vials were rapidly cooled in ice water, and the contents were ground to a fine powder. The melting points were determined in capillary tubes in an oil bath whose temperature was raised at 0.2–0.3°/min. (Table II). A calibrated precision thermometer was employed.

TABLE II

| Mole fraction of dimethyl terephthalate | M.p., °C. |
|---|---|
| 0.000 | 128–129.2 |
| 0.111 | 124.1–125.6 |
| 0.159 | 124.6–125.5 |
| 0.301 | 125.8–127.6 |
| 0.500 | 129.4–131.1 |
| 0.739 | 134.0–135.3 |
| 0.876 | 136.5–137.8 |
| 1.000 | 140.4–141.1 |

The first temperature corresponds to the first visible appearance of liquid, and the second corresponds to the disappearance of the last solid. The results indicate that these components form a simple eutectic system at their melting point.

**Properties of a 1 : 1 Mixture of 17 and 15.**—A mixture of 0.2047 g. (0.001055 mole) of dimethyl terephthalate and 0.2070 g. (0.001055 mole) of dimethyl cyclohexa-1,4-diene-1,4-dicarboxylate was melted rapidly, quenched, and ground to a fine powder with a spatula.

*Anal.* Calcd. for $C_{20}H_{22}O_8$: C, 61.53; H, 5.68. Found: C, 61.55, 61.75; H, 5.84, 5.76.

The ultraviolet, infrared, and n.m.r. spectra were essentially linear combinations of those of the constituents: $\nu_{max}$ 698, 728, 806, 815, 874, 932, 955, 1008, 1020, 1087, 1103, 1118, 1198, 1273, 1320, 1387, 1410, 1443, 1509, 1650, 1715, 1730, 2840, 2890, 2950, 3010 cm.$^{-1}$; ultraviolet spectrum, $\lambda_{max}$ m$\mu$ (log $\epsilon$), 240 (4.024), 285 (2.928), 294 (2.848) [these agree fairly well with the values reported by Smith, Warren, and Vaughan[10] for their "diene IV": $\lambda_{max}$ m$\mu$ (log $\epsilon$), 240 (4.069), 286 (3.107), 294 (3.090). Closer agreement was obtained by a mixture containing 5% of **5** (see below)]; n.m.r. (*cf.* Table I) $\tau$ 1.73 [2.0] s, 2.86 [1.0] fs, 5.97 [3.1] s, 6.17 [3.1] s, 6.81 [2.1] fs. The corresponding values reported for "diene IV"[10] are $\tau$ 1.72 [2] s, 2.83 [1] fs, 5.97 [3] s, 6.16 [3] s, 6.80 [2] fs, and 6.13 "buried."

**Properties of a Mixture of 5, 15, and 17.**—A mixture of 0.0191 g. of **5**, 0.1926 g. of **15**, and 0.1976 g. of **17** was prepared as described: m.p. 126.0–130.4°; $\lambda_{max}$ m$\mu$ (log $\epsilon$ based on av. mol. wt. = 195), 240 (4.012), 286 (3.071), 294 (3.070); n.m.r. $\tau$ 1.70 [2.0] s, 2.80 [1.0] fs, 5.94 [3.0] s, 6.15 [3.2] s, 6.80 [1.9] fs, 7.39 [0.2] fs. To check the analytical procedure used to analyze mixtures of **5**, **15**, and **17** (see below), the above mixture gave the following values (mole %) by integration of the n.m.r. peaks at $\tau$ 5.94, 6.15, 6.80, and 7.39: calcd. for **5**, 4.7%; **15**, 46.9%; **17**, 48.5%; found for **5**, 5.1%; **15**, 46.1%; **17**, 48.8%.

