aluminum hydride slurry, there was obtained 44% of *trans*-1,2-cycloöctanediol isopropylidene ketal and 31% of *trans*-1,3-cycloöctanediol, based on the weight of crude glycols, isolated in 82% yield.

2-Cycloöcten-1-one.—2-Cycloöcten-1-ol (5.00 g.) was dissolved in pure pentane (80 ml.) and active manganese dioxide[19] (23.5 g.) was added. After 6 hr. the slurry was filtered. The filtrate yielded 4.02 g. (82%) of a mixture of 2-cycloöcten-1-one and 2-cycloöcten-1-ol which was found to contain 59% of the ketone by comparison of the ultraviolet spectrum with the spectrum of the pure ketone.[13] Repetition of the oxidation gave 3.02 g. (62% over-all) of 2-cycloöcten-1-one of 98% purity as indicated by the ultraviolet spectrum.

2,3-Epoxycycloöctan-1-one.—In a modification of the method of Weitz,[20] sodium hydroxide (10 ml. of a 6 *N* solution) was added to a cooled mixture of 10 ml. of 30% hydrogen peroxide in 75 ml. of methanol. While maintaining a temperature of 0–5°, 2-cycloöcten-1-one (2.00 g.) in methanol (10 ml.) was added. After an hour the mixture was poured into 80 ml. of ice-water, and the solution was extracted with ether. The ether extract yielded 0.095 g. (5%) of recovered 2-cycloöcten-1-one, b.p. 83–84° (11 mm.), and 0.809 g. (36%) of 2,3-epoxycycloöctan-1-one, b.p. 115–116° (5 mm.). The latter compound was a solid which after sublimation had m.p. 92.0–93.0°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.46; H, 8.40.

Oxidation of *cis*- and *trans*-1,4-Cycloöctanediol with Chromic Anhydride–Pyridine Complex.—*cis*-1,4-Cyclooctanediol (0.100 g.) in dry pyridine (2 ml.) was added to the preformed complex[21] prepared from 0.555 g. of chromic anhydride and 6 ml. of pyridine. After stirring the mixture 30 minutes, it was allowed to stand overnight. The mixture was poured into 25 ml. of ice-water and extracted with four 40-ml. portions of chloroform. The extract was washed with dilute hydrochloric acid and dilute sodium bicarbonate and dried. Evaporation of the chloroform and treatment of the residue with 2,4-dinitrophenylhydrazine (0.270 g.) in ethanol (15 ml.) containing concentrated hydrochloric acid (5 drops) gave 1,4-cycloöctanedione bis-2,4-dinitrophenylhydrazone (0.250 g., 68%), m.p. 211.0–212.0° dec. after boiling the crude derivative with a large volume of ethanol. Recrystallization from nitrobenzene–ethanol gave an analytical sample, m.p. 211.8–212.0° (inserted at 205°).

Anal. Calcd. for $C_{20}H_{20}O_8N_8$: C, 48.00; H, 4.03. Found: C, 48.20; H, 4.15.

Oxidation of *trans*-1,4-cycloöctanediol (0.101 g.) by the same procedure gave 0.147 g. (42%) of 1,4-cycloöctanedione bis-2,4-dinitrophenylhydrazone, m.p. 211.3–211.5° after recrystallization from nitrobenzene–ethanol (1:1). No depression of melting point on admixture with an authentic sample was noted.

1,3-Cycloöctanedione Bis-2,4-dinitrophenylhydrazone.—Oxidation of *trans*-1,3-cycloöctanediol (0.100 g.) with chromic anhydride–pyridine complex followed by treatment with 2,4-dinitrophenylhydrazine as described for *cis*-1,4-cycloöctanediol gave 1,3-cycloöctanedione bis-2,4-dinitrophenylhydrazone (0.090 g., 26%), which had m.p. 233–234° (inserted at 225°) after recrystallization from nitrobenzene–ethanol.

Anal. Calcd. for $C_{20}H_{20}O_8N_8$: C, 48.00; H, 4.03. Found: C, 47.90; H, 4.16.

1,2-Cycloöctanedione Bis-2,4-dinitrophenylhydrazone.—Suberoin[4] (2.97 g.) was oxidized with cupric acetate monohydrate (8.36 g.) in methanol (2 ml.) and 50% aqueous acetic acid (20 ml.).[22] Distillation gave 1.76 g. (60%) of 1,2-cycloöctanedione, b.p. 58–60° (1 mm.), $n^{25}D$ 1.4699. Part of the diketone (0.276 g.) was treated with 2,4-dinitrophenylhydrazine reagent, giving 0.970 g. (99%) of 1,2-cycloöctanedione bis-2,4-dinitrophenylhydrazone. Recrystallization from nitrobenzene gave a sample with m.p. 216.0–216.5° (dec., inserted at 210°).

