to the oxazolidone in 8.5% yield based on amino alcohol; the over-all yield was 2%. The oxazolidone was recrystallized from carbon tetrachloride. This product was identical with the corresponding product obtained from the reaction between potassium cyanate and the epoxide in the absence of water.

Registry No.—Potassium cyanate, 590-28-3.

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Structural Isomer Distribution in Ring Polymers of Propylene Oxide

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The structural isomer distributions in the cyclic dimer and tetramer of propylene oxide formed by the homogeneous catalyst BF_3 have been determined and found to be random. By a combination of gas chromatography, nuclear magnetic resonance, and mass spectroscopy, four out of four of the geometrical isomers of the dimer and 22 out of 23 of the geometrical isomers of the tetramer have been observed, the majority isolated, characterized, and assigned to a structural configuration.

In addition to a high molecular weight residue, a distillable liquid (in yields up to 60%) is obtained from the reaction of propylene oxide with triethyloxonium tetrafluoroborate or boron trifluoride. Analysis by gas chromatography, nuclear magnetic resonance, and mass spectroscopy has shown this liquid to be ring polymers of propylene oxide (designated as $(PO)_n$ where n, the number of PO units in the ring, is 2, 4, 5, and higher). This paper establishes the ring nature and structural isomer distributions (head to tail, head to head, and tail to tail) of $(PO)_2$ and $(PO)_4$.

Experimental Section

The details of the synthesis of the ring polymers of propylene oxide are given elsewhere.[1]

Separation of isomers of $(PO)_n$ by gas chromatography was possible by the use of glpc columns containing Carbowax 20M plus various metal salts, prepared in the following way. Anhydrous $AgNO_3$, $CuCl_2$, $CdCl_2$, or $NiCl_2$ was dissolved in methanol followed by addition of Carbowax 20M in dichloromethane. The mixture was stirred until homogeneous. Chromosorb CL (60–80 mesh) was added and the solvent removed by evaporation. The resulting columns had a composition of 1.0% (w/w) metal salt, 20% (w/w) Carbowax 20M. The packing was poured into copper tubing having dimensions of 0.25 in. × 10 ft. The $AgNO_3$ packing was used for preparative purposes and a $^{3}/_{8}$ in. × 10 ft. column was made to accommodate a larger sample size. All columns were conditioned overnight at 200° prior to use.

$(PO)_n$ fractions were collected at the exit of an F & M Model No. 720 gas chromatograph in 2, mm (o.d.) glass capillary tubing, coiled to increase trapping efficiency. A separation of the $(PO)_4$ mixture into four preliminary fractions was made on the $AgNO_3$–Carbowax 20M preparative column. Each fraction was then further separated by use of one or more of the other metal salt columns. The separated materials were examined by nmr and mass spectroscopy.

The majority of the proton nmr spectra of the isomers of $(PO)_n$ were obtained at 100 MHz using a Varian HA-100 spectrometer in conjunction with a time averaging computer. Spectra of the separated isomers (in $CDCl_3$) were obtained at room temperature. For purposes of interpretation, the spectra of a few isomers were obtained at 60 MHz using a Varian A-60 spectrometer. Mass spectra of glpc fractions were obtained using a Consolidated Electrodynamics Corporation mass spectrometer (Model no. 21-103C) using a source temperature of 300°, an ionizing potential of 70 ev, and an ionizing current of 20 μa.

Results

1. $(PO)_2$, 2,5- and 2,6-Dimethyldioxanes.—The lowest boiling fraction of the BF_3-catalyzed reaction of propylene oxide was determined by vapor phase osmometry to have a molecular weight in the range of 112 to 118. Infrared spectra showed the presence of C–O stretching vibrations and the absence of a characteristic hydroxyl frequency. Using the glpc column $NiCl_2$–Carbowax, this distillate separated into six peaks. Nmr analysis showed the first two of these peaks (in order of elution and constituting about 5% of the fraction) to be the *cis* and *trans* isomers of 2-ethyl-4-methyl-1,3-dioxolane easily identifiable by the characteristic resonance patterns of the $O_2\mathit{CH}CH_2CH_3$ and $O_2CHCH_2\mathit{CH}_3$ protons. The last four glpc peaks all had nmr spectra consisting of a single methyl region doublet (due to spin–spin coupling) and similar methine and methylene regions and so correspond to the *cis* and *trans* isomers of 2,5- and 2,6-dimethyldioxane.

