broad), 9.08 (s), 9.92 (s), 9.49 (m), 9.82 (m), 10.53 (s), 10.84 (s), 11.13 (m), 11.27 (m), 12.0 (s), 12.7 (m), 13.8 (m), 14.7 (m) μ; nmr ($CDCl_3$) δ 5.66 (broad m, 1), 3.1–3.5 (m, 5), 1.78 (d, 3, J = 2 Hz), 1.51 ppm (s, 3).

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.65; H, 5.39.

Aromatization of 4 in Aqueous Solution. In a typical experiment, 0.1–0.2 g of freshly prepared **4** was added to 10 ml of 0.1 *M* aqueous buffer solution having the desired pH value, and the mixture was shaken vigorously for 10 min. The resultant solution was extracted with three 10-ml portions of ether, the combined extracts were dried (Na_2SO_4), and the solvent was removed by evaporation under reduced pressure at room temperature. A few milliliters of CCl_4 was added to the residue and the solution was again evaporated under reduced pressure. The addition and removal of CCl_4 was repeated several times, and the residue was then utilized for ir, nmr, and gc analysis.

The ir and nmr spectra of these products were composites of the spectra of 2,4- and 2,5-xylenol. No attempt was made to estimate quantitatively the relative amounts of the two phenols in these mixtures on the basis of the spectroscopic absorption data, but variations in the relative intensities of characteristic absorption bands were consistent with the compositions determined by gc analysis.

For gc analysis, 50 mg of the product mixture to be examined was treated with 0.5 ml of Tri-Sil[6] to convert the phenols to their more volatile trimethylsilyl ethers, and the resultant mixture was analyzed on a Carle Basic Gas Chromatograph, Model 6500, at 150°, using a column packed with 8% di-*n*-nonyl phthalate on 60–80 mesh diatomite. The peaks corresponding to the TMS derivatives of 2,4- and 2,5-xylenol were identified by calibrating the instrument with the silylation products prepared from authentic samples of the xylenols; the retention time for the 2,4-xylenol TMS derivative was 15–20% longer than that for the 2,5-xylenol TMS derivative. Relative peak areas (Table I) were determined by cutting out and weighing the paper enclosed by the peaks. Calibration of this procedure with xylenol mixtures of known composition indicated that the results were accurate to within approximately ±2%.

Isolation and Identification of Aromatization Products. A solution of 0.50 g of the oxide–oxepin mixture **4** in 10 ml of ether was shaken with 20 ml of 0.1 *N* HCl until the yellow color disappeared. The aqueous layer was washed with several small portions of ether, and the combined ether layers were dried ($MgSO_4$) and evaporated under vacuum at room temperature to give 0.42 g (84% recovery) of a pale yellow oil. This was dissolved in benzene and chromatographed on a 2 × 50 cm column of silica gel (SilicAR CC-7), using benzene–petroleum ether (1:1, gradually increasing to 3:1) as the eluting solvent. Removal of the solvent from appropriate fractions of the eluate in a rotary evaporator at room temperature provided 274 mg of a faster moving product as a crystalline solid (fraction I) and 73 mg of a slower moving product as a colorless oil (fraction II).

Fraction I was recrystallized from cyclohexane to provide colorless crystals, mp 74–75°, which showed no depression when mixed with authentic 2,5-xylenol and which gave an ir spectrum identical with that of the latter compound.

Fraction II gave an ir spectrum identical with that of 2,4-xylenol and, on treatment with 3,5-dinitrobenzoyl chloride in pyridine, it was converted into a crystalline 3,5-dinitrobenzoate which melted at 162.5–163.0° after recrystallization from ethanol; lit. mp of 2,4-dimethylphenyl 3,5-dinitrobenzoate, 164.6°.[15]

Acknowledgment. The author is indebted to Karin M. Rauch and Cynthia A. DeMarkey for assistance in carrying out portions of the experimental work.

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(15) M. Phillips and G. L. Keenan, *J. Amer. Chem. Soc.*, **53**, 1924 (1931).

Stereochemical Factors in Epoxide Polymerization by Base and Coordination Catalysts

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Abstract: The amorphous fraction accompanying isotactic poly(propylene oxide) or poly(*tert*-butylethylene oxide) formed by coordination catalysts was shown by degradation to the dimer glycols to involve inversion of configuration at every ring opening at the secondary carbon atom for (*R*)- (or (*S*)-) PO and to involve *no* stereoselection in the coordination step for *tert*-BuEO. The crystalline poly(*tert*-BuEO) formed by polymerization with *tert*-BuOK was similarly shown to give equal amounts of erythro and threo dimer glycol. It is proposed that these dimer units arise from regular alternate isotactic and syndiotactic placements (iso,syn). Aryl glycidyl ethers polymerized by *tert*-BuOK gave crystalline fractions shown to be isotactic (by comparison with crystalline polymer formed by coordination catalysts). The amount of the crystalline fractions decreased in the order $p\text{-}CH_3O > p\text{-}CH_3 > H > Cl \simeq 2,6\text{-}(CH_3)_2$. Crystallinity for both *tert*-BuEO and aryl glycidyl ethers was markedly diminished in the presence of DMSO, HMPT, or dicyclohexyl-18-crown-6 macrocyclic ether. All of these observations are in accord with a model for the transition state involving coordination of the potassium ion at the active chain end with at least the next two adjacent ether groups.

