[CONTRIBUTION FROM THE CORPUS CHRISTI RESEARCH LABORATORIES, COLUMBIA–SOUTHERN CHEMICAL CORP.]

Synthesis and Reactions of 3,4-Epoxycyclopentene

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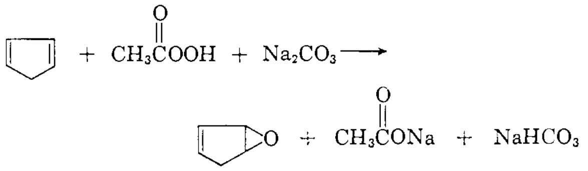
RECEIVED FEBRUARY 8, 1960

The epoxide of cyclopentadiene has been synthesized by reaction of cyclopentadiene and peracetic acid in an inert solvent in the presence of anhydrous sodium carbonate. This reactive epoxide is easily hydrolyzed to a mixture of 1,2- and 1,3-cyclopentenediols.

Although the preparation of cyclopentenediol or its esters from cyclopentadiene and hydrogen peroxide and peracids has been reported several times,[1–4] no report has been found of the isolation of the monoepoxide of cyclopentadiene. Attempts to prepare this compound from cyclopentadiene and either monoperphthalic acid[5] or peracetic acid formed *in situ* from acetic acid and hydrogen peroxide[6] were unsuccessful. Even with monoperphthalic acid at 0° no epoxide was isolated. Instead, the main products were cyclopentenediol and its ester, indicating that the epoxide is too reactive to isolate in the presence of acids even under relatively mild conditions. However, when the reaction was run with 40% peracetic acid in an inert solvent in the presence of anhydrous sodium carbonate, a 70–75% yield of epoxide was obtained. The purified product was shown to have the formula C_5H_6O by elemental analysis, and the presence of an oxirane ring and double bond was indicated by titration with pyridine hydrochloride and iodine number determination, respectively.

The success of the epoxidation of cyclopentadiene is dependent on relatively anhydrous conditions, a fast neutralization of acetic acid by sodium carbonate, a fast epoxidation step and a slow reaction of peracetic acid with sodium carbonate. Acetic acid is neutralized by anhydrous sodium carbonate in methylene chloride approximately 2000 times as fast as is peracetic acid, and the latter reacts with cyclopentadiene approximately 50 times as fast as it is neutralized by sodium carbonate. Olefins that are epoxidized more slowly than cyclopentadiene would presumably give lower yields because of neutralization of the peracetic acid.

The use of magnesium oxide or dibasic sodium phosphate in place of sodium carbonate gave epoxycyclopentene in yields of only 37 and 14%, respectively. Other bases, such as calcium hydroxide, calcium oxide, sodium bicarbonate, pyridine and sodium hydroxide gave little or no epoxide. The stoichiometry of the reaction, as shown below, requires at least one mole of Na_2CO_3 for each mole of acid present for maximum yields. At lower ratios of Na_2CO_3: total acid, yields were lower, although a 200% increase in the amount of sodium carbonate did not increase the yield of epoxide. Independent experiments showed that an almost quantitative recovery of acetic acid was obtained when glacial acetic acid was added to a suspension of anhydrous sodium bicarbonate in methylene chloride and filtered after being allowed to stand at room temperature with occasional agitation for 1 hour.



The solvent plays an extremely important part in the epoxidation of cyclopentadiene. When methylene or ethylene chlorides were used as solvents, yields of 65–75% were obtained. With carbon tetrachloride, cyclohexane, diethyl ether or perchloroethylene as solvents, yields were only 6–20%. Other solvents, such as chloroethyl ether, *o*-dichlorobenzene, acetonitrile, chloroform, chlorobenzene and benzene gave yields of 50 ± 5%.

The use of anhydrous peracetic acid[7] or peracetic acid free of acetic acid, H_2O and H_2O_2[8] had no effect on yields. Apparently the only advantage pure, dilute peracetic acid had in this case was that less sodium carbonate was required.