These assignments are confirmed by the mass spectra presented in Table I. The spectra of all four isomers displayed identical cracking patterns differing only in relative intensities. A high-intensity parent ion peak was observed at m/e 116 (2 × 58) and a low-intensity, pressure-dependent, parent ion plus one peak at m/e 117. Nothing was observed at higher values of m/e and a significant M − 15 peak was observed. The relative intensities of some other mass peaks are given in Table I. For the 2,5- and 2,6-dimethyldioxanes, structural configuration is expected to be more important than geometrical configuration

Table I

Some Major Mass Peaks of Isomers of 2,5- and 2,6-Dimethyldioxane[a,b]

Glpc fraction[c]	m/e							Mole % of total
	44	57	58	59	72	101	116	
A	0.988	2.04	0.200	0.440	2.67	1.88	5.19	33
B	0.575	1.36	0.682	1.74	2.77	2.85	5.57	18
C	0.932	1.98	0.197	0.450	2.76	2.15	4.82	22
D	0.625	1.32	0.676	1.78	3.17	3.27	5.25	27

[a] Expressed as % Σ 28. [b] BF_3 was the catalyst. [c] In order of elution from a $NiCl_2$–Carbowax 20M column.

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[1] J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959); R. J. Kern, *J. Org. Chem.*, **33**, 388 (1968).

in determining the relative intensities of the mass fragments.[2] Thus (by inspection of Table I) glpc fractions A and C can be assigned to one structural configuration and B and D to the other. The relative concentrations of the geometrical isomers of 2,5- and 2,6-dimethyldioxane based on peak area measurements of a glpc chromatogram are given in Table I. The observed distribution of structural configurations in $(PO)_2$ is 55/45, close to random.

2. **$(PO)_4$, Tetramethyl-1,4,7,10-tetraoxacyclododecane.**—The largest part of the BF_3–catalyst reaction mixture was distilled at 61–65° (0.07 mm). Vapor phase osmometry placed the molecular weight of this fraction in the range 231–237. Infrared spectra revealed C–O stretching vibrations at 8.73, 9.00, 9.30, and 9.73 μ and the absence of any characteristic carbonyl or hydroxyl group frequencies. The nmr spectrum of this fraction was similar to that of the composite dimethyldioxane spectrum with the methyl region appearing as a collection of many doublets. Resonances analogous to those displayed by the dioxolanes were absent. The mass spectrum showed a parent ion peak at m/e 232 (4 times 58) and a very low-intensity, pressure-dependent, parent ion plus one peak at m/e 233 with nothing observable at higher m/e values. These results suggest that the material is the cyclic tetramer of propylene oxide $(PO)_4$, a conclusion consistent with the elemental analysis.

Anal. Calcd for $C_{12}H_{24}O_4$: C, 62.1; H, 10.3. Found: C, 62.4; H, 10.5.

The four structural (head to head, head to tail, etc.) isomers of $(PO)_4$ are

AAAA	AA*AA*	AAA*A*	AAAA*
I	II	III	IV

A = -CH(CH$_3$)CH$_2$O-   A* = -CH$_2$CH(CH$_3$)O-

While a 12-membered ring containing four ether-like oxygens will be flexible enough at room temperature to remove the stereochemical distinctions of axial and equitorial,[3] geometrical *cis* and *trans* isomers are still possible. The 23 geometrical isomers of $(PO)_4$ are listed in Table II. Because of the symmetry properties of the structural configurations, the only possible number of nmr unique methyl groups of any isomer is 1, 2, or 4.

