38-3; II (*trans–trans–trans–trans*), 15042-39-4; II (*cis–trans–trans–cis*), 15042-40-7; III (*cis–cis–cis–cis*), 15042-41-8; III (*cis–trans–cis–trans*), 15042-42-9; III (*trans–trans–trans–trans*), 15042-43-0; III (*trans–cis–trans–cis*), 15042-44-1; III (*cis–cis–trans–trans*), 15042-45-2; III (*trans–trans–cis–cis*), 15042-46-3; IV (*cis–cis–cis–cis*), 15042-47-4; IV (*cis–cis–trans–trans*), 15042-48-5; IV (*cis–trans–trans–cis*), 15042-49-6; IV (*cis–trans–cis–trans*), 15042-50-9; IV (*trans–trans–cis–cis*), 15042-51-0; IV (*trans–trans–trans–trans*), 15042-52-1; IV (*trans–cis–cis–trans*), 15042-53-2; IV (*trans–cis–trans–cis*), 15042-54-3; *cis*-2-ethyl-4-methyl-1,3-dioxolane, 1568-99-6; *trans*-2-ethyl-4-methyl-1,3-dioxolane, 1860-13-5; *cis*-2,5-dimethyldioxane, 15042-57-6; *trans*-2,5-dimethyldioxane, 15042-58-7; *cis*-2,6-dimethyldioxane, 15042-59-8; *trans*-2,6-dimethyldioxane, 15042-60-1.

Acknowledgments.—The authors wish to acknowledge the assistance of Dr. J. J. Daly (Monsanto Research S. A., Zurich) for the X-ray analysis, M. T. Jackson, R. C. Scheibel, and J. Mesa (Monsanto Central Research Department, St. Louis) for obtaining the mass spectra, and Dr. J. M. S. Henis (Monsanto Central Research Department, St. Louis) for suggestions concerning their interpretation.

Twelve-Membered Polyether Rings. The Cyclic Tetramers of Some Olefin Oxides

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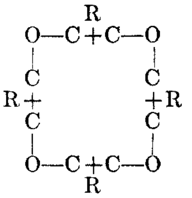
Received August 4, 1967

Twelve-membered ring polyethers have been obtained from propylene oxide, epichlorohydrin, and 1,2-butylene oxide in 30–40% conversions by treating the epoxide with $(C_2H_5)_3OBF_4$ or BF_3. Larger rings and a cyclic dimer are present in smaller amounts but no cyclic trimer forms.

The literature records many studies relating to the polymerization of epoxides employing various Lewis acid initiators.[1] Formation of polymeric resins and dopes is a common and undisputed result. On the other hand appreciable amounts of readily distillable products arise from the reactions of some olefin oxides with triethyloxonium tetrafluoroborate or boron trifluoride. These products prove to be principally cyclic tetramers, 1,4,7,10-tetraoxacyclododecanes (I).[2,3] No cyclic trimers and only small amounts of cyclic dimers (dioxanes) form.



I

Proof of ring structure relies upon data precluding end groups. Molecular weight by mass spectrometry and elemental analyses do not allow for end groups. No hydroxyl or ethyl groups are detectable in proton nmr or infrared spectra. The same products are obtained regardless of whether $(C_2H_5)_3OBF_4$ or BF_3 is employed as the catalyst.

There are four structural (head to tail) and twenty-three geometrical (*cis,trans*) isomers of the generalized structure I ($R \neq H$). These have been intensively studied in a companion article.[4] Twenty-two isomers were detected. The proton nmr patterns in the methyl region for the various propylene oxide derived isomers provides additional confirmation of ring structure.

Rings of other than 12 members could conceivably result if acetal groups, –O–CHR–O, were incorporated. Their presence would have been revealed by unique readily detectable nmr features which were not observed. However, the cyclic dimer (dioxane) families were accompanied by shrunken acetal-containing rings. For example, *cis*- and *trans*-2-ethyl-4-methyl-1,3-dioxolane formed from propylene oxide[4] (fraction 1 in Experimental Section).