Distillation of the filtered reaction mixture occasionally results in a rapid, exothermic polymerization. During large scale batch distillations, the rapid increase in temperature and pressure resulting from such a polymerization may result in rupture of the distillation column. The most convenient and safest way to distil crude epoxycyclopentene is to separate the latter from the higher boiling fraction by a rapid distillation at temperatures below 40°. Redistillation of the purified epoxide fraction has been carried out numerous times at temperatures up to the atmospheric boiling point without incident. The higher boiling fraction, on the other hand, gave the previously mentioned exothermic polymerization when heated slowly to 100–120° and occasionally a brisant explosion when heated rapidly to 140–150°. Although the exothermic polymerization has been duplicated on a small scale by heating a mixture of distilled epoxycyclopentene containing traces of aqueous or anhydrous hydrogen chloride to 60–100° under adiabatic conditions, the brisant explosion could not be duplicated. It is assumed that the latter was caused by traces of peroxidic impurities, small amounts of which were detected by analysis.

Epoxycyclopentene is the most reactive epoxide encountered in these laboratories. Hydrolysis occurs within a few seconds after addition to water at room temperature. The yield of mixed cyclo-

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(1) K. H. Bauer and O. Bahr, *J. prakt. Chem.*, **122**, 201 (1929).

(2) N. A. Milas and L. S. Maloney, THIS JOURNAL, **62**, 1841 (1940).

(3) P. Sequin, *Compt. rend.*, **216**, 667 (1943).

(4) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4035 (1952).

(5) H. Bohme, *Org. Syntheses*, **20**, 70 (1940).

(6) R. J. Gall and F. P. Greenspan, *J. Am. Oil Chemists Soc.*, **34**, 161 (1957).

(7) F. P. Greenspan, U. S. Patent 2,490,800, Dec. 13, 1949.

(8) B. Phillips, P. S. Starcher and B. D. Ash, U. S. Patent 2,814,641, November 26, 1957.

pentenediols is almost quantitative when either the purified epoxide or the filtered reaction mixture is added with rapid stirring to a large excess of water at temperatures below 20°. The poor yields at lower ratios of water:epoxide are attributed to polyether formation as indicated in Fig. 1. An increase in temperature above 20° results in a gradual decrease in yields, until at 90–100° the yield, with a 50:1 molar ratio of water:epoxide, was only 74%.

The hydrolysis product of epoxycyclopentene apparently consists primarily of a mixture of two isomeric cyclopentenediols. Hydrogenation of the hydrolysis product followed by distillation yields a liquid boiling at 92–99° (1.5 mm.) and a solid. Vicinal hydroxyl analyses of the two fractions showed 18.2 and 6.0 meq./g., respectively, indicating that, although the separation was rather crude, the liquid was mostly 1,2-diol and the solid was mostly 1,3-diol. With the exception of the bis-*p*-nitrobenzoate, derivatives of the liquid agree well with literature values for *cis*-1,2-cyclopentanediol. Derivatives of the solid agree with those for the *cis*-1,3-diol as shown in Table I. No other isomers were detected.

TABLE I

MELTING POINTS OF CYCLOPENTANEDIOL DERIVATIVES (°C.)

Cyclopentanediol derivative	Bis-*p*-nitrobenzoate	Bis-phenylurethan	Bis-toluene-sulfonate
cis-1,2	116.5–117.5,[a] 117[b]	205,[a] 197[b]	92[b]
trans-1,2	145–154.2,[a] 143[b]	221[a,b]	109[b]
cis-1,3	182,[a] 186,[b] 179–181[c]	171,[a] 173,[b] 168–171[c]	93[b]
trans-1,3	207,[a] 153[b]	184,[a] 163[b]	115–116[b]
Liquid	105–107.5	204–205	91–92
Solid	182–185	173.5–174	90.5–92

[a] A. T. Blomquist and W. G. Mayes, *J. Org. Chem.*, 10, 134 (1954). [b] Ref. 4. [c] Ref. 2.

Several typical epoxide and glycol reactions were applied to epoxycyclopentene and the mixed cyclopentenediols. In most cases the reaction was run only once, and no attempt was made to obtain optimum yields. Epoxycyclopentene is stable at room temperature if stored in tightly capped bottles. In contact with atmospheric moisture, however, the epoxide hydrolyzes to give cyclopentenediol and polyethers.