I. Amorphous Polymer from Coordination Catalysts

By ozone degradation to dimeric glycol, it has been previously shown that the principle irregularity in the structure of the amorphous poly(propylene oxide) accompanying the isotactic polymer prepared by coordination catalysts does not arise from random configurations (atactic sequences), but from head-to-head sequences.[2] Price and Tumolo[2] advanced the hypothesis, based only on the optical rotation of such amorphous polymer fractions from the (*R*) (or (*S*)) monomer, that each insertion of a head-to-head unit involved an

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(1) From the doctoral dissertations of M. K. Akkapeddi (Stereochemistry and Kinetics of Base-Catalyzed Polymerization of Epoxides, 1971), B. T. DeBona (The Stereochemistry of Abnormal Diads in Amorphous Poly(propylene oxide), 1971), and B. C. Furie (The Structures of Poly(*tert*-butylethylene oxides), 1970).

(2) C. C. Price and A. L. Tumolo, *J. Polym. Sci., Part A-1*, **5**, 175 (1967); C. C. Price, R. Spector, and A. L. Tumolo, *ibid., Part A-1*, **5**, 407 (1967).

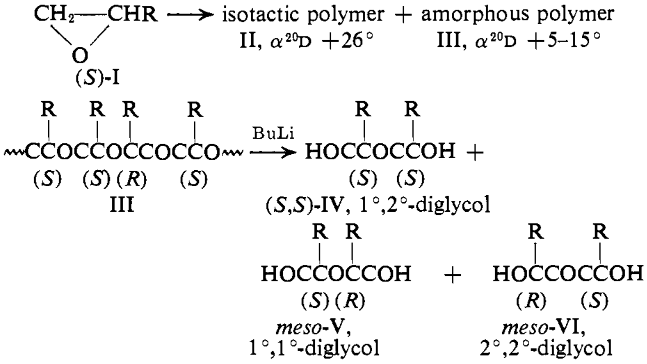
Table I. Amorphous Poly(propylene oxide) Samples and Their Degradation to Dimer Glycols

					Degradation results (dipropylene glycols, % rel)[f]			
Monomer	Catalyst	% yield[a]	[α]D, deg	$\bar{M}_n$[b]	1°,2°	2°,2° (% meso)[g]	1°,1° (% meso)	Calcd % meso[h]
RS	$Et_2Zn–H_2O$	80[c]	0.0		81.0	8.9 (40)	10.3 (67)	50
RS	$Et_2Zn–H_2O$	50[d]	0.0	2800	69.7	15.0 (40)	15.3 (69)	50
RS	$FeCl_3$–PO	82[c]	0.0	5000	70.0	15.2 (42)	14.7 (64)	50
R	$Et_2Zn–H_2O$	85[d]	−9.2	3000	66	16 (87)	18 (94)	90
R	$Et_2Zn–H_2O$	60[d]	−5.9	2500	61.5	18.3 (79)	20.1 (84)	78
S	$Et_2Zn–H_2O$	75[c]	−13.9	6500	80.8	8.8 (78)	10.4 (84)	82
S	$FeCl_3$–PO	87[c]	+13.0	6000	69.1	13.7 (90)	17.2 (96)	88
S	$FeCl_3$–PO	69[d]	+4.0	3500	60.8	20.2 (78)	19.0 (85)	76
RS	$Et_2Zn–H_2O$	*e*	0.0		98	~1	~1	

[a] Per cent yield after separation of crystalline fraction. [b] Vapor pressure osmometer. [c] Soluble in acetone at −30°. [d] Soluble in *n*-hexane at −78°. [e] Crystalline polymer, mp 58° (capillary); $\bar{M}_v$ = 110,000. [f] Average of at least two mixtures. [g] Estimated from ir spectra of bis-*p*-nitrobenzoate esters. [h] Calculated as $100(N_S^2 + N_R^2)$, where N_S (mole fraction of (*S*)-propylene oxide in monomer) was estimated from the relationship $[\alpha]_D = -16.78°N_S + 8.39°$.

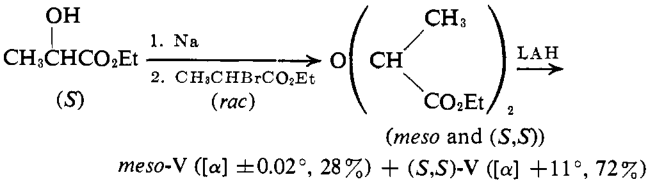
inversion of configuration in the structurally inverted monomer. In other words, the SN2 ring opening which must occur at the asymmetric secondary carbon atom of the epoxide must, as expected, proceed with inversion of configuration at that atom.

The earlier degradation studies[2] were carried out on a polymer prepared from racemic monomer. We here report studies on the diad sequences in amorphous polymer fractions from (*R*) (or (*S*)) monomer. Examination of the sequences in such a polymer chain, III, reveals that if inversion of configuration accompanies structural inversion, the abnormal head-to-head (or tail-to-tail) diads will produce the two symmetrical dimer glycols V and VI in the meso configuration only.