Anal. Calcd. for $C_{20}H_{20}O_8N_8$: C, 48.00; H, 4.03. Found: C, 48.32; H, 3.96.

***p*-Nitrobenzoates.**—The *p*-nitrobenzoates of the various cycloöctenols and cycloöctanediols prepared during this study were obtained by treating the alcohols with *p*-nitrobenzoyl chloride in pyridine at room temperature for 0.5 to 3.0 hr. followed by isolation in the usual manner,[23] except that in some cases *p*-nitrobenzoic acid and other impurities were removed by passing a solution of the crude *p*-nitrobenzoate through a column of neutral alumina. The melting points and analyses of the new derivatives appear in Tables I and II.

Di-*p*-toluenesulfonates.—The preparations of the new di-*p*-toluenesulfonates (Table II) were similar to the one reported for *cis*-1,4-cycloöctanediol di-*p*-toluenesulfonate.[4]

(19) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(20) E. Weitz and A. Scheffer, *Ber.*, **54B**, 2327 (1921).

(21) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, **75**, 422 (1953).

(22) H. S. Corey, Jr., Ph.D. Thesis, M.I.T., 1954.

(23) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 164.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Proximity Effects. IX. Solvolysis of *trans*-Cycloöctene Oxide

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trans-Cycloöctene oxide has been prepared from *trans*-cycloöctene and peracetic acid. This oxide reacts exothermically with formic acid, forming a mixture of products that was isolated in 55% yield. Components of this mixture that have been isolated and the mole percentage of each include the following: first, products formed by a transannular hydride shift of the kind observed in previous work in this series: *trans*-1,4-cycloöctanediol, 33%; *trans*-1,3-cycloöctanediol, 1%; 4-cycloöcten-1-ol, 12%. In addition, three compounds formed by ring contraction were isolated. These were hexahydro-*o*-tolualdehyde (isolated as the acid), 25%; a liquid glycol $C_8H_{16}O_2$ (A) containing a C-methyl group, 16%; a second liquid glycol $C_8H_{16}O_2$ (B), also containing a C-methyl group, 13%.

trans-Cycloöctene oxide has been described by Ziegler and Wilms,[2] who prepared it from a sample of cycloöctene that is now known to be a mixture of *trans*- and *cis*-cycloöctene in a ratio of approximately 3:2.[3] In this work, *trans*-cycloöctene oxide was prepared from the pure *trans*-olefin and peracetic acid in 93% yield. Unlike *cis*-cycloöctene oxide, which is a crystalline solid, the *trans*-oxide is a liquid; differences in its infrared spectrum from the spectrum of the *cis*-oxide show that it is not contaminated by the *cis* isomer, and vapor phase chromatography indicated that the oxide prepared in this way is homogeneous.

(1) National Science Foundation Fellow, 1953–1954.