Separation of the geometrical isomers of $(PO)_4$ was possible by use of metal salt–Carbowax 20M glpc columns.[4] Sufficient amounts of a fraction were collected from one column to allow successive passes through different columns so that separation of $(PO)_4$ into 19 distinct glpc fractions was achieved. An example of a typical chromatogram is given in Figure 1. The glpc fractions, their relative concentrations, the column sequence used in their separation and a summary of their nmr spectra are given in Table III. Nmr spectra of the methyl regions of the glpc fractions are presented in Figures 2–7. Inspection of these spectra immediately allows the assignment of some of the geometrical isomers to the appropriate structural configurations. Thus, the two-line (one methyl group gives rise to two lines due to spin–spin coupling) methyl region spectra of glpc fractions B, C, and G place them in either structural configurations I or II.

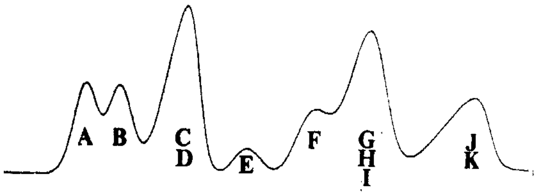

Figure 1.—Chromatogram obtained from $(PO)_4$ fractions 1 and 2 collected from an $AgNO_3$–Carbowax 20M glpc column as they appear on a $CdCl_2$–Carbowax 20M glpc column. Time axis goes from left to right. The letters correspond to the glpc fraction designations given in Table III. Fractions C and D were subsequently separated using a $CuCl_2$–Carbowax 20M glpc column. Other separations are given in Table III.

TABLE II
GEOMETRICAL ISOMERS OF THE FOUR STRUCTURAL CONFIGURATIONS OF $(PO)_4$

Structural confign[a]	Isomer no.	Number of nmr unique methyl groups	Geometry
I	1	1	*cis–cis–cis–cis*
	2	1	*trans–trans–trans–trans*
	3	2	*cis–trans–cis–trans*
	4	4	*cis–cis–trans–trans*
II	5	1	*cis–cis–cis–cis*
	6	1	*cis–trans–cis–trans*
	7	1	*trans–cis–trans–cis*
	8	1	*trans–trans–trans–trans*
	9	4	*cis–trans–trans–cis*
III	10	2	*cis–cis–cis–cis*
	11	2	*cis–trans–cis–trans*
	12	2	*trans–trans–trans–trans*
	13	2	*trans–cis–trans–cis*
	14	4	*cis–cis–trans–trans*
	15	4	*trans–trans–cis–cis*
IV	16	4	*cis–cis–cis–cis*
	17	4	*cis–cis–trans–trans*
	18	4	*cis–trans–trans–cis*
	19	4	*cis–trans–cis–trans*
	20	4	*trans–trans–cis–cis*
	21	4	*trans–trans–trans–trans*
	22	4	*trans–cis–cis–trans*
	23	4	*trans–cis–trans–cis*

[a] Structural configurations identified in the text.

The four-line spectra of glpc fractions A, E, I, P, and S place four of these isomers in configuration III and the remaining isomer in configuration I. Glpc fraction E was actually crystalline with a melting point of 93°. Large single crystals were grown and X-ray analysis established that these crystals were monoclinic with space group $P2_1/C$ (cell dimensions: $a = 4.82$, $b = 16.49$, $c = 8.58$ A, $\beta = 99.6°$). From the measured density of 1.13 and molecular weight of 232, n must be 2 ($M = \rho v/n$). The crystal is therefore centrosymmetric and (considering its nmr spectrum) can only belong to configuration I. The fractions A, I, P, and S therefore belong to configuration

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[2] See, for example, K. Bieman, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] Even eight-membered rings will probably be this flexible: F. A. L. Anet and M. St. Jacques, *J. Am. Chem. Soc.*, **88**, 2585 (1966).

[4] For a statement on the ability of cyclic ethers to form metal complexes and hence a clue as to the possible nature of mechanism of separation, see C. J. Pedersen, *ibid.*, **89**, 2495 (1967).