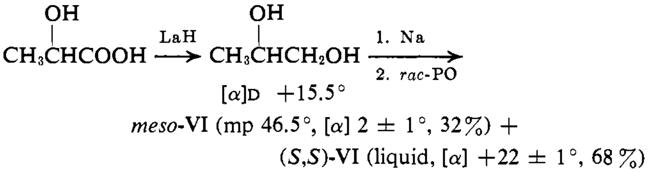


By glc, the diglycols from butyllithium degradation[3] of III can be resolved into four fractions. In order of increasing retention times, these are VI (meso and racemic), IV (erythro and threo), V (racemic), and V (meso).

Samples of meso and active dimer glycols V and VI were synthesized and characterized both to confirm the identity for the glc-separable isomers of V and to work out an assay procedure for the glc-inseparable isomers of VI. The synthesis for the diprimary glycols is outlined below.



The synthesis of the disecondary glycols started with (*S*)-(+)-lactic acid. *meso*-VI was separated by crystallization of the mixture from ether at −60°.



A procedure for determination of the relative amounts of *meso*- and active VI in the inseparable mixtures obtained from degradation of polymer was developed from the observation of significant difference in the ir spectra of the bis-*p*-nitrobenzoate esters in the 8.5–9- and 9.5–11.5-μ regions. The bands actually used were those at 8.69 (*meso*- and *rac*-VI) and 8.51 μ (*meso*-VI only).

The properties of the polymer samples studied and their degradation to dimer are summarized in Table I. Note that the fractions prepared from acetone at −30° have a higher molecular weight and higher optical rotation that those from *n*-hexane at −78°, indicating that the latter procedure is significantly more selective.

One problem of concern to our interpretation of the degradation data is the extent to which an assumption of random cleavage to dimer glycols is justified. We have no experimental evidence for the random cleavage down to dimer, but the equally disturbing possibility of nonrandom further cleavage of dimer we have tested. The results are summarized in Table II.

The data do indeed indicate some degree of selectivity, the rate of degradation being in the order *rac*-V > *meso*-V ≃ IV > VI. However, the differences, even for the more severe conditions of the experiments reported in Table II, suggest that we do not err substantially in interpreting the dimer glycol fractions from polymer degradation (Table I) as being reasonably accurate reflections of the diad sequences in the original polymer.

The data in Table I clearly show that the amorphous polymer from racemic monomer (samples 1, 2, and 3) gave the diprimary and disecondary glycols in roughly equal amounts of their meso and racemic diastereoisomeric forms. The lower amount for the racemic diprimary is in accord with its more rapid destruction by *n*-butyllithium (see Table II).

The amorphous polymer from optically active monomer degraded to give largely *meso*-V and -VI. The

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(3) E. J. Vandenberg, *J. Polym. Sci., Part A-1*, 7, 525 (1969).

Table II. Control Degradations of Dimer Glycol Mixtures

Mixed glycols	Composition Before %	 After %	BuLi/glycols
Sample A			
disecondary	37	40	
primary–secondary	45	47	
diprimary (active)	8	6	2/1
diprimary (meso)	9	6	
Sample B			
disecondary	37	50	
primary–secondary	45	39	3/1
diprimary (active)	8	2	
diprimary (meso)	9	8	
Sample C			
disecondary	50	58	3/1
primary–secondary	50	42	
Sample D			
diprimary (active)	72	67	3/1
diprimary (meso)	28	33	
Sample D	72	52	10/1
	28	48	

fact that these are not more nearly 100% meso is not due to incomplete inversion of the head-to-head units, but due to the optical impurity of the monomer as shown in the last column of Table I. Franzus and Surridge[4] have shown that, in the conversion of optically pure propylene glycol to bromohydrin, two isomers are formed. One is optically pure 1-bromo-2-propanol, which gives optically pure propylene oxide, [α]D −8.39° ($CHCl_3$). The other is 2-bromo-1-propanol, which gives propylene oxide of [α]D −1.50°. Our intermediate bromohydrins had about 20% of the 2-bromo isomer by glc. On the basis of the observed rotations of our monomer samples, one can calculate the enantiomer composition as indicated in the last column of Table I. Considering the sources of error in analysis and in nonrandom degradation, the agreement of the observed results with those calculated in Table I based on the assumption of inversion at every ring opening at the secondary oxirane carbon is quite satisfactory. Further support for this hypothesis comes from the correlations of observed amount of diprimary plus disecondary glycols with that calculated from optical rotations of the amorphous polymer samples, assuming that all such diads would always be formed by inverting the configuration of the monomer unit inserted by attack at the secondary carbon atom (Table III).

Table III. Comparison of the Observed Amounts of Abnormal Dipropylene Glycols Isomers with those Calculated from the Optical Rotation Values of the Corresponding Polymers

[α]D of polymer, deg	Total diprimary and disecondary glycols, % Obsd[a]	 Calcd[b]
−9.2	34	32
−5.9	38.4	39
+13.9	19.2	23
+13.0	30.9	25
+4.3	39.2	42

[a] Sum of the values from Table I. [b] Assuming one inversion for each head-to-head unit; [α]D ±26.3° for pure isotactic polymer.