**Reaction of 5 and 15 with Aqueous Potassium Hydroxide.**—These experiments were carried out several times in the presence or absence of air and with variations in agitation and method of heating (oil bath or electric heating mantle). In all cases **5** yielded mixtures of **5**, **15**, and **17**, while **15** yielded **15** and **18** with at most only traces of **5**. The relative proportions of products could be estimated by integration of the n.m.r. peaks at $\tau$ 5.95 for **17** ($OCH_3$), at $\tau$ 6.8 for **15** ($CH_2$), at $\tau$ 7.38 for **5** ($CH_2$), and at $\tau$ 6.1–6.2 for **5** and **15** ($OCH_3$). In a typical experiment 1.0 g. of **5** was heated at reflux (oil bath, magnetic stirrer, air) in a solution of 1.1 g. of 85% potassium hydroxide in 1.0 ml. of water for 3.5 days. The mixture was cooled and acidified with hydrochloric acid. The resulting product was filtered, washed with water, and vacuum dried. The product (1.02 g.) was gently warmed with 5 g. of phosphorus pentachloride for 30 min. It was cooled in ice, and 10 ml. of methanol was added dropwise. The solution was refrigerated and yielded 0.54 g. of a mixture of 13% **17**, 43% **15**, and 44% **5**. After one recrystallization from ethyl acetate these values were 14, 68, and 18%, respectively. After a second recrystallization the values were 36, 62, and 2%.

When **15** was treated similarly (electric heating mantle, magnetic stirrer, air), the product after one recrystallization from ethyl acetate consisted of **15** (51%), **17** (47%), and **5** (2% max.)

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# Free-Radical Additions to Vinylcyclopropane and Butadiene Monoxide[1]

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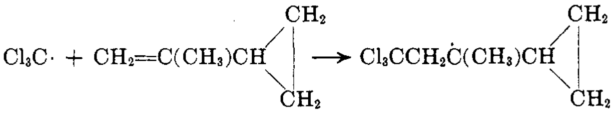
The light-induced addition of bromotrichloromethane to vinylcyclopropane gave a mixture of *cis*- and *trans*-1,1,1-trichloro-6-bromohex-3-ene. The additions of cyclopentane, cyclohexane, and cyclooctane to butadiene monoxide in di-*t*-butyl peroxide induced reactions yielded the corresponding *trans*-4-cycloalkylbut-2-en-1-ols. Isopropyl alcohol was added to butadiene monoxide in a similarly induced reaction yielding *trans*-5-methylhex-2-en-1-ol. The formation of these addition products is proposed to proceed by a $\beta$-elimination reaction involving the opening of the three-membered ring. The stereochemistry of the $\beta$-elimination reaction is discussed in terms of the conformational factors encountered in the transition states of the reactions.

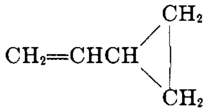
In an earlier report,[3] the free-radical additions of polyhalomethanes and mercaptans to 2-cyclopropylpropene (I) were shown to yield unsaturated products that required the opening of the cyclopropyl ring. The ring opening in these reactions was a $\beta$-elimination reaction that involved the adduct radical A· yielding a rearranged radical B· which reacted with the adding reagent to produce the addition product. These steps are illustrated in the following chain sequence (eq. 1–3) for the addition of bromotrichloromethane to I. This system did not lend itself readily to a study of the stereochemistry of the $\beta$-elimination reaction. For this reason we undertook the investigation of free-radical addition reactions to vinylcyclopropane (II) and butadiene monoxide (III). These two unsaturated compounds undergo similar $\beta$-elimination reactions in free-radical additions yielding 1,2-disubstituted ethylenes as addition products, making the configura-

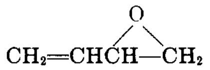

(1)

I A·

$$\mathrm{A\cdot} \longrightarrow \underset{\mathrm{B\cdot}}{\mathrm{Cl_3CCH_2C(CH_3){=}CHCH_2\dot{C}H_2}} \tag{2}$$

$$\mathrm{B\cdot} + \mathrm{BrCCl_3} \longrightarrow \mathrm{Cl_3CCH_2C(CH_3){=}CHCH_2CH_2Br} + \mathrm{Cl_3C\cdot} \tag{3}$$


II


III

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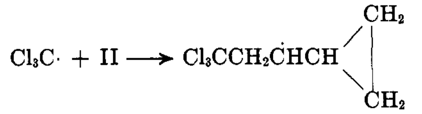
[1] This work was supported by Grant No. 512-A from the Petroleum Research Fund.