(2) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

(3) A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

Ziegler and Wilms heated *trans*-cycloöctene oxide with water at 120° and dilute aqueous sulfuric acid at 170–180°. No change in volume of the water-insoluble layer was noted in the absence of acid, while in the presence of acid a water-insoluble fraction was separated from the aqueous solution, but no products were isolated from either phase. We have found that *trans*-cycloöctene oxide reacts exothermically with formic acid to form a complex mixture. The products that were formed were separated into two fractions by distillation. A low-boiling fraction, b.p. 66–105° (22 mm.), was removed by distillation and contained 40% of the total product. The infrared spectrum of this mixture contained bands at 3000 and 1640 cm.$^{-1}$ (olefinic), 2700 cm.$^{-1}$ (aldehyde C–H), 1723 cm.$^{-1}$ (carbonyl) and 1180 cm.$^{-1}$ (formate ester). This mixture was treated with silver oxide and excess aqueous sodium hydroxide, in order to oxidize the aldehyde to an acid and at the same time to saponify the formate. Acidification of the alkaline solution formed a mixture of acids, $C_8H_{14}O_2$, which was saturated to permanganate and accordingly was composed of alicyclic acids. The infrared spectrum of the mixture contained an absorption band at 1375 cm.$^{-1}$, indicating the probable presence of a C-methyl group, and a Kuhn–Roth C-methyl determination (54% of one C-methyl group) indicated that one such group was present. The alicyclic carboxylic acids containing one C-methyl group that could be derived from *trans*-cycloöctene oxide with minimal ring contraction are *cis*- and *trans*-hexahydrotoluic acids. An amide prepared from the mixture of acids had m.p. 172.8–178.8°, a value consistent with the possibility that the mixture was composed of *cis*- and *trans*-hexahydro-*o*-toluic acids, whose amides melt at 151–153° and 181°, respectively.[4] *cis*-Hexahydro-*o*-toluic acid was prepared by the catalytic reduction of *o*-toluic acid[5] and converted to the *trans* isomer by heating with β-naphthalenesulfonic acid. The *p*-bromophenacyl ester of the *trans*-acid, m.p. 104–106°, proved to be identical with the corresponding derivative of the major component of the mixture of acids derived from the product obtained by rearrangement of *trans*-cycloöctene oxide. The mixture derived from the rearrangement product also contained some of the *cis*-acid, and an impure solid isolated from the mother liquors from recrystallization of the *p*-bromophenacyl ester prepared from the mixture contained characteristic bands at 1730, 1375, 890 and 758 cm.$^{-1}$ that are present in the spectrum of the *p*-bromophenacyl ester of *cis*-hexahydro-*o*-toluic acid, in addition to the bands present in the spectrum of the derivative of the *trans* isomer. Accordingly, the aldehyde formed from *trans*-cycloöctene oxide is hexahydro-*o*-tolualdehyde. It is uncertain from these results whether the aldehyde formed initially is the *cis* or *trans* isomer, for the *cis* isomer might be isomerized to the more stable *trans* form either in the formic acid solvolysis medium or in the presence of base during oxidation with silver oxide. Quite drastic conditions were required to isomerize the *cis*- to the *trans*-acid with β-naphthalenesulfonic acid, and vigorous acid treatment also has been used by others[6,7] to effect the isomerization. It was also shown that the *cis*-acid was affected relatively little if any by heating with aqueous sodium hydroxide at 180° for 8 hr. However, conversion of the *cis*- to the *trans*-aldehyde *via* an enol form would be expected to occur much more easily.

The alcohol formed by hydrolysis of the formate ester during treatment of the low-boiling fraction with alkaline silver oxide was shown to be composed principally of 4-cycloöcten-1-ol by preparation of the phenylurethan, which was compared with an authentic sample.[8] The alcohol was not examined in a manner that would detect the presence of 3-cycloöcten-1-ol unless it was the major component; both of these alcohols now are known to be formed in the solvolysis of *cis*-cycloöctene oxide.[9]

The high-boiling residue (60% by weight of the product) was saponified, and the alcohols that were formed were separated by chromatography on alumina. The first fraction contained 4-cycloöcten-1-ol, identified as the phenylurethan. The next fraction was a liquid glycol $C_8H_{16}O_2$ (A) that formed a bis-*p*-nitrobenzoate, m.p. 154–155°. Another liquid glycol $C_8H_{16}O_2$ (B) that formed a bis-*p*-nitrobenzoate, m.p. 175.5–180.4°, was eluted next. Both of these glycols were shown to be different from the eight isomeric cycloöctanediols by comparison of the infrared spectra of the bis-*p*-nitrobenzoates. Both glycols A and B gave negative periodate tests, indicating that they were not 1,2-glycols, and each contained one C-methyl group according to the Kuhn–Roth C-methyl determinations. From the broad melting range of the bis-*p*-nitrobenzoate, this derivative of glycol B may be a mixture of isomers, possibly stereoisomers. Further work is required to determine the structures of glycols A and B.

2-Hydroxy-2-methylcyclohexanemethanol was prepared from 2-hydroxymethylcyclohexanone and methylmagnesium iodide and shown not to be identical with either glycol A or B by conversion to the bis-*p*-nitrobenzoate, m.p. 214–215°. However, this synthesis apparently yielded predominantly one stereoisomer, and the structure of either glycol A or B may correspond to the other stereoisomer, or both may be position isomers of this formula or indeed may not have six-membered alicyclic rings.

The glycol eluted next from the chromatogram was *trans*-1,4-cycloöctanediol, identified as its bis-*p*-nitrobenzoate, m.p. 155.4–156.6°, which was identical with an authentic specimen. Finally, a small amount of crystalline *trans*-1,3-cycloöctanediol was eluted and identified by comparison with an authentic sample,[9] m.p. 109–111°.

The formation of *trans*-1,4- and *trans*-1,3-cycloöctanediol can be accounted for by hydride shifts across the eight-membered ring with concurrent attack by formic acid on the carbon atom from which the hydride shifts, as postulated for the con-

(4) K. v. Auwers and F. Dersch, *J. prakt. Chem.*, [2] **124**, 233 (1930).