The polymerization of *tert*-butylethylene oxide (*tert*-BuEO) by coordination catalysts gives a crystalline polymer, mp 150°, assumed to be isotactic.[5–7] We have found by butyllithium degradation that this polymer gives a single dimer glycol VIIe, mp 48°. There was only about 3–7% of the threo isomer, VIIt, mp 60°, which may arise either from imperfections in the isotactic chains or imperfect separation of the amorphous polymer.

When the amorphous polymer fraction accompanying the isotactic poly(*tert*-BuEO) was similarly degraded,[3] all three isomeric dimer glycols were observed on glc, as indicated in Table IV.

Table IV. Dimer Glycols from Amorphous Poly(*tert*-BuEO) ($Et_2Zn \cdot H_2O$ Catalyst)

	IX	VIII	VII	% VIIe[a]
Sample I	20.0	40.8	39.1	42.6
	25.5	39.2	35.4	43.3
	26.5	42.0	31.5	39.3
Sample II	23.2	46.1	30.7	42.7
	24.8	44.6	30.6	42.7

[a] Based on VII only.

As has been shown to be the case for amorphous poly(propylene oxide)[2] formed *via* coordination catalysts, the amorphous fractions of poly(*tert*-BuEO) from such catalysts have many units incorporated in a head-to-head, tail-to-tail sequence. In fact, despite the neopentyl-like hindrance which might have been expected for ring opening at the secondary carbon in *tert*-BuEO there is considerably more head-to-head polymer than for propylene oxide (compare Tables III and IV). If such sequences degraded purely randomly, there should have been an equal amount of the symmetrical dimer glycols VIII and IX formed. In every case (Table IV), the amount of the 1°,1°-isomer IX is less. This may well be due to the fact that an ether link flanked by two *tert*-butyl groups (which would need to be preserved to give IX) is so strained that it degrades preferentially.

Another interesting feature which emerges from the data in Table IV is that the sites which produce amorphous polymer are not only indiscriminate in the mode of ring opening, but must also be indiscriminate in the selection of D and L monomers, since the 1°,2°-dimer VII is nearly equally threo and erythro.

Most of the isomeric dimer glycols were identified by comparison with synthetic samples. The successful syntheses for the 1°,2°-dimer glycols VIIe and VIIt and for the 2°,2°-dimer glycol VIII are outlined in Chart I. Since the preparation of VIII utilized racemic *tert*-BuEO and racemic glycol, it should have produced a mixture of *meso*- and *rac*-VIII. We were unable to separate the mixture by recrystallization or glc. This leave the possibility open that the reaction to form dimer glycol may have been stereoselective for only one isomer. The synthesis of the dimer glycol VII led to isomers which were separable by distillation, recrystallization, or glc, in contrast to the case of propylene oxide where the corresponding 1°,2°-dimer glycols were not resolvable. The identity of the erythro isomer VIIe

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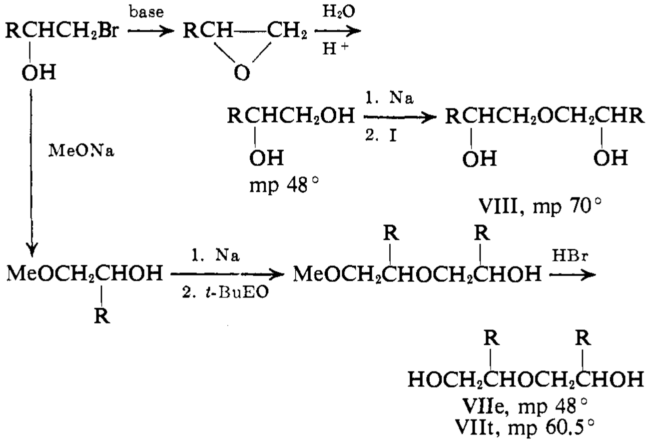
(4) B. Franzus and J. H. Surridge, *J. Org. Chem.*, **31**, 4286 (1966).

(5) C. C. Price and D. C. Carmelite, *J. Amer. Chem. Soc.*, **88**, 4039 (1966).

(6) C. C. Price and H. Fukutani, *J. Polym. Sci., Part A-1*, **6**, 2653 (1968).

(7) G. Allen, C. Booth, and S. J. Hurst, *Polymer*, **8**, 385 (1967).

Chart I



R = *tert*-Bu; Me = CH_3

was assumed from the fact that this isomer was 93–98% of the dimer glycol fraction from isotactic poly(*tert*-BuEO). A number of attempts to prepare the 1°,1°-isomer IX were unsuccessful so that the identification of the long-retention peak as IX must be regarded as tentative. The glc characteristics of the glycols are summarized in Table V.

Table V. Some Properties of Dimer Glycols of *tert*-BuEO

Compound	Glc ret time, min	Mp, °C
VIII, synth	38.4	67.0–68.5
from degrad	38.4	66.0–68.5
VIIe, synth	48.8	45.5–48.0
from degrad	48.8	46.0–49.0
VIIt, synth	52.1	58.0–60.5
from degrad	52.1	58.0–61.0
IX, from degrad	60	*a*

[a] This peak, appearing only for amorphous polymer from coordination catalysts, was always the least plentiful isomer (see Table IV) and we were not able to isolate enough to characterize the material by melting point or analysis.