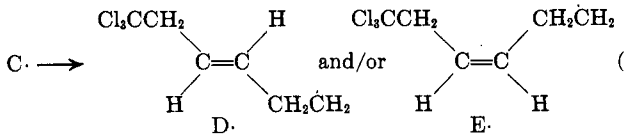
[2] Taken from the thesis submitted by L. R. M. in partial fulfillment of the requirements for the M.S. degree from the University of Kansas, 1964.

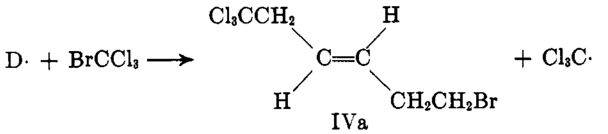
[3] E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).

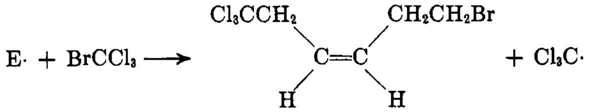
tion of the products easily determined by infrared analysis.

The light-induced addition of bromotrichloromethane to vinylcyclopropane yielded a mixture of *cis*- and *trans*-1,1,1-trichloro-6-bromohex-3-ene as evidenced by infrared absorptions at 966 and 699 cm.$^{-1}$ due to the *cis* and *trans* olefinic linkages, respectively. Attempts to isolate the two isomers by preparative gas chromatography failed and, without the pure isomers in hand, a quantitative estimation of their relative amounts was not possible. Treatment of the addition product mixture with iodine[4] and with methyl mercaptan[5] in attempting to isomerize the mixture to an equilibrium mixture of the *cis* and *trans* products failed to cause any change in the intensities of the infrared absorptions at 966 and 699 cm.$^{-1}$, suggesting that an equilibrium mixture of the two products was obtained in the addition reaction. However, it was not possible to conclude from these experiments that an equilibrium mixture of the *cis* and *trans* isomers resulted in this case from a nonstereospecific $\beta$-elimination reaction of radical C· yielding a mixture of radicals D· and E· which react with the bromotrichloromethane to yield the two isomers. The equilibration of a single isomeric product, either IVa or IVb, caused by free bromine atoms present in the reaction mixture produced by the photolytic decomposition of bromotrichloromethane may well have occurred. Such an equilibration of a single isomer could readily be accomplished by addition of the bromine atom to the double bond of a single product yielding either radical F· or G· (or both). Free rotation about the 3,4-carbon–carbon bond is possible in such radicals and the $\beta$-elimination of the bromine atom would yield a mixture of the *cis* and *trans* isomers. This process could repeat itself many times and eventually the equilibrium mixture of IVa and IVb would be obtained. The equilibration of *cis–trans* isomers by iodine or by methyl mercaptan involves essentially the same sequence of reactions except that the adding radicals are the iodine atom and methyl thiyl radical, respectively.


C·
(4)

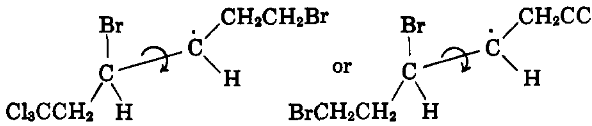

D· E·
(5)


IVa
(6)


IVb
(7)

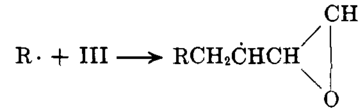
$$\mathrm{BrCCl_3} \xrightarrow{h\nu} \mathrm{Br\cdot} + \mathrm{Cl_3C\cdot} \qquad (8)$$

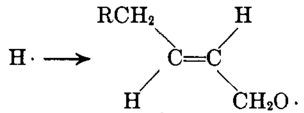
IVa or IVb + Br· ⟶

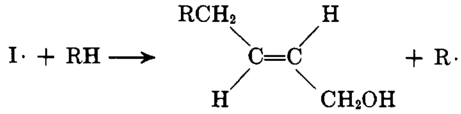

F· G·
(9)

F· (or G·) ⟶ IVa + IVb + Br· (10)