Experimental

Epoxycyclopentene.—Cyclopentadiene of 95–96% was prepared by pyrolysis of commercial dicyclopentadiene.[9] The product was stored in a tightly capped bottle at Dry Ice temperatures until immediately before use. Peracetic acid was prepared by the method of Greenspan.[10]

To a rapidly stirred suspension of 106 g. (1.0 mole) of anhydrous sodium carbonate in a solution of 56 g. of 95.6% cyclopentadiene (0.81 mole) and 670 g. of methylene chloride was added 75 g. of 41% peracetic acid (0.405 mole). The peracetic acid had been previously treated with 2 g. of sodium acetate to neutralize the sulfuric acid. The temperature was maintained at 20° during the addition, which required approximately 0.5 hour. After being allowed to stir for an additional hour, titration of a filtered aliquot showed that all of the peracid had been consumed. The reaction mixture was filtered, and the solid filter cake, consisting of sodium acetate, sodium bicarbonate and sodium carbonate, was washed three times with a total of 225 ml. of methylene chloride. Analysis of the combined filtrate and washings by addition of an aliquot to excess pyridine hydrochloride and back titrating with alcoholic sodium hydroxide indicated a 70% yield of epoxide. The bulk of the methylene chloride was removed by atmospheric pressure distillation, utilizing a 104 × 1.4 cm. column packed with $^3/_{32}''$ Pyrex helices. Distillation was continued until the pot temperature reached 65°. Epoxycyclopentene, along with some methylene chloride and dicyclopentadiene, was stripped from the residue and collected in an ice-cooled receiver by distillation through a short Vigreux column at 15 mm. pressure. Redistillation of the latter fraction through the 104 × 1.4 cm. column gave 33.2 g. of epoxide, b.p. 112° (760 mm.), 63° (93 mm.), f.p. −53 to −55°, n^{25}_D 1.4575, d^{25}_4 1.0217, η^{25} 0.6886, vapor pressure 20° (18.8 mm.), 25° (23. 8 mm.), 30° (31.2 mm.), 40° (49.7 mm.), 50° (77.8 mm.). Analysis of the purified epoxide by the pyridine hydrochloride method showed 18.7% of epoxy oxygen (theoretical 19.5%). The iodine number was 298 (theoretical 310).

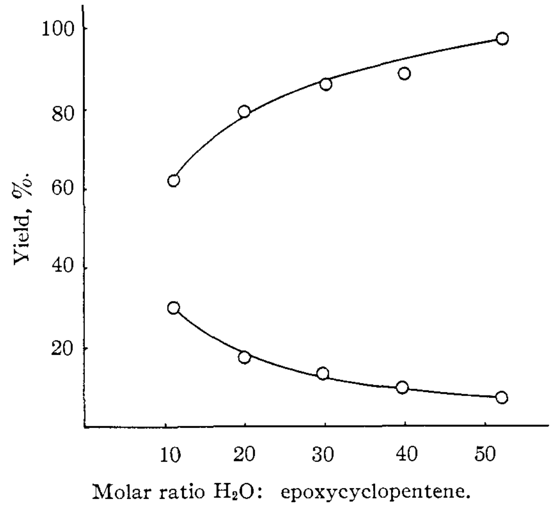

Fig. 1.—Hydrolysis of epoxycyclopentene; effect of excess water on product distribution: upper curve, diol; lower curve, polyether.

Anal. Calcd. for C_5H_6O: C, 73.15; H, 7.37; O, 19.49. Found: C, 73.03; H, 7.31; O, 19.15.

Cyclopentenediol.—To 310 g. of distilled water was added 500 g. of a 5.42% solution of epoxycyclopentene (0.331 mole) in methylene chloride over a period of 1 hour at temperatures maintained between 5 and 10°. The reaction mixture was stirred rapidly during the addition and for 1 hour thereafter at 15–20°. Distillation of the aqueous layer gave 32.1 g. (97% yield) of a mixture of cyclopentenediols, b.p. 82–105° (0.8 mm.), d^{25}_4 1.1574, n^{25}_D 1.5001, η^{25} 119, vapor pressure 119° (7 mm.), 146° (33 mm.).

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.06; O, 31.96. Found: C, 59.92; H, 7.71; O, 32.43.