When the composite family of cyclic tetramers from propylene oxide (I, $R = CH_3$) is cooled several days a portion crystallizes, mp 92–93°. Mass analysis showed the parent ion at m/e 232. X-Ray diffraction and nmr data[4] establish this solid to be the completely head to tail structural isomer, 2,5,8,11-tetramethyl-1,4,7,10-tetraoxacyclododecane.

Fraction 3 (see Experimental Section) of the propylene oxide reaction mixture was broken into parts by gas chromatography. Subsequent mass analysis of each of the five parts isolated showed the existence of a parent ion at m/e 290 (5×58). This corresponds to the cyclic pentamer of propylene oxide $(PO)_5$. Fraction 4 had a molecular weight of about 360 as determined by vapor phase osmometry. The mass spectrum of this fraction had peaks at m/e values above 290 but no detectable peak as 348 (6×58). Thus, the existence of a cyclic hexamer of propylene oxide $(PO)_6$ is not certain. No cyclic trimer was observed. The relative yields of $(PO)_2$, $(PO)_4$, $(PO)_5$, and resin were 1, 10, 2, and 5, respectively.

Large ring formation is not general to Lewis acid initiators. Tin tetrachloride, for example, is not effective in this respect, nor is this behavior common to all olefin oxides. Ethylene oxide gives rise to dioxane and resinous polymer.[5] 2,3-Butylene oxide proves re-

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(1) (a) A. M. Eastham, *Fortschr. Hochpolym. Forsch.*, **2**, 18 (1960); (b) A. E. Gurgiolo, *Rev. Macromol. Chem.*, **1**, 123 (1966).

(2) A "cyclic tetramer of propylene oxide" is reported[3] without characterization or structure proof in a study on the solubility of alkali metals in ethers.

(3) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

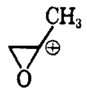
(4) R. J. Katnick and J. Schaefer, *J. Org. Chem.*, **33**, 384 (1968).

(5) See also D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 900 (1957).

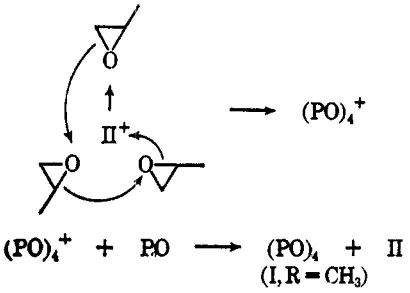
luctant to react at all. The tetraoxacyclododecanes derived from epichlorohydrin (I, R = $-CH_2Cl$) and 1,2-butylene oxide (I, R = C_2H_5-) are described in the Experimental Section.

The reactions of $(C_2H_5)_3OBF_4$ have been interpretable in terms of carbonium ion mechanisms.[6] A cationic propagation coupled with the formation of 7–8 moles of cyclic tetramer per mole of boron suggest a chain transfer of hydride ion from monomer (species II). Hydride ion transfer has been shown in the cationic polymerization of tetrahydrofuran[7] and suggested for the dimerization of styrene oxide.[8] The dominance of cyclic tetramer over other ring sizes suggests that ring-forming propagation involves a preferred number of monomer units in a coordination or solvation shell.

Speculation along this line leads to an interesting suggestion. There is no apparent difference in products or product distributions whether BF_3 or $(C_2H_5)_3OBF_4$ is used. Thus, coordination centers operative in the two routes are similar if not identical. Possibly II is solvated by (predominantly) three epoxide units. The entire cluster then collapses to a 12-membered ring.



II



Experimental Section

Triethyloxonium Tetrafluoroborate.—An adaptation of Meerwein's method[9] was employed. BF_3 gas (40 g, 0.59 mole) was dissolved in 100 ml of anhydrous diethyl ether. To this solution under nitrogen in a stirred 500-ml flask fitted with reflux condenser was added a solution of 56 g (0.60 mole) of epichlorohydrin in 50 ml ether at a rapid drop-by-drop rate. Ether refluxed continually. Stirring was continued 2 hr during which time the oxonium salt crystallized. Liquors were decanted under nitrogen and replaced with fresh ether and stirred. Such decantation, washing to remove the organic borate also formed, was repeated three times. Solids, very hygroscopic, were stored under ether in the dark. Solids were removed by spatula and used ether-wet as needed.