(5) H. H. Hamby and R. Schaufelber, *loc. cit.*, **431**, 29 (1923).

(6) A. Skita, *ibid.*, **431**, 23 (1923).

(7) W. Goodwin and W. H. Perkin, *J. Chem. Soc.*, **67**, 127 (1895).

(8) A. C. Cope and B. C. Anderson, THIS JOURNAL, **79**, 3892 (1957).

(9) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, **79**, 3900 (1957).

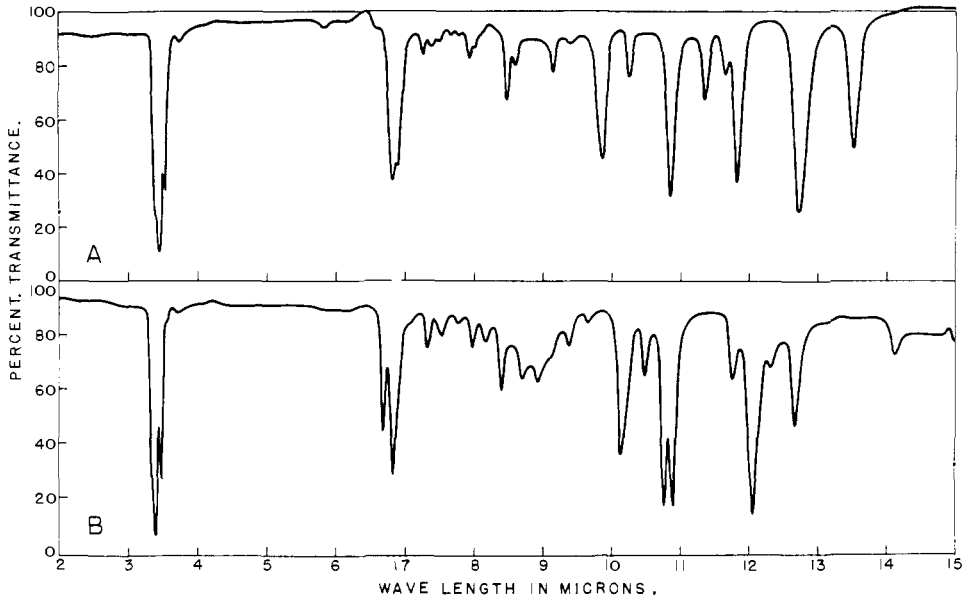
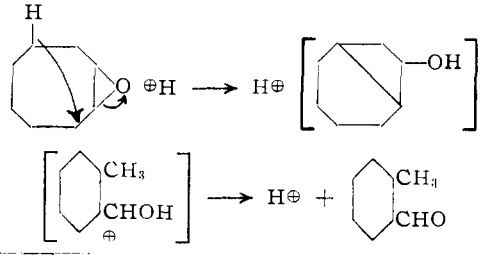


Fig. 1.—Infrared absorption spectra, determined with a Baird double beam infrared recording spectrometer, model B, fitted with a sodium chloride prism: curve A, *cis*-cycloöctene oxide; curve B, *trans*-cycloöctene oxide, both as solutions (100 mg./ml.) in carbon tetrachloride in the region 2–8μ and in carbon disulfide in the region 8–16μ, in a 0.1-mm. cell.

version of *cis*-cycloöctene oxide to *cis*-1,4-cycloöctanediol.[10] 4-Cycloöcten-1-ol may be formed in a similar manner, with loss of a proton accompanying the hydride shift,[9] or could be formed by the dehydration of *trans*-1,4-cycloöctanediol.

The formation of hexahydro-*o*-tolualdehyde in the solvolysis of *trans*-cycloöctene oxide is unusual in that ring contraction by two carbon atoms has occurred. Ring contraction of the oxides of cyclic olefins by one carbon atom has been described previously. For example, 1,4-dihydronaphthalene oxide on treatment with magnesium bromide yields 2-indanaldehyde in addition to β-tetralone.[11] 1-Methylcyclohexene oxide passed over kieselguhr at 220–230° forms 1-methylcyclopentanecarboxaldehyde as well as 2-methylcyclohexanone.[12] It seems likely that the spatial proximity of opposite sides of the eight-membered ring as well as the high degree of strain undoubtedly present in the *trans*-cycloöctene oxide are responsible for the unusual ring contraction that occurs in conversion of the oxide to hexahydro-*o*-tolualdehyde and glycols A and B. One reaction path by which the aldehyde could be formed is formulated below. It is quite possible that the bicyclo[4.2.0]cycloöctan-7-ol that is represented as an intermediate would be stable in formic acid under conditions used for the rearrangement. However, if such an intermediate is formed, cleavage of the four-membered ring could occur as formulated before the energy derived from cleavage of the strained *trans*-oxide was dissipated.



