gave white crystals melting at 121° (undepressed upon admixture with authentic benzoic acid).

Hydrogenation. Hydrogenation of 0.195 g. (1.05 mmol.) of product was performed in ethyl alcohol using palladium on charcoal in the usual way[21] at room temperature. The first molar equivalent of hydrogen was absorbed within 15 min. while 24 hr. was required for the second mole.

Ozonization. To a 0.8409-g. sample dissolved in 100 ml. of anhydrous methanol as participating solvent was added ozone at −40° from a Welsbach T 23 ozonizer at a flow rate of 17 l. per hr. and an ozone concentration of 66.5 mg. per l.; oxygen pressure was eight p.s.i. and potential was 90.[22] It was estimated that at this rate 23.2 min. would be required for complete ozonization of two double bonds. After 20 min. the first traces of ozone broke through to the ozone meter and the reaction was stopped at 23 min. Now 2 g. of zinc dust was added and after warming to room temperature, 10 ml. of 5% sulfuric acid was added to destroy remaining peroxides. The solution was steam distilled until the distillate tested negative with 2,4-dinitrophenylhydrazine, the volume at this point being nearly 3 l. The first 1500-ml. portion of distillate was made just acid and 3 g. of dimedone in 50 ml. of 50% aqueous ethanol added.[23] A fluffy precipitate formed slowly which when dried gave the proper melting point for the formaldehyde-dimedone adduct, 196° (hot stage), and was not lowered by mixing with authentic adduct.

The filtrate from the dimedone reaction was steam distilled and 2,4-dinitrophenylhydrazine added. The mixed derivatives were collected by filtration, dried, dissolved in chloroform and chromatographed first on Fisher alumina and then on Woelm alumina using chloroform as eluent in both cases. The wide range of melting points for acetone–2,4-dinitrophenylhydrazone that may be found in the literature attests to the difficulty in its purification. Several recrystallizations of the twice chromatographed product failed to raise the melting point from 123° to the desired 126°.[24] However, chromatography on Florosil with benzene eluent raised the melting point to the desired temperature and the identification was completed by mixed melting point and comparison of the infrared spectrum (Nujol mull)[25] with an authentic sample.

NMR spectrum.[7] This was obtained using a Varian Dual-Purpose 60-mc. NMR Spectrometer coupled to a Varian 60-mc. magnet with flux stabilizer. In addition to the gross features of the spectrum described above it was noticed that the hydrogens in the olefinic region consisted of a nonequivalence quartet and one sharp peak of intensity two. The quartet implies the presence of two lone hydrogens on adjacent carbons and the single spike the presence of two equivalent hydrogens on a carbon adjacent to another carbon bearing no hydrogens (*i.e.*, the methylene hydrogen on carbon-1). The lower of the nonequivalent lone hydrogens is that on carbon-4 of the 1,4-hexadiene chain and the higher one is presumably on carbon-3 and is shifted to its low position by its proximity to two trigonal carbons.

Acknowledgment. The writer is glad to express his appreciation to Professor Robert Levine of this Department and Dr. Bothner-By of Mellon Institute for critical readings of this manuscript.

PITTSBURGH 13, PA.

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(22) These conditions were chosen by Dr. R. H. Callighan of Mellon Institute who performed the ozonization for us. We are grateful for this help from him.

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[CONTRIBUTION FROM THE AGRICULTURAL RESEARCH DIVISION, SHELL DEVELOPMENT COMPANY AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

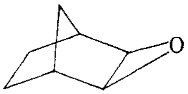
Bridged Polycyclic Compounds. XI.
Epoxidation of Norbornene and of *exo*-Dihydrodicyclopentadiene[1]

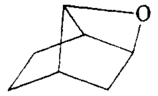
S. B. SOLOWAY AND STANLEY J. CRISTOL

Received September 23, 1959

Epoxidation of norbornene has been shown to give 2,3-epoxynorbornane and epoxidation of *exo*-dihydrodicyclopentadiene (*exo*-5,6-cyclopentano-2-norbornene) has been shown to give *exo*-2,3-epoxy-*exo*-5,6-cyclopentanonorbornane. Thus both epoxidations occur without rearrangement and by *exo* addition to the bicycloheptene ring.