II. Stereoselection Factors in Base-Catalyzed Polymerizations

The polymerization of *tert*-butylethylene oxide by potassium *tert*-butoxide has been found[5,6] to give a crystalline polymer differing in configuration from that produced by coordination catalysts.[5–7] This behavior contrasts to that of phenyl glycidyl ether which gives crystalline polymer by base catalysis of the same isotactic configuration as by coordination catalysts.[8,9]

On the basis of nmr data, it was proposed that the configuration of crystalline base-catalyzed poly(*tert*-BuEO) was syndiotactic, with two skew conformations at the C–C backbone bond.[6] Tani and Oguni[10] have suggested the alternative possibility, that the two sets of nmr lines for the backbone hydrogens arise from roughly equal numbers of isotactic and syndiotactic placements, although they made no decision between long blocks or a regular alternating sequence.

Degradation of this polymer by butyllithium has now shown it does indeed contain equal numbers of isotactic and syndiotactic placements as suggested by Tani and Oguni.[10] The results as summarized in Table VI clearly show that this polymerization proceeds almost exclusively to form head-to-tail sequences, presumably due to highly preferential SN2 attack at the primary carbon. It is also evident that the polymer has roughly equal amounts of isotactic and syndiotactic sequences, as indicated by the relative amounts or *erythro*- and *threo*-VII. The fact that the polymer, at least when prepared in bulk, is crystalline indicates that the equal proportions of VIIe and VIIt cannot be due to atactic polymer sequences. The two alternatives would seem to be long blocks of isotactic and syndiotactic sequence in roughly equal amounts, or regularly alternating "iso,syn" sequences, *i.e.*, regularly alternating isotactic and syndiotactic placements.

Table VI. Dimer Glycols from Poly(*tert*-BuEO) (*tert*-BuOK Catalyst)

Polymer[a]	VIII	VII	VIIe, %[b]
Bulk, prep I	0.95	99.1	56.4
	1.37	98.6	58
	2.11	97.9	57.2
prep II	3.95	96.1	54.8
	3.85	96.2	54.1
DMSO, prep I	4.24	95.8	47.5
	4.37	95.6	48.1
prep II	6.10	93.9	46.7
	9.16	90.9	49.1

[a] The bulk polymer is crystalline, while that prepared in DMSO is amorphous. Two different samples of each polymer were degraded two or three times each. [b] Based on VII only.

It seems highly unlikely that a single propagating species could produce crystalline block copolymers of isotactic and syndiotactic sequences without producing a great deal of atactic polymer as well. We therefore prefer the latter structure for the polymer. In fact, a reasonable mechanism for forming such a structure, involving chelation of ether groups by the potassium cation, is proposed below. The importance of ether groups in coordinating with cations has been demonstrated by Pederson[11] and is believed to be involved in the biological function of the macrocyclic antibiotics.[12]

An interesting feature of the regular isosyn stereochemical sequence *ddllddll*, etc., is that incoming configuration is always opposite to that of the penultimate unit at the growing end, *i.e.*, $k_{ddl^*} \gg k_{ddd^*}$ and $k_{dll^*} \gg k_{dld^*}$. Models approximating the transition state which account for such a sequence of relative reactivities are indicated below (XIA and XIB). These models assume that the growing chain end (XA or XB) will exist principally with an ion-pair bond between the terminal alkoxide anion and potassium cation and with the latter coordinated to *at least* two of the nearest ether oxygens. In the transition involving addition of a new monomer unit (M), the initial geometry will have the terminal O^-, the primary oxirane carbon, and the oxirane oxygen in the essentially linear geometry required for an SN2 displacement reaction at the carbon. As the reaction proceeds, with negative charge developing on the oxirane oxygen, this oxygen will move as quickly and easily as possible to coordinate with the K^+, as indicated by XIA (or XIB).

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(8) C. C. Price and A. Noshay, *J. Polym. Sci.*, **34**, 165 (1959); C. C. Price, Y. Atarashi, and R. Yamamoto, *ibid.*, *Part A-1*, 7, 569 (1965).

(9) Y. Tanaka and H. Kakiuchi, *ibid.*, *Part A-1*, 4, 109 (1966).

(10) H. Tani and N. Oguni, *Polym. Lett.*, 7, 803 (1969).

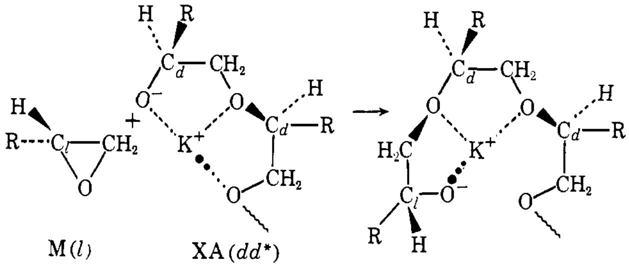
(11) C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386, 391 (1970).