Dark-colored decomposition products develop in time. Product may be purified by dissolving the contaminated material in about 5–10 vol. of CH_2Cl_2. A two-phase liquid-liquid system develops. The clear oxonium-rich phase can be easily separated by syringe and needle. When injected into dry ether or CCl_4, white $(C_2H_5)_3OBF_4$ crystallizes out rapidly.

Proton nmr spectra were run on oxonium-saturated phases (above) from $CHCl_3$, CH_2Cl_2, and $ClCH_2CH_2Cl$ solutions (*ca.* 1 *M*). All revealed the same chemical shifts. The 1.0 to 10.0 τ spectra consisted of a methyl triplet centered at 8.44 and a CH_2 quartet centered at 5.42 (J = 7.0 cps).

Reaction of Propylene Oxide.—To a nitrogen-purged stirred 1-l. flask fitted with a Dry Ice reflux condenser was added 200 ml (166 g) of propylene oxide. Solid $(C_2H_5)_3OBF_4$ (30–40 mmoles), wet with diethyl ether, was added in pea-sized portions. The resulting exothermic reaction can become vigorous and may require external cooling initially. The mixture remains fluid without pronounced viscosity increase. One hour after this addition was completed sodium carbonate (5 g) and 4 drops of water were added and stirred for 2 hr. The filtered reaction solution was then fractionally distilled. Besides unreacted propylene oxide and small amounts of unidentified low-boiling, carbonyl-containing materials, the fractions given in Table I were obtained.

TABLE I

Fraction	Boiling range, °C	Amount, g	n^{23}D, deg	d^{23}	Mol wt[a]	Principal species
1	117–130 (1 atm)	7	1.4142		116,118	$(PO)_2$
2	61–65 (0.07 mm)	67	1.4453	0.996	232,237	$(PO)_4$
3	77–83 (0.07 mm)	15	1.4455	1.001	306,308	$(PO)_5$
4	90–150 (0.07 mm)	6	1.4427		369,371	
5	Residue	36	1.4430	1.009	609,611	Resin

[a] Molecular weight by vapor phase osmometer.

Anal. of fraction 2, $(PO)_4$. Calcd for $C_{12}H_{24}O_4$: C, 62.1; H, 10.3. Found: C, 62.4; H, 10.5.

Infrared spectra (IR-4) of fraction 2 reveal no carbonyl or hydroxyl groups. The spectrum is that of poly(propylene oxide) except for absence of OH and the resolution of the broad C–O stretching band of the polymer into four strong overlapping bands at 8.73, 9.00, 9.20, and 9.37 μ. The nmr spectrum is discussed elsewhere.[4]

Boron trifluoride may be employed as the catalyst instead of the oxonium salt mentioned above. Short bursts of the gas were introduced into the reaction solution taking care not to overstimulate the reaction. Occasionally induction periods before reaction occur before heat is evolved. When additional BF_3 (after an initial reaction has occurred) failed to cause heat evolution, the reaction mixture was allowed to stand overnight under nitrogen, then worked up as above. No difference was observed between products resulting from BF_3 or from $(C_2H_5)_3OBF_4$ catalysts. $SnCl_4$ failed to produce a cyclic tetramer.

Crystalline Isomer of Cyclic Propylene Oxide Tetramer.—Fraction 2 above was stored at 0° for 3 weeks. About 3 wt % crystallized. Two recrystallizations from cyclohexane and two from acetone gave natural-white crystals, mp 92–93°. Its molecular weight by mass spectrometry was 232.

Reaction of Epichlorohydrin.—Epichlorohydrin (30 ml) and carbon tetrachloride (30 ml) were placed in a mechanically stirred 200-ml flask under nitrogen. $(C_2H_5)_3OBF_4$ (about 2 mmoles) was introduced. After a few minutes vigorous heat evolution occurred requiring external cooling. Similar $C_2H_5OBF_4$ addition was carried out three more times. The solution was gently refluxed 1 hr, cooled under N_2, and then stirred with 1 g of anhydrous Na_2CO_3 for 1 hr. This mixture was centrifuged, and the liquors were fractionally distilled. A fraction (7 g), bp 195–205 (1 mm), was diluted with 4 vol. of toluene and cooled to about 0° overnight. Well-shaped, needle-like crystals of fraction 6 formed with mp 133–136°. Liquors were stripped of solvent and redistilled while collecting the 195–205° (1 mm) cut 7.