The epoxidations of norbornene (bicyclo(2,2,1)-heptene-2) with monoperoxyacetic acid[2] and monoperoxyphthalic acid[3] have been reported. The structure of the oxide was formulated as *exo*-2,3-epoxynorbornane (I) in view of its reduction by lithium aluminum hydride to *exo*-2-norborneol[2] and its ring opening to a 2,7-dihydroxynorbornane.[2,3] This formulation of the epoxide as the 2,3-isomer suggests that Wagner-Meerwein rearrangement has occurred in the ring-opening step, but the facts available in the literature are also consistent with the formulation of the epoxide as the 2,7- isomer, if the assumption is made that reduction by lithium aluminum hydride involves attack at the bridge carbon atom. We had pre-


I


II

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(1) Previous paper in series: S. J. Cristol, W. K. Seifert, and S. B. Soloway, *J. Am. Chem. Soc.*, in press (1960).

(2) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

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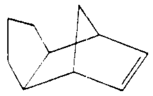
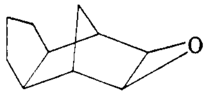
pared this epoxide from norbornene and peroxybenzoic acid, and had found properties and reactions similar to those reported in the other preparations.

Barrow and Searles[4] have shown that, while 1,2-epoxides have strong infrared absorption bands at about 11.9μ,[5] trimethylene oxides have bands at about 10.3 μ and tetrahydrofurans at about 9.2μ. Accordingly, structure I should have a strong band at about 11.9μ, and structure II, which may be classified as having both four- and five-membered oxide rings, should have a strong absorption peak or peaks in the range 9.1 to 10.3μ.

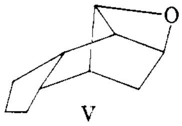
An infrared spectral analysis showed the position of a strong band at 11.85μ for the epoxide of norbornene and this result, coupled with the lithium aluminum hydride reduction to *exo*-2-norborneol confirms the structure *exo*-2,3-epoxynorbornane (I).[2,3]

We felt it worthwhile to study a system in which a *chemical* proof could be added to the infrared analysis result. Accordingly, epoxidation of *exo*-5,6-cyclopentano-2-norbornene (III) was carried out, using peroxybenzoic acid in chloroform.

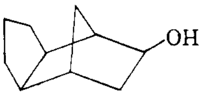

III



IV



V



VI

If the epoxidation occurred without rearrangement, product IV would result, and lithium aluminum hydride reduction would give *exo*-5,6-cyclopentano-*exo*-2-norborneol (VI). On the other hand, addition with rearrangement would give V, which on reduction would give an alcohol related to *endo*-5,6-cyclopentanonorbornane.

The epoxide product was an oil, which had a strong absorption band at 11.84μ; it was reduced by lithium aluminum hydride in refluxing tetrahydrofuran very slowly to give slightly impure *exo*-5,6-cyclopentano-*exo*-2-norborneol[6] m.p. 37–46° (lit.[1,7] m.p. 53–54°). The alcohol was converted to the *p*-nitrobenzoate and acid phthalate esters, and melting point and mixed melting-point determinations with esters prepared from authentic alcohol confirmed the identity of the alcohol as VI.

Thus, addition of an oxygen atom to the olefinic bond in norbornene and one of its derivatives involves *exo* addition without rearrangement.

EXPERIMENTAL

exo-2,3-Epoxynorbornane, I. A chloroform solution, 1340 ml., containing 104 g. (0.75 mole) of peroxybenzoic acid[8] was added slowly to 65.8 g. (0.7 mole) of solid norbornene,[9] producing a strongly exothermic reaction. The addition was completed with cooling, and the resulting solution was kept in a refrigerator for 4 days; at this time, titration with sodium thiosulfate showed the consumption of 96.2 g. of peroxybenzoic acid (theory 96.6 g.). The chloroform solution was washed with alkali and water, dried over anhydrous sodium sulfate, and distilled through a modified Claisen flask at atmospheric pressure (630 mm.). After the chloroform was removed there was obtained a forerun of 3 g., b.p. 142–146° (m.p. 121–122°) and 59 g. of product, b.p. 146–148°, which solidified in the receiver as fern-like crystals, m.p. 121–125° (total yield 80%). Recrystallization of a specimen from cold hexane gave I as needle-like crystals, m.p. 125.5–126.5° (lit. m.p. 125–127°;[2] 118–119°[3]).