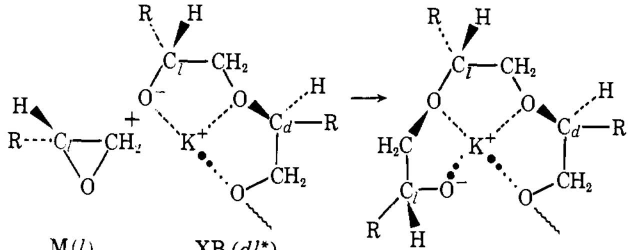
(12) M. Eigen, Lecture, Munich, West Germany, Oct 1970.

It should be pointed out that the models XIA (*ddl**) and XIB (*dll**) are diastereoisomeric. They would not be expected to have equal energies, nor equal rates of formation. What is essential is that the rate of formation of XIA (*ddl**) be considerably greater than that of *ddd** (which would give iso,iso sequences) and that the rate of formation of XIB (*dll**) be considerably greater than that of *dld** (which would give syn,syn sequences).

In order to clarify the steric features which would lead to the expectation of the observed regular iso,syn sequences, consider the model XA. Note that in the two fused rings, the planes of the two five-membered rings have a sharp angle, dictated largely by the COC bond angle. Each ring has a *tert*-butyl group, one on a carbon α to the ring junction, one on a carbon β to the ring junction. Models indicate that the van der Waals radii of an α-*cis-tert*-butyl group and an α' cis hydrogen would overlap by about 2.0 Å and thus α-*cis-tert*-butyl would be strongly disfavored compared to α-*trans*-. A β-*cis-tert*-butyl group would fail to overlap α' (or β') hydrogens by *ca.* 0.2–0.5 Å and so would be disfavored but little compared to a β-*trans-tert*-butyl. It is on this basis that we have chosen the indicated conformations of XA and XB with the α-*tert*-butyl trans to the adjacent ring.

Model XIA does involve an α-*cis-tert*-butyl placement of the central *tert*-butyl group. However, the alternative of adding a D monomer to give iso,iso sequences would involve an α-*cis-tert*-butyl–β-*cis-tert*-butyl interaction. This would be strongly disfavored because of a severe interference (~2.5 Å) of the van der Waals radii of two *tert*-butyl groups.


M(*l*) XA(*dd**) XIA (*ddl**)


M(*l*) XB (*dl**) XIB (*dll**)

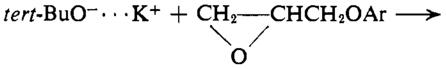
For model XIB, there is a mildy unfavorable β-*cis-tert*-butyl interaction for the central *tert*-butyl group. However, if the D monomer were to add, giving syn,syn sequences, there would be a second mildly unfavorable β-*cis-tert*-butyl interaction.

A simplified statement of the stereochemistry producing preferred iso,syn sequences is that (1) the models XA and XB have their conformation dictated by preference for the α-*tert*-butyl to be trans and (2) the transition states XIA and XIB then select monomer to put the incoming β-*tert*-butyl in a β-trans position.

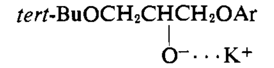
The failure to obtain a crystalline polymer from *tert*-BuEO by *tert*-BuOK polymerization in DMSO is in accord with the hypothesis that chelated structures X and XI are important in determining stereoselection. With HMPT as solvent amorphous polymer is also produced, but in this case the molecular weight is not lowered, as it is by chain transfer with DMSO molecules. The strongly polar DMSO or HMPT molecules, with a strong negative field around the oxygen atom, would tend to displace the less polar ether oxygens from the K^+ in X and XI. Similarly, the observation that dicyclohexyl-18-crown-6 macrocyclic ether[11] produced amorphous polymer also fits with the importance of chelation to stereoselection. The 18-crown-6 ethers have strong tendencies to coordinate with potassium and would thus markedly diminish its capacity to order the structure of the growing polymer chain as shown in models X and XI.

On the basis of the fact that polymerization of phenyl glycidyl ether (PGE) in DMSO with potassium *tert*-butoxide as catalyst gave increased (although low) yields of crystalline, acetone-insoluble isotactic polymer with increased catalyst concentration, it was suggested that ion-pair association of K^+ with the growing alkoxide unit in base-catalyzed polymerization was important in promoting stereoselection.[8] It was also suggested that chelation of this K^+ with adjacent ether groups including the aryl ether was involved.[6]

Evidence in support of chelation by the aryl ether group in PGE has been obtained by polymerization of analogs of PGE in which such chelation would be enhanced (*p*-methyl- and *p*-methoxy-) or inhibited (*p*-chloro- and 2,6-dimethyl-). As seen in Table VII, the *p*-methoxy derivative (Hammett $\sigma = -0.27$) gave more crystalline polymer than did the *p*-methyl ($\sigma = -0.17$), while the *p*-chloro ($\sigma = +0.23$) gave no polymer of sufficient isotacticity to be insoluble in acetone at room temperature. A negative σ constant would be expected to enhance the ability of the aryl ether to coordinate with potassium while a positive σ constant would have the opposite effect. Two *o*-methyl groups, while promoting the basicity of the aryl ether electronically, would be expected to offer strong steric interference with chelation.