Anal. Calcd for $C_{12}H_{20}O_4Cl_4$: C, 38.9; H, 5.4; Cl, 38.4; mol wt, 370. Found for fraction 6 (crystals): C, 38.8; H, 5.1; Cl, 38.0; mol wt (differential vapor pressure thermistor), 372, 377. Found for fraction 7 (liquid): C, 38.8; H, 4.9; Cl, 38.0; mol wt (differential vapor pressure thermistor), 354, 362.

Infrared and proton nmr spectra revealed no hydroxyl, carbonyl, or ethyl groups in either fraction 6 or 7.

Reaction of 1,2-Butylene Oxide.—A mixture of 200 ml (2.3 moles) of 1,2-butylene oxide (Union Carbide Chemicals Co.), bp 61–62° (740 mm), in 100 ml of CH_2Cl_2 was placed in a stirred nitrogen-purged, 1-l. flask. Crystallized $(C_2H_5)_3OBF_4$, which had been stored under diethyl ether, was added as ether-wet lumps about 1 cm in diameter. When about 30 mmoles had been added over a 5-hr period, noticeable heat evolution ceased. After standing overnight under nitrogen 4 g of powdered $NaHCO_3$ was added to the reaction mixture and stirred 2 hr. The filtered reaction mixture was then distilled under reduced pressure in stages until 150° (0.1 mm) was obtained in the

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[6] H. Meerwein, *Angew. Chem.*, **67**, 374 (1955).

[7] I. Kuntz, *J. Polymer Sci.*, **B4**, 427 (1966).

[8] W. M. Paskia, *ibid.*, **A3**, 4287 (1965).

[9] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfiel, *J. Prakt. Chem.*, **147**, 257 (1937).

head. Distillates were fractionated again using an 8-in. Vigreaux column to obtain the fractions given in Table II.

Table II

Fraction	Boiling range, °C	Amount, g	n^{25}D, deg
8	69-70 (27-28 mm)	7	1.4248
9	99-101 (0.1 mm)	73	1.4503
10	115-130 (0.07 mm)	16	
11	Residue	45	1.4470

Fraction 9, d^{23} 0.968, revealed no hydroxyl or carbonyl group in its infrared spectrum. Its nmr was consistent with a cyclic structure, and its molecular weight by differential vapor phase thermistor was 271. A mass spectrum revealed an intense *m/e* peak at 288 (4 × 72, the molecular weight of butylene oxide).

Ethylene Oxide.—Ethylene oxide was treated in a manner similar to that described for propylene oxide above. Both $(C_2H_5)_3OBF_4$ and BF_3 were tested. Only dioxane and nondistillable semicrystalline poly(ethylene oxide) were obtained.[5]

Registry No.—*cis*-2-Ethyl-4-methyl-1,3-dioxolane, 1568-99-6; *trans*-2-ethyl-4-methyl-1,3-dioxolane, 1860-13-5; 2,5,8,11-tetramethyl-1,4,7,10-tetraoxacyclododecane, 15129-24-5; triethyloxonium tetrafluoroborate, 14323-65-0; dioxane, 123-91-1.