Work is in progress to determine the structures of glycols A and B.

Experimental[13]

trans-Cycloöctene Oxide.—*trans*-Cycloöctene (24.0 g.), purified by the aqueous silver nitrate extraction procedure,[3] was added dropwise during a period of 1 hr. with stirring to 65 ml. of commercial 40% peracetic acid[14] to which 13 g. of sodium acetate trihydrate had been added to neutralize the sulfuric acid present, with cooling to maintain a temperature of 0°. The mixture was stirred for 3 hr. at room temperature and then stored overnight at 5°. It was then placed in a separatory funnel containing crushed ice and neutralized to litmus by adding 30% sodium hydroxide solution. The aqueous solution was extracted with three 125-ml. portions of ether, and the combined extracts were washed with water and dried over magnesium sulfate. The solution was concentrated and the residue fractionated through a semi-micro column. The yield of *trans*-cycloöctene oxide, b.p. 85–86° (22 mm.), n^{25}D 1.4741, was 25.4 g. (93%). An analytical sample had b.p. 85.5° (22 mm.), n^{25}D 1.4740. Its infrared spectrum is shown in Fig. 1, together with the spectrum of *cis*-cycloöctene oxide.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.95; H, 10.98.

Solvolysis of *trans*-Cycloöctene Oxide with Formic Acid.—A 100-ml. three-necked flask equipped with a dropping funnel, thermometer and stirrer was charged with 24 ml. of 88% formic acid heated to 48°. *trans*-Cycloöctene oxide (6.7 g.) was added dropwise with stirring in a nitrogen atmosphere, while the temperature was maintained at 48–51° by cooling with an ice-bath. The reaction mixture was heated at 90–95° for 1 hr., cooled and poured into 95 ml. of water. The product was extracted with four 80-ml. portions of ether, and the combined extracts were washed with saturated sodium bicarbonate solution, water and dried over Drierite. Material with b.p. 66–105° (22 mm.),

(10) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

(11) B. Tchoubar, *Compt. rend.*, **214**, 117 (1942).

(12) M. Tiffeneau, THIS JOURNAL, **195**, 1284 (1932).

(13) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Infrared spectra were determined with a Baird double beam recording spectrometer, model B, fitted with a sodium chloride prism.

(14) Obtained from the Becco Sales Corp., Buffalo, N. Y.

$n^{25}D$ 1.4487–1.4657 (2.7 g.), was removed by distillation through a semi-micro column and the residue was set aside. An infrared spectrum of the low-boiling material indicated the presence of an aldehyde and a formate ester and showed the presence of an olefinic double bond.

Oxidation of the Aldehyde and Saponification of the Formate.—The low-boiling material was shaken overnight at room temperature with freshly precipitated silver oxide prepared from silver nitrate (9 g.), sodium hydroxide (5.3 g.) and 40 ml. of water (the excess sodium hydroxide also was present in the reaction mixture). The solids were removed by filtration, the basic solution extracted with three 20-ml. portions of ether and the combined extracts containing the alcohol formed by the saponification of the formate were set aside.

The basic solution was acidified and extracted with three 20-ml. portions of chloroform. The combined extracts were dried over magnesium sulfate, concentrated and the residue was distilled in a short-path still to give 1.03 g. of an analytically pure mixture of acids, $n^{25}D$ 1.4580. The infrared spectrum of the mixture had, in addition to the usual carboxylic acid absorption bands, a band of medium strength at 1375 $cm.^{-1}$ (C-methyl).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92; one C-methyl group, 10.55. Found: C, 67.79; H, 9.73; C-methyl, 5.78.[15]

A portion of the acid mixture (90 mg.) was refluxed with thionyl chloride for 30 min. and the reaction mixture poured into iced concentrated ammonium hydroxide. The product was filtered and a very poor yield of a mixture of amides was obtained. After two recrystallizations from water, it had m.p. 172.8–178.8°.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.70. Found: C, 68.19; H, 10.80.

Identification of *cis*- and *trans*-Hexahydro-*o*-toluic Acid.—The acid mixture (208 mg.) was treated with *p*-bromophenacyl bromide (408 mg.) according to the method of Shriner and Fuson.[16] A crude derivative was obtained (343 mg., 70%) with m.p. 80–96°. After four recrystallizations from hexane an analytical sample was obtained with m.p. 104–106° (hot-stage).