$$\textit{tert}\text{-BuO}^-\cdots K^+ + \underset{\text{O}}{CH_2\text{—}CHCH_2OAr} \longrightarrow$$

XII, Ar = C_6H_5
XIII, Ar = $p\text{-}CH_3C_6H_4$
XIV, Ar = $p\text{-}CH_3OC_6H_4$


$$\textit{tert}\text{-BuOCH}_2\underset{\text{O}^-\cdots K^+}{\text{CH}}\text{CH}_2\text{OAr}$$

XV, Ar = $p\text{-}ClC_6H_4$
XVI, Ar = $2,6\text{-}(CH_3)_2C_6H_3$
XVII, Ar = $2,4,6\text{-}(CH_3)_3C_6H_2$

Even XIV, which gave 36% of crystalline polymer in bulk polymerizations, gave only 14% in DMSO and 6% in HMPT. It was also shown that dicyclohexyl-18-crown-6 macrocyclic ether reduced the amount of crystalline polymer formed from XIV from 36 to 7%.

The experimental evidence thus supports the view that chelation of ion-paired K^+ at the growing chain end promotes stereoselection in favor of isotactic sequences. The evidence indicates that coordination at the aryl ether oxygen is important. In fact, this extra ether oxygen must be crucial in directing the propaga-

Table VII. Preparation and Properties of Poly(phenyl glycidyl ethers)

	By $Et_2Zn \cdot H_2O$					By *tert*-BuOK, cryst				Amorphous		
Subst	% yield	% benzene insol	Mp, °C	[η]	Major X-ray spacings, Å	% yield	Mp, °C	Major X-ray spacings, Å	[η] (mol wt)[f]	% yield	Sp, °C	[η][e]
H	96	97	200–203	1.12	8.0, 8.5, 4.1, 3.8	20	96–102	8.0, 4.7, 4.1, 3.8	0.08 (6400)	80	60–72	0.07
p-Me	90	96	200–205	1.0	4.6, 4.1, 3.5	25[b]	105–112	4.6, 4.1 3.5	0.08 (12,000)	75	50–65	0.05
p-MeO	98	94[d]	190–200	1.0	4.5, 4.1, 3.7, 3.4	36[c,d]	113–115	4.6, 4.2, 3.9, 3.6	0.1 (17,000)	64	75–85	0.08
p-Cl	74	98	185–192	2.09	7.5, 4.5, 4.0	None			(5500)	98	Semisolid	0.04
2,6-Me$_2$	85	68[a]	125	1.04	6.9, 4.0	None			(3900)	82	Semisolid	

[a] *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.19; H, 7.86. Found: C, 73.90; H, 7.88. [b] In DMSO, 12%, mp 105–112°. [c] In DMSO, 14%, mp 110–115°; in HMPT, 6%; in bulk with dicyclohexyl-18-crown-6 added equivalent to catalyst, 6.7%, mp 110–115°. [d] The crystalline polymer from Et_2Zn on *tert*-BuOK showed bands at 1352, 1150, 890, and 870 cm^{-1} in KBr which were not present in $CHCl_3$ or CS_2 solutions nor in the acetone–soluble polymer from *tert*-BuOK nor in polymer prepared in DMSO or HMPT or with dicyclohexyl-18-crown-6 added. The latter polymers were all amorphous glasses, softening point ~75–90°. [e] In benzene at 30°, dl g^{-1}. [f] By Mechrolab Vapor Osmometer.

tion isotactically rather than in the regular isosyn sequence found for polymerization of *tert*-butylethylene oxide by the same catalyst under the same conditions. Actually, the only modification necessary in models XA and XIA is to recognize that the aryl ether group in incoming monomer could coordinate to K$^+$ in XA only if the aryl ether group were up (D configuration), leading to an isotactic sequence (*ddd**) in XIA.

Experimental Section

Dimer Glycol IV was prepared by the method of Sexton and Britton,[13] bp 134–135° (10 Torr) (lit.[13] bp 96–96.5° (4 Torr), 94% purity by glc. The nmr ($CDCl_3$) shows two doublets at δ 1.12 and 1.3 ($J \simeq 7$ Hz, 6 H), multiplets centered at 3.51 (4 H) and 3.90 (2 H), and a broad singlet at 4.38 ppm (2 H). The latter was shown to be due to hydroxyl by deuterium exchange. The infrared spectrum was the same as that reported by Tumolo.[14]

Dilactic acid diethyl ester[15] was prepared from sodium dispersion, ethyl lactate, and ethyl α-bromopropionate, bp 118° (15 Torr). 99% pure by glc. The nmr ($CDCl_3$) showed a methyl triplet at δ 1.22 ($J \simeq 7$ Hz, 6 H), a methyl doublet at 1.34 ($J \simeq 7$ Hz, 6 H), a methylene quartet at 4.17 ($J \simeq 7$ Hz, 4 H), and a methine quartet at 4.06 ppm ($J \simeq 7$ Hz, 2 H).