In order to investigate the stereochemistry of the $\beta$-elimination reaction, it became necessary to find a system that would not involve any free radicals that were capable of addition and rapid elimination from the double bond in the product causing isomerization of a single product if it is indeed formed. The di-*t*-butyl peroxide induced additions of cycloalkanes and of isopropyl alcohol to butadiene monoxide (III) proved to be a system that not only involved a $\beta$-elimination essentially identical with that encountered in the vinylcyclopropane reactions but was also free of any radicals that could cause isomerization of the products. The additions of cyclopentane, cyclohexane, and cyclooctane to III yield the corresponding *trans*-4-cycloalkylbut-2-en-1-ol as the major 1:1 addition product. These unsaturated alcohols were formed by the following sequence of reactions (eq. 11–13) where R = $C_5H_9$, $C_6H_{11}$, or $C_8H_{15}$. A similar ring opening was observed by Sabatino and Gritter in the di-*t*-butyl peroxide induced reaction of cyclohexene oxide which yielded, among other products, 3-cyclohexenol.[6] Although the yields of these unsaturated alcohols were low (see Table I), the infrared and n.m.r. spectra were consistent with the assigned structures. In each case, the infrared spectra showed a strong oxygen–hydrogen stretching absorption at 3333 cm.$^{-1}$ and an absorption at 968 cm.$^{-1}$ due to the *trans* olefinic linkage. There was no absorption in the 715–690-cm.$^{-1}$ region indicating the absence of any *cis* olefinic linkages. The n.m.r. spectra of all three addition products were basically the same, each having a vinyl proton resonance with essentially identical splitting centered at 5.61, a doublet at 4.08 assigned to the allylic protons bonded to the hydroxyl-bearing carbon, a singlet in a region ranging from 3.9 to 4.4 (depending on the dryness of the sample) due to the hydroxyl proton, and a generally complex pattern in the region of 0.9–2.2 p.p.m. resulting from the remaining


H·
(11)


I·
(12)


(13)

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[4] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Am. Chem. Soc.*, **67**, 1319 (1945); R. M. Noyes and R. G. Dickinson, *ibid.*, **65**, 1427 (1943); R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

[5] C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).

[6] E. C. Sabatino and R. J. Gritter, *J. Org. Chem.*, **28**, 3437 (1963).

TABLE I

DI-*t*-BUTYL PEROXIDE INDUCED FREE-RADICAL ADDITIONS OF CYCLOALKANES AND ISOPROPYL ALCOHOL TO BUTADIENE MONOXIDE

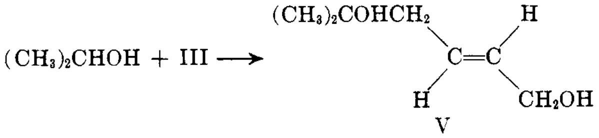
| Adding reagent (mmoles) | mmoles of butadiene monoxide | mmoles of peroxide | mmoles of recovered butadiene monoxide | Product (mmoles) | % yield[a] | Residue, g. |
|---|---|---|---|---|---|---|
| Cyclopentane (2280) | 143 | 15 | *b* | *trans*-4-Cyclopentylbut-2-en-1-ol (8.2) | 5.8[c] | 3.8 |
| Cyclohexane (4000) | 71.5 | 15 | 24.3 | *trans*-4-Cyclohexylbut-2-en-1-ol (6.5) | 13 | 3.3 |
| Cyclooctane (2460) | 143 | 18 | 83.5 | *trans*-4-Cyclooctylbut-2-en-1-ol (25.7) | 43 | 6.7 |
| Isopropyl alcohol (4430) | 143 | 30 | 12.9 | *trans*-5-Methylhex-2-ene-1,5-diol (14.4) | 11 | . . . |

[a] Yield determination based on butadiene monoxide that reacted unless indicated otherwise. [b] Unreacted butadiene monoxide codistilled with excess cyclopentane. [c] Based on the amount of butadiene monoxide initially present.

protons. The integrations of these absorptions were consistent in all cases with these assignments.