Anal. Calcd. for $C_7H_{10}O$: C, 76.3; H, 9.15. Found: C, 76.7; H, 9.24.

The compound smelled like camphor and sublimed readily at room temperature. It did not react with potassium permanganate in acetone, nor with bromine in carbon tetrachloride. Its infrared spectrum had a strong peak at 11.85 μ characteristic of 1,2-epoxides.[10]

This epoxide could be reduced to *exo*-2-norborneol by heating at reflux with a solution of lithium aluminum hydride in tetrohydrofuran for seven days. A similar reduction, using *N*-ethylmorpholine as solvent, has already been reported.[2]

exo-2-syn-7-Norbornanediol diacetate. A solution of 5.5 g. (0.05 mole) of I, and 4.9 g. (0.05 mole) of potassium acetate in 100 ml. of acetic acid was heated at reflux for 48 hr. The product was isolated by diluting with water and extracting with pentane. The oil remaining after evaporation of the pentane was distilled; 5.2 g. (49%), b.p. 134–135° (15 mm.), n^{20}_{D} 1.4657, was obtained.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.2; H, 7.60; sapon. equiv., 106. Found: C, 62.0; H, 7.60; sapon. equiv., 109.

exo-2-syn-7-Norbornanediol. A solution of 24.5 g. (0.115 mole) of the diacetate in 75 ml. of dry ether was added slowly with stirring to 11.9 g. (0.345 mole) of lithium aluminum hydride in 600 ml. of ether, and the mixture was stirred for 24 hr. The excess lithium aluminum hydride was destroyed with 35 ml. of ethyl acetate, the complex was decomposed, and the inorganic hydroxides were coagulated by the addition of 125 ml. of water. The ether solution was then filtered through a plug of dry cotton. Evaporation of the solvents at reduced pressure gave 13.8 g. (93% yield) of a crystalline residue, m.p. 177–181°. Recrystallization from nitromethane gave 5.5 g. (37%) of pure *exo-2-syn*-7-norbornanediol as fern-like crystals, m.p. 191–192° (lit. m.p. 179–181°;[2] 174–176°[3]).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.44. Found: C, 65.6; H, 9.56.

The water-soluble diol gave a negative test for a vicinal diol with periodic acid.

exo-2,3-Epoxy-exo-5,6-cyclopentanonorbornane (*exo-5,6-epoxyoctahydro-exo-4,7-methanoindene*, IV). A chloroform solution, 250 ml., containing 15.2 g. (0.11 mole) of peroxybenzoic acid was added slowly to 13.4 g. (0.10 mole) of *exo*-dihydrodicyclopentadiene (III),[1] with cooling to moderate the exothermic reaction. After the reaction solution was kept in a refrigerator overnight, titration with sodium thiosulfate showed that all of the peracid had been consumed.

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Additional chloroform solution, 110 ml., containing 6.6 g. (0.048 mole) of peroxybenzoic acid was added. After 4 hr. at room temperature, 0.044 mole of peracid was still present. The chloroform solution was then washed repeatedly with sodium carbonate solution and dried over anhydrous sodium sulfate. The chloroform was removed at atmospheric pressure and the residual oil was distilled to yield 12.0 g. (80%) of IV as a colorless oil, b.p. 50–51.5° (0.7 mm.), n_D^{28} 1.5031.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.39. Found: C, 80.0; H, 9.50.