Mono-β-hydroxyethyl Ether of Cyclopentenediol.—To a solution of 2 drops of BF_3 etherate in 160 g. (2.58 moles) of ethylene glycol was added 30 g. of 58% epoxycyclopentene (0.213 mole) over a period of 1.5 hours at temperatures maintained between 24 and 35°. Distillation at reduced pressure gave 22.4 g. (73% yield) of the β-hydroxyethyl ether of cyclopentenediol, b.p. 102–202° (0.1 mm.). Redistillation gave a product boiling at 123–131° (0.9 mm.).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31, H, 8.39; O, 33.29. Found: C, 58.12; H, 8.18; O, 33.69.

Monoallyl Ether of Cyclopentenediol.—To a solution of 195 g. (3.36 moles) of allyl alcohol containing 2 drops of BF_3 etherate was added over a period of 2.3 hours 30 g. of 58% epoxycyclopentene (0.213 mole) at temperatures maintained between 24 and 35°. Distillation of the reaction mixture yielded 24.8 g., b.p. 70–102° (5.5 mm.). Upon redistillation the product boiled at 80–87° (1.5 mm.).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63; O, 22.83. Found: C, 68.94; H, 8.53; O, 22.69.

Diacetate of Cyclopentenediol. (a) From Epoxycyclopentene.—A mixture of 40 g. of acetic anhydride, 0.35 mole of epoxycyclopentene and 2 g. of sodium acetate was heated to

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[9] "High Purity Dicyclopentadiene and Methyl Cyclopentadiene Dimer," Enjay Co., Inc., Market Development Division (4).

[10] F. P. Greenspan, THIS JOURNAL, **68**, 907 (1946).

145° for 1 hour. Distillation gave 26.7 g. boiling between 76 and 97° at 2.9 mm. (42% yield). Analysis indicated 11.2 meq. of ester/g. (theoretical for diacetoxy cyclopentene 10.87).

(b) **From Cyclopentenediol.**—Cyclopentenediol (108.6 g., 1.086 moles) was added over a period of 1.5 hours to 220 g. (2.16 moles) of acetic anhydride at 65–90°. After the complete addition the acetic acid was distilled through a Widmer column at 69–72° at 152 mm. until 129.4 g. had collected. Distillation of the residue afforded 195.9 g. (98% yield) of diacetate boiling between 75 and 87° (4.5 mm.). Analysis indicated 11.0 meq. of ester/g. (theoretical 10.87).

CORPUS CHRISTI, TEX.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

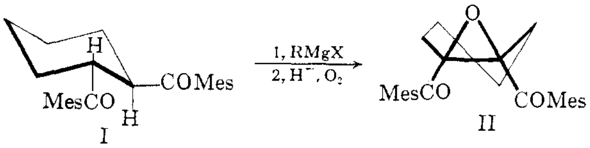
Autoxidation of the Enol Form of 1,2-Dimesitoylcyclohexane. A New Route to Epoxy Ketones[1]

BY REYNOLD C. FUSON, WILLIAM R. HATCHARD, ROGER H. KOTTKE[2] AND JAMES L. FEDRICK[3]

RECEIVED AUGUST 20, 1959

Enolization of *trans*-1,2-dimesitoylcyclohexane by treatment with a Grignard reagent followed by air oxidation of the enol in strongly acidic solution gives *cis*-1,2-dimesitoyl-1-cyclohexene oxide. Autoxidation in dilute acidic solution produces this oxide, along with 2-mesitoyl-1-cyclohexen-1-ol and mesitoic acid. Platinum-catalyzed oxidation of the monoenol of *trans*-1,2-dimesitoylcyclohexane yields 1,6-dimesitoyl-1-cyclohexene. This olefin has been made also by treatment of the dienol salt of the diketone with iodine. Epoxidation of the olefin has been accomplished with alkaline hydrogen peroxide.

Treatment of *trans*-1,2-dimesitoylcyclohexane (I) with a Grignard reagent followed by air oxidation of the resulting enol has been found to yield the symmetrical *cis*-1,2-dimesitoylcyclohexene oxide (II). When the liberation and autoxidation were conducted in strongly acidic solution, the epoxide was obtained in 89% yield.