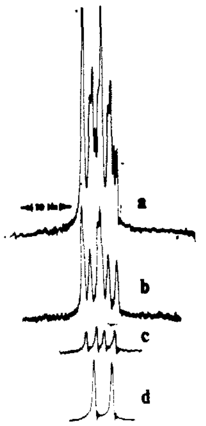

Figure 2.—100-MHz spectra of methyl regions of (PO)$_4$ glpc fractions. (a) Fraction 1 from AgNO$_3$–Carbowax 20M glpc column. This fraction was subsequently separated using a CdCl$_2$–Carbowax 20M column into glpc fractions (b) C and D, (c) A, and (d) B. The sum of the spectra b, c, and d equals the spectrum a illustrating the absence of isomer rearrangements by the glpc columns.

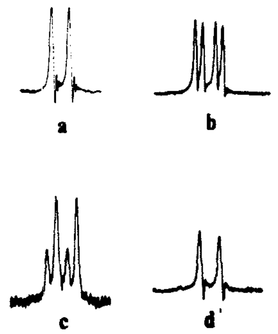

Figure 3.—100-MHz spectra of methyl regions of (PO)$_4$ glpc fractions (a) C, (b) E, (c) F, and (d) G. All sweep scales are equal.

TABLE III

CHROMATOGRAPHIC FRACTIONS OF (PO)$_4$[a]

Glpc fraction	Glpc columns used in separation[b]	No. of observable nmr methyl lines	No. of isomers in fraction	Mole % of total
A	a(1)b(1)	4	1	10
B[c]	a(1)b(2)	2	1	11
C	a(1)b(3)c(2)	2	1	5
D	a(1)b(3)c(1)	8	1	16
E[d]	a(2)b(4)	4	1	3
F	a(2)b(5)	4	2	8
G	a(2)d(4)	2	1	3
H	a(2)b(6)	>12	≥2	13
I[e]	a(2)b(6)	4	1	5
J	a(2)b(7)	8	1	8
K	a(2)b(7)[f]	8	1	6
L	a(3)d(9)	8	1	3
M	a(3)d(10)	8	1	2
N	a(3)d(11)	8	1	4
O	a(3)d(12)	8	1	0.5
P	a(4)c(7)	4	1	0.5
Q	a(4)c(8)	10	2	1
R	a(4)c(9)	8	1	1
S	a(4)c(10)	4	1	0.5

[a] BF$_3$ was the catalyst. Almost identical results are obtained if triethyloxonium tetrafluoroborate was used as the catalyst. [b] Columns are designated by letter: a is AgNO$_3$–Carbowax 20M; b is CdCl$_2$–Carbowax 20M; c is CuCl$_2$–Carbowax 20M; d is NiCl$_2$–Carbowax 20M. Numbers in parentheses indicate order of elution from a given column. [c] Melting point 44°. [d] Melting point 93°. [e] Melting point 85°. [f] K separated from J by use of plain Carbowax 20M column.

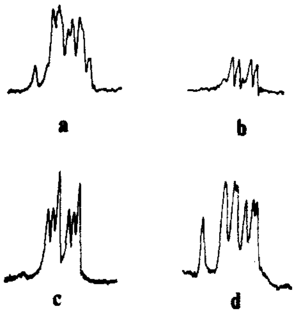

Figure 4.—100-MHz spectra of methyl regions of (PO)$_4$ glpc fractions (a) H, (b) I, (c) J, and (d) K. All sweep scales are equal.

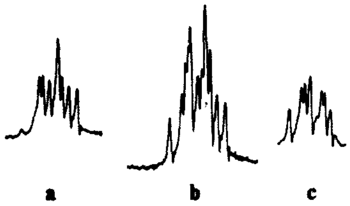

Figure 5.—100-MHz spectra of methyl regions of (PO)$_4$ glpc fractions (a) L, (b) M, and (c) N. All sweep scales are equal.

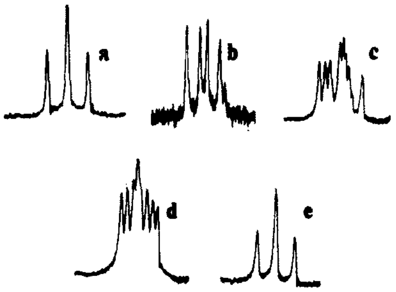

Figure 6.—100-MHz spectra of methyl regions of (PO)$_4$ glpc fractions (a), P, (c) Q, (d) R, and (e) S; b is a 60-MHz spectrum of glpc fraction P. All sweep scales are equal.