Anal. Calcd. for $C_{16}H_{19}BrO_3$: C, 56.66; H, 5.62. Found: C, 56.91; H, 5.62.

A mixture of this derivative with authentic *trans*-hexahydro-*o*-toluic acid *p*-bromophenacyl ester showed no depression and the infrared spectra of the two derivatives were identical.

The mother liquors from the recrystallization of the *p*-bromophenacyl ester of the acid mixture were concentrated to give a residue which after recrystallization from hexane had m.p. 52–90° (hot-stage). The infrared spectrum of this mixture indicated it to be mostly *cis*-hexahydro-*o*-toluic acid *p*-bromophenacyl ester, contaminated with the *trans* isomer.

***cis*-Hexahydro-*o*-toluic Acid *p*-Bromophenacyl Ester.**—A solution of *o*-toluic acid (15 g.) in glacial acetic acid (50 ml.) containing concentrated hydrochloric acid (0.5 ml.) was hydrogenated at room temperature in the presence of 3.3 g. of Adams platinum catalyst at 38–30 p.s.i. The reduction was complete in 2.5 hr. After filtration, the solvent was removed under reduced pressure and the product distilled to give 12.9 g. (81%) of *cis*-hexahydro-*o*-toluic acid, b.p. 83–85° (1 mm.), $n^{25}D$ 1.4620.

A portion of the acid was converted to the amide, which after two recrystallizations from water had m.p. 154.5–156° (lit.[4] m.p. 151–153°).

cis-Hexahydro-*o*-toluic acid (302 mg.) was converted to the *p*-bromophenacyl ester in 82% yield in the usual way.[16] After three recrystallizations from hexane, it had m.p 83.0–84.2°.

Anal. Calcd. for $C_{16}H_{19}BrO_3$: C, 56.66; H, 5.62. Found: C, 56.54; H, 5.69.

***trans*-Hexahydro-*o*-toluic Acid *p*-Bromophenacyl Ester.**—*cis*-Hexahydro-*o*-toluic acid (4 g.) was refluxed for 30 min. with 200 mg. of β-naphthalenesulfonic acid. The residue was distilled in a short-path still at 120° (5 mm.) to give 3.8 g. of an oily solid. After three recrystallizations from benzene there was obtained pure *trans*-hexahydro-*o*-toluic acid, m.p. 52.4–54.4° (lit.[7] m.p. 50–52°).

The *trans*-acid (151 mg.) was treated with *p*-bromophenacyl bromide (280 mg.) in the usual way[16] to give 288 mg. or 80% of *trans*-hexahydro-*o*-toluic acid *p*-bromophenacyl ester, m.p. 102–103° (hot-stage). An analytical sample recrystallized from hexane had m.p. 104–106° (hot-stage).

Anal. Calcd. for $C_{16}H_{19}BrO_3$: C, 56.66; H, 5.62. Found: C, 56.88; H, 5.93.

Identification of 4-Cycloöcten-1-ol in the Low-boiling Fraction after Treatment with Silver Oxide.—The ether extracts of the alkaline solution obtained by treating the low-boiling fraction with silver oxide and sodium hydroxide were concentrated to give 0.67 g. of product. Chromatography on 21 g. of alumina (Activity II) in a 15-mm. column, collecting 20-ml. fractions, gave a small amount of material that gave a positive test with 2,4-dinitrophenylhydrazine reagent but which did not give a derivative that could be purified. The main bulk of material (115 mg.) was distilled in a short-path still and the distillate treated with phenyl isocyanate. After removal of excess reagent under reduced pressure, a crude product was obtained which after one recrystallization from hexane had m.p. 73–135°. The product was sublimed, and the sublimate after two recrystallizations from hexane had m.p. 92.0–94.5° (hot-stage). Its infrared spectrum was identical to the spectrum of 4-cycloöcten-1-ol phenylurethan.[8] The alcohol fraction was not examined in a way that would have detected the presence of 3-cycloöcten-1-ol as a minor component.

Saponification of the Residue of Diformates.—The residue (4.1 g.) from the distillation of the low-boiling product obtained by treating *trans*-cycloöctene oxide with formic acid was refluxed overnight with alcoholic potassium hydroxide (5.5 g.). The ethanol was removed under reduced pressure and replaced by 50 ml. of water. The product was extracted with three 40-ml. portions of chloroform, and the combined extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure to give 3.2 g. of product which was chromatographed on 105 g. of Merck acid-washed alumina (Activity II) in a 22-mm. column, collecting 100-ml. fractions. Fractions 1, 8–10, 60, 61–62 and 68–70 were discarded.