The infrared spectrum of IV showed a characteristic 1,2-epoxide peak at 11.84 μ.[10]

exo-5,6-Cyclopentano-exo-2-norborneol (octahydro-exo-4,7-methanoinden-exo-5-ol, VI). Lithium aluminum hydride, 3.8 g. (0.1 mole) was dispersed in 50 ml. of tetrahydrofuran by refluxing with stirring, 5.0 g. (0.033 mole) of epoxide IV was added, and the reaction mixture was heated at reflux for 5 days. The excess lithium aluminum hydride was destroyed with 10 ml. of ethyl acetate and the complex was decomposed with 100 ml. of water. Extraction of both the solid and liquid phases with pentane, drying and evaporation of the solvents, and, finally, distillation yielded 1.15 g. of a forerun, b.p. 50–73° (0.5 mm.), which was about 65% epoxide by infrared analysis, and 3.14 g. (62%) of impure alcohol VI, b.p. 75–79° (0.7 mm.), which solidified, m.p. 37–46°.

The *acid phthalate* derivative was prepared by heating 1.0 g. (6.6 mmoles) of the reduction product with 1.27 g. (8.6 mmoles) of phthalic anhydride in 15 ml. of pyridine on the steam bath. Water and 6*N* hydrochloric acid were added and the precipitated oil was taken up in ether. The ethereal solution was dried over anhydrous sodium sulfate and the solvent was evaporated to yield 1.9 g. (96%) of product, m.p. 151–153.5°. Crystallization from acetone gave 0.81 g. of pure acid phthalate, m.p. 157.5–158°; mixed m.p., 157.5–158°, with the acid phthalate of authentic VI.[1,6,7]

Treatment of 0.5 g. (3.3 mmoles) of the alcohol with 0.73 g. (3.9 mmoles) of *p*-nitrobenzoyl chloride in 5 ml. of pyridine yielded 0.6 g. (60%) of crude product, m.p. 86–90°. Two crystallizations from hexane gave 0.25 g. of *p*-nitrobenzoate, m.p. 91.5–93°; mixed m.p. 93.5–94° with the *p*-nitrobenzoate of authentic VI[1,6] (m.p. 94–94.5°).

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BOULDER, COLO.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL SCIENCE, KANSAS STATE COLLEGE]

Condensation Reactions of Carbon Monoxide with Aluminum Chloride and Aromatic Systems

ELBERT W. CRANDALL, C. H. SMITH,[1] AND R. C. HORN[2]

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Carbon monoxide reacts with aromatic hydrocarbons in the presence of molar quantities of aluminum chloride at 60° and a pressure of 50 p.s.i. to give substituted anthracenes. Toluene gives a dimethylanthracene, diphenylmethane gives a dibenzylanthracene, and *p*-xylene yields 1,4,5,8-tetramethylanthracene. Diphenyl ether forms xanthydrol at 80°.

Aromatic aldehydes, benzyl alcohol, and benzhydrol are cleaved in the presence of excess aluminum chloride to give carbon monoxide. If an aryl hydrocarbon is present, polynuclear systems are formed.[3–7] Carbon monoxide should then react with aromatic hydrocarbons to form derivatives of anthracene.

In the present investigation, carbon monoxide under 50 p.s.i. pressure was shaken with various aromatic hydrocarbons and diphenyl ether in the presence of aluminum chloride over a period of 12–18 hours. Pressure drops of 5–15 pounds were noted in most cases.

At 60°, toluene reacts with carbon monoxide to form a mixture of dimethylanthracenes which is regarded as a eutectic mixture of the 2,6- and 2,7-isomers.[8] Diphenylmethane gives a dibenzylanthracene, while *p*-xylene gives a tetramethylanthracene, probably the 1,4,5,8 isomer.[4]

The dimethyl and dibenzylanthracenes were analytically and spectroscopically identical with the products obtained from the reactions of benzaldehyde with toluene and diphenylmethane.[3,4,6] Each is regarded as a mixture of the 2,6- and 2,7-isomers[8].

The reaction is temperature dependent. At 30°, toluene reacts to give some *p*-tolualdehyde along with dimethylanthracene. At 40°, only a trace of aldehyde is observed. The yield of dimethylanthracene increases to a maximum at 60° (Table I). A comparison of this reaction with the Gattermann-Koch reaction was carried out.[9] Toluene, saturated with dry hydrogen chloride, failed to give increased yields of dimethylanthracene at 60°.

Diphenyl ether is unique in that the carbon monoxide bridges the *ortho-* positions to give xanthydrol.

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[2] From the master's thesis of R. C. Horn, Kansas State College, Pittsburg, Kan.

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