored solid. Water (100 ml.) was added with heating and the solution was treated with 0.5 teaspoon of Darco G60. Filtration yielded a very slightly yellow filtrate. Removal of the solvent under reduced pressure gave a white solid, 1.31 g., m.p. 125.5–129.5°, mixed m.p. 127–130° with authentic *meso*-1,4-dichloro-butane-1,2-diol.

DL-4,5-Bis(iodomethyl)-2,2-diphenyldioxolane. Sodium iodide (30 g., 0.2 mole) was mixed with 100 g. of acetylacetone and heated to 115°. The resulting dark colored solution was cooled to 40° and 16.25 g. (0.05 mole) of DL-4,5-bis(chloromethyl)-2,2-diphenyldioxolane was added. The solution was then heated to 155–165° for 4 hr. during which time the solution turned black and water and 2,5-dimethylfuran were distilled. The black solution was diluted with water and filtered to yield a black, highly crystalline residue. The residue was washed with sodium iodide solution, ether, and carbon tetrachloride. The residue was then washed very thoroughly with hot water, followed again by ether and carbon tetrachloride to yield 7.40 g. of a dark brown, highly crystalline solid, m.p. 191–193°. This solid on ignition liberated iodine and left no residue. The infrared spectrum of this material was nearly identical with the starting material. An analytical sample was prepared by recrystallizing twice from carbon tetrachloride and twice from *n*-butyl alcohol to a constant melting point, 190–191°.

Anal. Calcd. for $C_{17}H_{16}I_2O_2$: C, 40.34; H, 3.19; I, 50.15; m.w. 506. Found: C, 40.32; H, 3.34; I, 49.93; m.w. 512 (Rast).

The ultraviolet spectrum of this compound in methylene chloride showed the expected benzenoid form and absorption at 258 m μ but the ϵ_{max} was three to four times the expected value (400–500) and showed marked changes with concentration: ϵ_{max} 1620 for $1.6 \times 10^{-3}M$, 1500 for $3.2 \times 10^{-3}M$, 1440 for $7.9 \times 10^{-3}M$, 1430 for $8.1 \times 10^{-3}M$, 1240 for $15.8 \times 10^{-3}M$, and 1170 for $16.2 \times 10^{-3}M$.

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