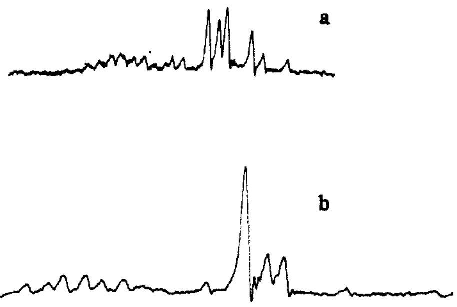

Figure 7.—100-MHz spectra of the nonmethyl region of (PO)$_4$ glpc fractions (a) B and (b) C. Even though the methyl region spectra of the two isomers are both single methyl doublets, the nonmethyl regions are distinct. The sweep scales are not equal.

III. Having accounted for all possible four-line methyl region spectra, the four lines of the spectrum of glpc fraction F (in approximately 1:2:1:2 intensity ratios) are only consistent with a 2:1 mixture of two isomers each having a single nmr unique methyl group. Both of these isomers are in either configuration I or II. The spectra of all other glpc fractions have eight or more lines.

In using the nmr data to assign geometrical isomers to a structural configuration, it is assumed that each isomer which has four different methyl groups will have an eight-line methyl region spectrum. The possibility of an eight-line methyl region spectrum appearing as a four-line spectrum, or a four as a two, can be neglected since inspection of Table III and Figures 2–6 shows that virtually all of the expected isomers of $(PO)_4$ are observed and that these isomers display the expected number of nmr unique methyls.[5] The ability to distinguish the subtle differences between isomers of $(PO)_4$ by nmr can be attributed directly to the cyclic nature of the tetramer system in which each methyl group is aware of the other three methyl groups, a situation which does not exist in linear tetramers of propylene oxide.

Some major mass spectrometric peaks of the glpc fractions of $(PO)_4$ are presented in Table IV. The cracking patterns of all fractions were identical, differing only in relative intensities thereby giving further confirmation that all of these fractions are isomeric. In addition to the peaks given in Table IV, lower intensity but still significant peaks were observed for all fractions for values of *m/e* of 103, 115, 116, 129, 130, 131, 143, 145, 159, and 161. All fractions displayed parent ion peaks at *m/e* 232. There were some significant differences from the dimethyldioxane cracking patterns apparent, *e.g.*, in the absence of a significant M − 15 peak and in the relative intensities at M − 57, M − 58, and M − 59.

TABLE IV

MAJOR HIGH MASS PEAKS OF ISOMERS OF $(PO)_4$

Glpc fraction[a]			*m/e*		
	59	73	87	117	175[e]
A	1.000	0.245	0.162	0.089	0.0125
B	1.000	0.107	0.132	0.108	0.0180
C	1.000	0.267	0.226	0.156	0.0362
D	1.000	0.238	0.185	0.116	0.0221
E	1.000	0.119	0.139	0.111	0.0172
F	1.000	0.237	0.252	0.158	0.0216
G	1.000	0.282	0.287	0.171	0.0402
H[b]	1.000	0.228	0.188	0.109	0.0149
I[c]	1.000	0.201	0.177	0.113	0.0162
J	1.000	0.259	0.177	0.092	0.0109
L	1.000	0.126	0.147	0.112	0.0165
M[d]	1.000	0.229	0.281	0.140	0.0192
N	1.000	0.252	0.241	0.143	0.0182
O	1.000	0.243	0.249	0.111	0.0130
P	1.000	0.236	0.166	0.081	0.0093
Q	1.000	0.201	0.266	0.094	0.0100
R	1.000	0.175	0.375	0.083	0.0121
S	1.000	0.244	0.168	0.086	0.0096

[a] Purity of fractions is 95% or better unless otherwise noted. [b] Contaminated with about 15% I. [c] Contaminated with about 20% H. [d] Contaminated with 50% L and N. [e] Reproducibility of ratios ±5%.