Structure of the Oxide II.—When the oxide was treated with 48% hydrobromic acid under vigorous conditions, it was converted to *o*-dimesitoylbenzene.[4] Prolonged treatment of the oxide with zinc and hydrochloric acid regenerated the original diketone I. The oxide proved to be stable to a hot mixture of acetic and sulfuric acids as would be expected if it had the 1,2-epoxy structure, since acid cleavage of such ring systems would generate a carbonium ion adjacent to a carbonyl group.

The spectroscopic data[5] support the symmetrical structure for the epoxide. The shift produced in the ultraviolet spectrum by the formation of the oxide from *trans*-1,2-dimesitoylcyclohexane is the same as that observed when 1,2-dimesitoylethane is converted to *trans*-1,2-dimesitoylethylene oxide. The nuclear magnetic resonance spectrum of *trans*-1,2-dimesitoylcyclohexane[6] has a peak (+2.2 p.p.m.) characteristic of tertiary hydrogen atoms adjacent to carbonyl groups. This peak (+2.2 p.p.m.) was identified by the relation of the area under its curve to that under the peak for methylene hydrogen (+3.5 p.p.m.) and by the fact that this same peak appears in the spectrum of cyclohexyl phenyl ketone in the required ratio to the methylene hydrogen peak. The tertiary hydrogen peak is absent in the spectrum of the oxide. A weak tertiary hydrogen atom band is present at 1315 cm.$^{-1}$ (carbon tetrachloride)[7] in the infrared spectra of *trans*-1,2-dimesitoylcyclohexane (I), 1,6-dimesitoyl-1-cyclohexene, 1,6-dimesitoyl-1-cyclohexene oxide and Δ^4-2,6-endoxo-*exo*-*cis*-tetrahydrophthalic anhydride. In agreement with the symmetrical epoxide structure, this band is absent in the spectrum of the oxide from *trans*-1,2-dimesitoylcyclohexane.

Confirmation of the structure assigned to the oxide is provided by the characteristic symmetrical epoxide bands at 1240, 1175 and 840 cm.$^{-1}$ (carbon tetrachloride) in the infrared spectra.[7] These bands are identified readily by comparing the spectra of the two model compounds, 1,2-dimesitoylethane and 1,2-dimesitoylethylene oxide; the bands are present only in the epoxide. It might be mentioned that the *unsym*-epoxide bands at 1100 and 910 cm.$^{-1}$ (chloroform) are quite different as can be seen by a comparison of the spectrum of duryl α-mesitylethyl ketone with that of 1-mesityl-1-duroylethylene oxide and the spectrum of *trans*-1,2-dimesitoylcyclohexane with that of 1,6-dimesitoyl-1-cyclohexene oxide. Any other bridged ether structure that might be proposed

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(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) Visking Corporation Fellow, 1954–1955.

(3) Toms–River Cincinnati Chemical Corp. Fellow, 1957–1958.

(4) R. C. Fuson, S. B. Speck and W. R. Hatchard, *J. Org. Chem.*, **10**, 55 (1945).

(5) The ultraviolet spectra were obtained by Mr. J. Chin with a Cary model 14 recording spectrophotometer. The spectra were measured in 1-cm., quartz cells at concentrations of about 5×10^{-5} mole per liter in absolute ethanol. The infrared spectra were recorded by Mr. James Brader, Mrs. Louise Griffing, Mr. Cy Portnow, Mr. Paul E. McMahon and Miss Mary DeMott. The proton magnetic resonance spectra were determined by Mr. Benjamin Shoulders at 40 mc. rf. with a Varian model V-4300 B high-resolution spectrometer fitted with a field-sensing stabilizer ("Super Stabilizer"). The measurements, were made in approximately 15% solutions. The chemical shifts expressed in p.p.m. relative to water were actually determined relative to methylene chloride by use of a concentric-tube cell with methylene chloride in the outer compartment. Subtraction of 0.65 p.p.m. from shifts relative to methylene chloride was used in calculating shifts in p.p.m. relative to water. The authors are grateful to Dr. N. F. Chamberlain and to The Humble Oil and Refining Co. for preliminary nuclear magnetic resonance studies.

(6) It was necessary to use as solvent a mixture of one part of phenol and two parts of carbon disulfide for the n.m.r. spectra of this and similar ketones; band splitting could not be determined because of poor resolution.

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