Diels-Alder Reactions Involving Azonia Polycyclic Aromatic Compounds and Nucleophilic Dienophiles

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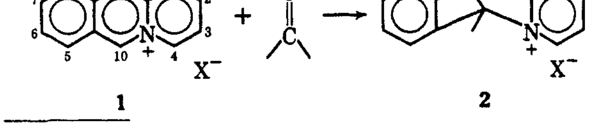
Received July 11, 1967

A study of Diels-Alder additions involving the 4a-azoniaanthracene ion, **1**, and a series of dienophiles shows that **1** is more reactive toward nucleophilic than toward electrophilic dienophiles. Furthermore, nmr analyses of adducts derived from **1** and unsymmetrical dienophiles indicate that the cycloadditions occur stereoselectively, giving one of the two possible positional isomers as a mixture, where possible, of two geometrically isomeric forms. Other azonia polycyclic aromatic compounds obeying the principle of "inverse" electron demand in Diels-Alder additions are shown to include azonianaphthacene, -benz[*a*]anthracene, and -dibenz[*a*,*c*]anthracene salts, a diazoniapentaphene salt, and an azonianaphthalene salt bearing electron-withdrawing substituents.

The concept of an "inverse" electron demand in Diels-Alder reactions was first proposed by Bachmann and Deno,[1a] and an experimental example of such a system involving 1,2,4,5-tetrazines was studied qualitatively by Carboni and Lindsey.[1b] The first kinetic study related to this phenomenon was recently provided by Sauer and Wiest[1c] through an investigation of the reaction of hexachlorocyclopentadiene with a series of dienophiles. Acting contrary to the "Alder rule,"[2] the electron-deficient hexachlorocyclopentadiene was shown to be much more reactive with electron-rich dienophiles, such as cyclopentadiene, styrene, and 2,3-dihydrofuran, than with typical electrophilic dienophiles, such as maleic anhydride and tetracyanoethylene. The 4a-azoniaanthracene ion, **1**,[3] is known to add maleic anhydride, esters of fumaric and maleic acids, and acrylonitrile across its 9,10 positions.[4] We report here a part of our study of the Diels-Alder reactions involving azonia polycyclic aromatic compounds, and **1** (eq 1) in particular, in which these compounds represent another general class of reactant which obeys the principle of Diels-Alder reaction with "inverse" electron demand.



(1)

1 **2**

Results and Discussion

Adduct Synthesis.—The dienophiles employed in condensations with **1** ($X^- = Br^-$), the reaction conditions, and the physical characterization of the products are tabulated in Table I. Adducts **2a**, **2b**, and **2c** were prepared by allowing a mixture of **1** and excess olefin in methanol to react in an autoclave at 70° for the periods indicated. The remaining adducts, which were derived from higher boiling dienophiles, were produced by allowing a mixture of **1** and a 5 *M* excess of dienophile in a suitable solvent to react either at room temperature or at reflux temperature until **1** was completely consumed as shown by the absence of 399-mμ absorbance in the ultraviolet region.

The resulting products were isolated by precipitation with ether and petroleum ether (bp 35-60°) and then recrystallized either directly or after being converted into perchlorate salts for improved solubility. No attempt was made to fractionate the mixture of isomers obtained in the majority of these reactions.

Adduct Structural Considerations.—The longer wavelength ultraviolet absorptions of the adducts of Table I are confined to the 260-275-mμ region indicative of the expected cycloaddition of the dienophile across the 9,10 positions of **1**. The possibility that the 1,3-diene adducts, **2c**, **2h**, and **2n**, were formed from 4 + 4 rather than 4 + 2 cycloadditions was excluded by relating **2c** to **2b** (eq 2) and **2n** to **2o** through

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[1] (a) W. E. Bachmann and N. C. Deno, *J. Am. Chem. Soc.*, **71**, 3062 (1949). (b) R. A. Carboni and R. V. Lindsey, *ibid.*, **81**, 4342 (1959). (c) J. Sauer and H. Wiest, *Angew. Chem. Intern. Ed. Engl.*, **1**, 269 (1962). This topic has recently been included in a review, J. Sauer, *Angew. Chem. Intern. Ed.*, **6**, 16 (1967), and in a chapter by R. Huisgen, R. Grashey, and J. Sauer in S. Patai, "The Chemistry of Alkenes," Interscience Publishers Ltd., London, 1964, p. 739.

[2] K. Alder, *Experientia*, *Suppl.* 2, 86 (1955).

[3] C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **77**, 4812 (1955).

[4] C. K. Bradsher and T. W. G. Solomons, *ibid.*, **80**, 933 (1958).