As might be expected, the classification of the fragmentation patterns of the isomers of $(PO)_4$ into four distinct patterns corresponding to the four structural configurations is somewhat unsatisfactory, owing in part to the great similarity between structures and to effects attributable apparently to the geometries of the isomers. However, classifications can be made on a strictly empirical basis. Configuration I contains isomers which have the lowest (by about a factor of 2) 73/59 and 87/59 ratios and intermediate 117/59 and 175/59 ratios. Configuration II contains isomers which have high 73/59 and 87/59 ratios and the highest 117/59 and 175/59 ratios. Configuration III contains isomers which have intermediate 73/59 and 87/59 ratios and the lowest 117/59 and 175/59 ratios.[6] Configuration IV contains isomers which have intermediate values for all ratios.

Using the above classifications and the nmr data, the assignments of geometrical isomers to structural configuration made with some degree of certainty are given in Table V. There are no obvious inconsistencies in using the mass data in this manner or in the resulting assignments (as, for example, the necessity of assigning two isomers having eight-line methyl region spectra to configuration I). In a few instances, the assignments are not unique. Thus, glpc fraction F could be composed of two parts of an isomer belonging to configuration II and one part of an isomer belonging to configuration I, rather than the indicated assignment of both isomers of F to configuration II.

TABLE V

PROBABLE $(PO)_4$ ISOMER ASSIGNMENTS[a]

Structural config	Glpc fractions within structural configuration
I	B
	E
	L
II	C
	F
	G
III	A
	I
	J
	P
	S
IV	D

[a] Several definite $(PO)_4$ isomer assignments can be made using nmr analysis alone. These place glpc fractions B, C, E, F, and G in structural configurations I and II and glpc fractions A, I, P, and S in III (see text).

Using only the nmr analysis (summarized in the footnote to Table V) the lower and upper limits[7] for the total relative normalized concentration of any of the four structural configurations are ≈0.15 and 0.40, respectively, compared to the random 0.25 concentration. Thus, although the distribution of geometrical isomers is far from random, the structural isomer distribution in $(PO)_4$ is random with any possible deviation from this randomness small.

Registry No.—I (*cis–cis–cis–cis*), 15038-19-4; I (*trans–trans–trans–trans*), 15038-20-7; I (*cis–trans–cis–trans*), 15038-21-8; I (*cis–cis–trans–trans*), 15042-35-0; II (*cis–cis–cis–cis*), 15042-36-1; II (*cis–trans–cis–trans*), 15042-37-2; II (*trans–cis–trans–cis*), 15042-

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[5] Ten of the expected twelve isomers which have eight-line spectra are definitely observed and of these only a few have even two exactly overlapping lines. Five out of the six expected two-line spectra and five out of the five expected four-line spectra are observed. The spectra of many isomers in solution in solvents other than $CDCl_3$ were obtained. Thus, the six-line spectrum (in $CDCl_3$) of glpc fraction D becomes eight well-resolved lines when *o*-dichlorobenzene is the solvent. The experimental ratio of one of these lines to the rest of the lines is 7.04 (calculated for a single pure isomer, 7.00).

[6] Of the five observed four-line methyl nmr spectra (four lines of equal intensity), two arise from crystalline fractions and the remaining three have almost identical mass spectra showing the lowest 117/59 and 173/59 ratios. Thus the unlikely possibility of a four-line spectrum arising from an equimolar mixture of two two-line spectra is justifiably neglected.

[7] Of those listed in Table V, glpc fractions D, J, and L are considered unassigned. The lower and upper limits are obtained by assigning to a structural configuration these and all other unassigned isomers in all ways consistent with their nmr spectra. The assigned isomers are listed in the footnote to Table V.

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.

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

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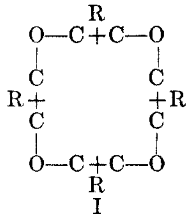
Twelve-membered ring polyethers have been obtained from propylene oxide, epichlorohydrin, and 1,2-butylene oxide in 30–40% conversions by treating the epoxide with $(C_2H_5)_3OBF_4$ or BF_3. Larger rings and a cyclic dimer are present in smaller amounts but no cyclic trimer forms.

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).