Fraction	Eluent	Weight, mg.
2–7	Benzene	331
11–13	Benzene–ether (9:1)	94
14–15	Benzene–ether (9:1)	156
16–19	Benzene–ether (9:1)	432
20–30	Benzene–ether (3:2)	483
31–36	Benzene–ether (1:1)	51
37–42	Ether	34
43–48	Ether–methanol (66:1)	725
50–59	Ether–methanol (97:3)	633
65–67	Ether–methanol (17:3)	38

4-Cycloöcten-1-ol.—Fractions 2–7 were distilled in a short-path still to give 170 mg. of distillate with an infrared spectrum that was identical to the spectrum of authentic 4-cycloöcten-1-ol. It was treated with phenyl isocyanate overnight to give, after removal of excess reagent under reduced pressure, a crude phenylurethan with m.p. 81–94°. After recrystallization from hexane, it had m.p. 94–96° (hot-stage). The infrared spectrum of the derivative was identical to the spectrum of an authentic specimen of 4-cycloöcten-1-yl phenylurethan.[8]

Glycol A Bis-*p*-nitrobenzoate.—Fractions 11–13 (96 mg.) were treated with *p*-nitrobenzoyl chloride (500 mg.) in a few milliliters of pyridine at room temperature, and the solution was allowed to stand overnight. The reaction mixture was poured into water and the product was extracted with three 10-ml. portions of benzene. The combined extracts were washed with three 80-ml. portions of water and with dilute hydrochloric acid, saturated sodium bicarbonate solution, water and saturated sodium chloride solution. The benzene solution was dried by concentrating to about 5 ml. at atmospheric pressure and passed over 5 g. of Activity II alumina. There was obtained after elution with benzene 201 mg. (68%) of a bis-*p*-nitrobenzoate with m.p. 137–147°. An analytical sample had m.p. 154–155°

(15) By the Microchemical Specialties Co., Berkeley, Calif.

(16) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 157.

after four recrystallizations from ethanol. A mixture with authentic *trans*-1,4-cyclooctanediol bis-*p*-nitrobenzoate[9] was depressed to 133–148°.

Anal. Calcd. for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01. Found: C, 60.08; H, 5.15.

A portion of fractions 14–15 (69 mg.) was converted in 83% yield to the corresponding bis-*p*-nitrobenzoate as above. After three recrystallizations from ethanol it had m.p. 154.0–155.2° and did not depress the m.p. of the derivative prepared from fractions 11–13.

An aliquot of fractions 16–19 (86 mg.) was treated with a 100% molar excess of *p*-nitrobenzoyl chloride as before to give 233 mg. or 87% of a bis-*p*-nitrobenzoate. After six recrystallizations from ethanol it had m.p. 154.0–155.2° and did not depress the m.p. of the derivative obtained from fractions 11–13.

Glycol B Bis-*p*-nitrobenzoate.—A portion of fractions 20–30 (137 mg.) was converted into a bis-*p*-nitrobenzoate in 78% yield. After seven recrystallizations from ethanol, it had m.p. 175.5–180.4°.

Anal. Calcd. for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01. Found: C, 59.89; H, 5.22.

A comparison of infrared spectra showed that the derivative prepared from fractions 20–30 was different from the bis-*p*-nitrobenzoates of the isomeric cyclooctanediols and of glycol A. A mixture of the bis-*p*-nitrobenzoates of glycol A and glycol B had m.p. 140–170°.

Fractions 31–36 (51 mg.) were treated with 280 mg. of *p*-nitrobenzoyl chloride in pyridine to give a derivative in 71% yield. After five recrystallizations from ethanol, it had m.p. 172–180°. A mixture with the derivative prepared from fractions 20–30 had m.p. 171.0–179.5°.

Periodate Tests and C-Methyl Determinations on Glycols A and B.—Both glycols A and B gave negative reactions with periodic acid (see ref. 16, p. 115). C-methyl determinations[15] gave the following values: glycol A, 9.57; glycol B, 8.98; calcd. for one C-methyl group, 10.55.

***trans*-1,4-Cyclooctanediol Bis-*p*-nitrobenzoate.**—A portion of fractions 43–49 (116 mg.) was treated overnight with a 100% excess of *p*-nitrobenzoyl chloride in a few milliliters of pyridine. There was obtained 284 mg. or 83% of crude *trans*-1,4-cyclooctanediol bis-*p*-nitrobenzoate, which after four recrystallizations from ethanol had m.p. 155.4–156.6°. A mixture with an authentic specimen[9] had m.p. 155.5–157.0°.