The major side product produced in these reactions is an aldehyde as indicated by a small carbonyl absorption at 1694 cm.$^{-1}$ in the infrared spectra of the crude 1:1 addition product mixture and a small doublet due to an aldehydic proton in the n.m.r. spectra at 9.5 p.p.m. Estimation of the aldehydic content from the integration of the n.m.r. spectra indicated that this material comprises about 5% of the crude product. It most likely arises from the di-*t*-butyl peroxide oxidation[7] of the alcohol produced as the major product of the reaction. Treatment of the crude 1:1 addition product with phenyl isocyanate gave the phenylurethan derivative of the unsaturated alcohol. In each reaction, a high-boiling residue was formed. Although no attempt was made to characterize this material, it is most likely a mixture of telomeric products resulting from reaction of either H· or I· with butadiene monoxide.

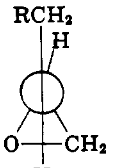
Isopropyl alcohol reacted with butadiene monoxide in a di-*t*-butyl peroxide induced reaction yielding *trans*-5-methylhex-2-ene-1,5-diol (V) as the 1:1 addition product. Reactions of *n*-butyraldehyde and *n*-butyl mercaptan induced with azobisisobutyronitrile at 80° failed to yield on distillation any isolable amounts of the expected addition products.



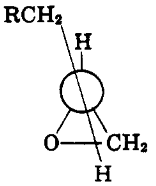
(14)

V

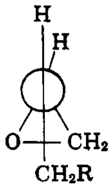
The observation that only a *trans* olefinic linkage was produced in the addition reactions to butadiene monoxide suggests that the elimination in these cases is stereospecific. The transition state for the reaction leading to the *trans* olefinic linkage likely involves a conformation intermediate between Ha and Hb whereas the transition state for the formation of the *cis* olefinic linkage would require a conformation intermediate between Hc and Hd. The most unfavorable situation in Ha or Hb requires eclipsing of the $RCH_2$ group or the methylene group of the epoxide ring with a hydrogen. In Hc, not only is there an eclipsing of two hydrogens but also two skew interactions between the $RCH_2$ group with the methylene and the oxygen of the epoxide ring. These skew interactions in Hc may well be greater than the normal skew interactions in ordinary aliphatic compounds since the angle described by the methylene and oxygen of the epoxide ring is only 60 rather than 120°. In Hd, there is eclipsing of the $RCH_2$ group with the methylene of the epoxide ring. The unfavorable conformational requirements for the transition state leading to the formation of the *cis* olefinic linkage may very likely raise the activation energy requirement for this reaction over that of the *trans* elimination enough to exclude formation of the *cis* product.



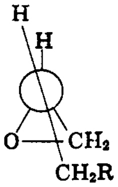
Ha



Hb



Hc



Hd

For the same conformational reasons outlined to account for the stereospecific formation of the *trans* olefinic linkage in the β-elimination reaction of H·, a stereospecific β-elimination might well occur to form only the *trans* radical D· in the addition reaction to vinylcyclopropane, but the addition product IVa is isomerized to the observed equilibrium mixture by bromine atoms. Although an attempt to add cyclohexane to vinylcyclopropane failed to yield any isolable amounts of a simple 1:1 addition product, a high-boiling residue was obtained which very likely was a mixture of telomeric products. The infrared spectra of this material showed an absorption at 961 cm.$^{-1}$ due to the *trans* olefinic linkage but no *cis* absorption in the 715–690-cm.$^{-1}$ region. It appears from this reaction, one which does not involve any radicals which could cause the isomerization of the product of the reaction, that the β-elimination reaction is also stereospecifically *trans* in the adduct radicals obtained by addition to vinylcyclopropane.

## Experimental[8]

**Materials.**—Vinylcyclopropane was prepared by the pyrolysis of 1-cyclopropylethyl-S-methyl xanthate in the manner reported previously.[9] The following reagents were commercial materials and were redistilled before using: bromotrichloromethane (Dow Chemical Co.), butadiene monoxide (Pittsburgh Plate Glass Co.), cyclopentane and cyclohexane (Matheson Coleman and Bell), cyclooctane (Aldrich Chemical Co.), and isopropyl alcohol (Fisher Scientific Co.). The following commercial reagents were used without further purification: azobisisobutyronitrile, *n*-butyl mercaptan, and *n*-butyraldehyde (Matheson Coleman and Bell); and di-*t*-butyl peroxide (Lucidol Division, Wallace Tierman, Inc.).

**Addition of $BrCCl_3$ to Vinylcyclopropane (II).**—A solution consisting of bromotrichloromethane (10.0 g., 0.05 mole) and vinylcyclopropane (1.7 g., 0.025 mole) was illuminated with a 275-w. Sylvania sun lamp for 3 hr. at 16°. Gas chromatographic analysis of the resulting reaction mixture showed that the olefin was completely consumed in this time. After removal of the unreacted

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[7] E. S. Huyser and C. J. Bredeweg, *J. Am. Chem. Soc.*, **86**, 2401 (1964).

[8] All melting and boiling points are uncorrected. The infrared analyses were performed on a Beckman IR-8 and the n.m.r. spectra obtained on a Varian Model A-60. Elemental analyses were performed by Weiler and Strauss, Oxford, England.

[9] C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 4896 (1960).

$BrCCl_3$ by distillation, the remaining residue was distilled under vacuum and yielded 5.0 g. (76% of theory) of 1,1,1-trichloro-6-bromohex-3-ene: b.p. 75–76° (1 mm.), $n^{20}\text{D}$ 1.5242.

*Anal.* Calcd. for $C_6H_8BrCl_3$: C, 27.05; H, 3.03; Br, 30.00; Cl, 39.92. Found: C, 26.98; H, 3.28; Br, 30.10; Cl, 40.00.

The n.m.r. spectra of this product showed a multiplet centered at 5.8 due to the vinyl hydrogens, a quartet centered at 2.8 due to the 5-methylene protons, a doublet at 3.4 p.p.m. due to the 2-methylene protons, and a triplet in the same region due to the 6-methylene protons. The integrated areas were consistent with these assignments. The pertinent features of the infrared spectra of this addition product are discussed in the text.

**Addition of Cyclopentane to Butadiene Monoxide (III).**—A solution consisting of cyclopentane (161 g., 2.28 moles), butadiene monoxide (10.0 g., 0.143 mole), and di-*t*-butyl peroxide (2.2 g., 0.015 mole) was heated in a stainless steel autoclave at 110–130° for 36 hr. Distillation of the reaction mixture gave some unreacted butadiene monoxide which codistilled with the unreacted cyclopentane. Vacuum distillation of the material remaining after removal of the unreacted cyclopentane and butadiene monoxide yielded 1.15 g. (5.8% of theory based on the initial amount of butadiene monoxide) of a crude reaction product consisting mainly of *trans*-4-cyclopentylbut-2-en-1-ol: b.p. 66–68° (0.03 mm.), $n^{20}\text{D}$ 1.4763. The salient features of the infrared and n.m.r. spectra are described in the text. Reaction of a portion of the crude mixture with phenyl isocyanate gave the phenylurethan derivative of the alcohol: m.p. 82.7–83.2°.

*Anal.* Calcd. for $C_{16}H_{21}NO_2$: C, 74.39; H, 7.80; N, 5.42. Found: C, 74.19; H, 7.98; N, 5.50.

After removal of the crude 1:1 addition product, a residue remained which amounted to 3.8 g.

**Addition of Cyclohexane to Butadiene Monoxide (III).**—A solution consisting of cyclohexane (336 g., 4.0 mole), butadiene monoxide (5.0 g., 0.072 mole), and di-*t*-butyl peroxide (2.2 g., 0.015 mole) was heated in a stainless steel autoclave at 125–135° for 24 hr. Distillation of the reaction mixture gave 1.7 g. of unreacted butadiene monoxide (b.p. 41°). Vacuum distillation of the high-boiling material remaining after removal of the unreacted cyclohexane gave 1.0 g. (13.8% yield based on butadiene monoxide consumed) of a crude reaction mixture consisting mainly of *trans*-4-cyclohexylbut-2-en-1-ol: b.p. 115° (5 mm.), $n^{20}\text{D}$ 1.4809. The infrared and n.m.r. spectra of this material are described in the text. The phenylurethan derivative of the alcohol was prepared by reaction of a portion of the crude mixture with phenyl isocyanate: m.p. 113.5–114°.