An aliquot of fractions 50–59 (169 mg.) was converted in 79% yield into a bis-*p*-nitrobenzoate in the same manner. After four recrystallizations from ethanol, it had m.p. 155.5–157.0°. A mixed m.p. with the derivative prepared from fractions 43–49 showed no depression.

***trans*-1,3-Cyclooctanediol.**—Fractions 65–67 (38 mg.) were sublimed at 70° (1 mm.) to give (after two recrystallizations from ethyl acetate) *trans*-1,3-cyclooctanediol, m.p. 109–111° (hot-stage). A mixture with an authentic specimen[9] showed no depression, and the infrared spectra of the two samples were identical.

Derivatives of 2-Hydroxy-2-methylcyclohexanemethanol.—A solution of methylmagnesium iodide was prepared from 6.9 g. of methyl iodide and 1.2 g. of magnesium in 30 ml. of ether. A solution of 2.4 g. of 2-hydroxymethylcyclohexanone[17] (b.p. 82° at 2.6 mm., $n^{25}D$ 1.4767) in 30 ml. of ether was added dropwise over a period of 20 min., and the mixture was refluxed for 1 hr. Water was added to the cooled mixture, followed by iced dilute hydrochloric acid. The ether layer and chloroform extracts of the aqueous layer were dried over magnesium sulfate and distilled, yielding 1.7 g. of 2-hydroxy-2-methylcyclohexanemethanol, b.p. 79° (0.15 mm.), $n^{25}D$ 1.4814, which was converted to the following derivatives.

2-Hydroxy-2-methylcyclohexanemethanol bis-*p*-nitrobenzoate was prepared by treating the glycol (402 mg.) with *p*-nitrobenzoyl chloride (1.6 g.) in a few milliliters of pyridine at room temperature for 1.5 days. The product was isolated in the usual manner and yielded 467 mg. (36%) of a derivative (calculated as the bis-*p*-nitrobenzoate). An analytical sample obtained after four recrystallizations from ethyl acetate had m.p. 214–215°.

Anal. Calcd. for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01. Found: C, 59.69; H, 5.08.

2-Hydroxy-2-methylcyclohexanemethanol mono-*p*-nitrobenzoate was prepared by treating 204 mg. of the glycol with 1.05 molar equivalent of *p*-nitrobenzoyl chloride in pyridine at 5° overnight. The product amounted to 382 mg. (92%) of a derivative (calculated as the mono-*p*-nitrobenzoate). After four recrystallizations from cyclohexane, it had m.p. 91.5–92.5°.

Anal. Calcd. for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.52. Found: C, 61.09; H, 6.72.

(17) Prepared from cyclohexanone and formaldehyde by the method of C. Mannich and W. Brose, *Ber.*, **56**, 841 (1923).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Structures of the Adducts of Cyclopentadiene and Methacrylic Acid and Some of its Derivatives[1]

BY JOHN S. MEEK AND WALTER B. TRAPP[2]

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The condensation of methacrylic acid and some of its derivatives with cyclopentadiene was studied in an effort to ascertain whether the methyl group or the negative group such as the carboxyl would be in the *endo* position in the major adduct. It was found that the carboxyl and the amide group showed a preference for the *exo* position. The aldehyde group showed an increasing tendency to prefer the *endo* position with longer reaction times and higher temperatures.

Methacrylic acid,[3] methyl methacrylate[3] and methacrolein[4,5] have been reported to give adducts with cyclopentadiene, but their structures were not proven. Recently the condensation of cyclopentadiene and methacrylic acid was reported to give both isomeric adducts I and II and the major product was tentatively assigned structure I[6] in accordance with Alder and Stein's orientation rule of diene syntheses.[7] However, we have found that the major adduct of cyclopentadiene and methacrylic acid is II.

Beckmann, Schaber and Bamberger attempted to prove structures of I and II by treatment with 50 volume per cent. sulfuric acid for 16 hours to see which acid would give a lactone. They re-

(1) This work was supported in part by the Office of Naval Research.

(2) Taken in part from the Ph.D. Thesis of W. B. Trapp, University of Colorado, 1952.

(3) A. A. Petrov and N. P. Sopov, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **18**, 1781 (1948).

(4) R. Morris, U. S. Patent 2,450,765.

(5) H. Joy and J. Rust, U. S. Patent 2,373,568.

(6) S. Beckmann, R. Schaber and R. Bamberger, *Chem. Ber.*, **87**, 997 (1954).

(7) K. Alder and G. Stein, *Ann.*, **514**, 1, 197 (1934).