*Anal.* Calcd. for $C_{17}H_{23}NO_2$: C, 73.56; H, 8.81; N, 5.36. Found: C, 73.71; H, 8.65; N, 5.36.

The residue remaining after distillation of the crude 1:1 addition product amounted to 3.3 g.

**Addition of Cyclooctane to Butadiene Monoxide (III).**—A solution consisting of cyclooctane (276 g., 2.46 moles), butadiene monoxide (10 g., 0.143 mole), and di-*t*-butyl peroxide (2.63 g., 0.018 mole) was heated in a stainless steel autoclave at 118–136° for 24 hr. The unreacted butadiene monoxide recovered by distillation (b.p. 40–41°) amounted to 5.85 g. Distillation of the material remaining after removal of the unreacted cyclooctane yielded 4.68 g. (43.2% yield based on butadiene consumed) of 1:1 addition product consisting mainly of *trans*-4-cyclooctylbut-2-en-1-ol: b.p. 103–104° (0.5 mm.), $n^{20}\text{D}$ 1.4942.

*Anal.* Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.03; H, 11.94.

The phenylurethan derivative of the alcohol melted at 83.2–84°.

*Anal.* Calcd. for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03. Found: C, 75.52; H, 9.03.

The residue remaining after removal of the 1:1 addition product amounted to 6.65 g.

**Addition of Isopropyl Alcohol to Butadiene Monoxide (III).**—A solution consisting of isopropyl alcohol (265 g., 4.43 moles), butadiene monoxide (10.0 g., 0.143 mole), and di-*t*-butyl peroxide (4.4 g., 0.03 mole) was heated in a stainless steel autoclave at 125–135° for 24 hr. After removal of the unreacted butadiene monoxide (0.9 g.) and isopropyl alcohol by distillation at atmospheric pressure, the remaining mixture was distilled under vacuum and yielded 1.85 g. (11.1 % yield based on butadiene monoxide consumed) of *trans*-5-methylhex-2-ene-1,5-diol: b.p. 93–94° (0.5 mm.), $n^{20}\text{D}$ 1.4662.

*Anal.* Calcd. for $C_7H_{14}O$: C, 64.58; H, 10.84. Found: C, 64.34; H, 10.88.

The n.m.r. spectra of this material showed a resonance at 5.7 p.p.m. due to the olefinic protons as well as other resonance absorptions consistent with the assigned structure. The infrared spectra showed an absorption at 966 cm.$^{-1}$ but no absorption in the 715–690-cm.$^{-1}$ region which indicated only a *trans* configuration for the olefinic linkage. Attempts to prepare solid derivatives of this diol with both phenyl isocyanate and 3,5-dinitrobenzoyl chloride yielded only oils.

**Reaction of Cyclohexane with Vinylcyclopropane (II).**—Cyclohexane (104 g., 1.24 moles), vinylcyclopropane (1.8 g., 0.027 mole), and di-*t*-butyl peroxide (2.2 g., 0.015 mole) were heated for 24 hr. in a stainless steel autoclave. After removal of the unreacted cyclohexane by distillation at atmospheric pressure, a residue amounting to 2.5 g. remained. Vacuum distillation of this residue failed to yield any distillable product. The infrared spectra of the residue showed a strong absorption at 966 cm.$^{-1}$ but no absorption in the 715–690-cm.$^{-1}$ region. No further attempt was made to characterize this material.

**Reactions of *n*-Butyl Mercaptan and *n*-Butyraldehyde with Butadiene Monoxide.**—Solutions of *n*-butyl mercaptan and *n*-butyraldehyde with butadiene monoxide in about a 10:1 ratio were heated with a small amount of azobisisobutyronitrile at 80° for several hours. Apparently reaction occurred as evidenced by the formation of higher boiling materials in each case, but on distillation we were unable to obtain any pure products that corresponded to the expected 1:1 addition products.

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