Racemic Dimer Glycol V. Reduction of the racemic dilactate above was accomplished with lithium aluminum hydride in ether to give V in essentially quantitative yield, bp 114° (8 Torr) (lit.[13] bp 102° (5 Torr). The nmr ($CDCl_3$) showed a methyl doublet at δ 1.10 ($J \simeq 7$ Hz, 6 H), an apparent methylene singlet at 3.50 (4 H), a complex methine multiplet centered at 3.65 (2 H), and a broad hydroxyl singlet at 4.10 ppm.

The **bis-*p*-nitrobenzoate** ester was prepared with *p*-nitrobenzoyl chloride and recrystallized from ethanol, mp 143–144° (lit.[13] mp 142–143°).

Meso and (*S,S*) Dimer Glycol V. (+)-(*S*)-lactic acid was esterified (bp 74–75°, (40 Torr); lit.[16] 58° (20 Torr)). The ester, 98% pure by glc, showed nmr bands ($CDCl_3$) for a methyl triplet at δ 1.30 ($J \simeq 7$ Hz), a methyl doublet at 1.36 ($J \simeq 7$ Hz), a methine quadruplet at 4.12, and a methylene quadruplet at 4.18 ppm. Conversion to the dilactate by reaction with sodium dispersion and *rac*-α-bromopropionate, then reduction by LAH, gave a mixture of *meso*- and (*S,S*)-V, bp 116–118° (10 Torr), [α]D 5.0° (neat), with the same ir and nmr spectra as the material from racemic lactate.

This mixture of diastereoisomers was separated by preparative glc by a 300 cm × 6 mm column of dioctyl sebacate on 60–80 mesh Chromosorb G; column 150°, detector 310°, injector 300°, collector 280°, He flow 80 ml/min. Two fractions of retention time 10 min (A) and 13 min (B) were obtained in a 2.5:1 ratio. Reinjection of 1-μl portions showed excellent separation; [α]D(A) +11° (c = 3 g/dl($CHCl_3$)), (B) 0 ± 0.02° (c = 3 g/dl ($CHCl_3$)).

Meso and (*S,S*) Dimer Glycol VI. **(+)-(*S*)-Propylene glycol** was prepared by LAH reduction of (+)-(*S*)-lactic acid in THF, bp 86–87° (11 Torr), 96% purity, glc, [α]D +15.5° (neat) (lit.[17] −15.0° for (−)-(*R*) enantiomer). Treatment with sodium and then *rac*-propylene oxide gave a mixture of *meso*- and (*S,S*)-VI, bp 118° (11 Torr), 98% purity by glc, [α]D +15–16° (neat).

By cooling a 10–20% ether solution to −60° and centrifuging, this mixture was separated into crystalline [mp 46.5° (lit.[13] 45–46.5°) and [α]^{50}D +2 ± 1° (neat)] and liquid fractions [[α]D +22 ± 1° (neat)]. By glc, the crystalline fraction was 99% pure while the liquid contained 4% of ether; both had the same retention time, as expected from their nonseparability by glc. The 15° rotation of the mixture thus indicates a composition of about 2:1 favoring the racemic diastereoisomer. The nmr spectra ($CDCl_3$) for the two isomers were very similar with methyl doublet at δ 1.14 ($J \simeq 7$ Hz), methylene multiplets at 3.4, methine multiplets at 3.95, and a broad hydroxyl singlet near 4.2 ppm.

Bis-*p*-nitrobenzoate Esters of VI. A mixture of *rac*- and *meso*-VI (10 g) was converted to the esters by treatment with 31 g of *p*-nitrobenzoyl chloride in 100 ml of dry refluxing pyridine. Crude ester was collected by pouring into water and then washing twice with 5% aqueous sodium carbonate at 50° for 5 min. The 95% yield of crude product was extracted thoroughly with 400 ml of boiling anhydrous ethanol. Decantation and cooling gave, after four more recrystallizations, *rac*-VI diester, mp 116.5–117.5°.

Anal. Calcd for $C_{20}H_{20}O_9$: C, 55.55; H, 4.66; N, 6.48. Found: C, 55.38; H, 4.44; N, 6.45.

Recrystallization of the ethanol-insoluble fraction four times from benzene gave the meso isomer, reported earlier,[13] mp 150–151° (lit.[13] 150–151°). *Anal.* Found: C, 55.54; H, 4.58; N, 6.51. The assignments of configuration are based on conversion of the pure *meso*-VI to the diester, mp 151°. The (*S,S*)-VI gave diester, mp 139°, identical with the *rac*-VI diester, mp 117°, in ir spectra.

(+)-(*R*)-Propylene oxide, bp 34.5–35.5°, [α]D +11.2° (neat), +6.3° (c = 10 g/dl ($CHCl_3$)) (lit.[18] [α]D +11.57° (neat)), was prepared from acetol through the glycol by yeast fermentaton.[18] The **(−)-(*S*)-isomer** was prepared from (+)-(*S*)-lactic acid through the glycol by LAH reduction, [α]D −11.4° (neat), −6.8° (c = 10 g/dl ($CHCl_3$)).

Polymerizations. Diethylzinc–water (1:1) catalyst was made up as a stock slurry in *n*-heptane, or prepared *in situ* in the presence of monomer. About 2 mmol of catalyst per 5 g of propylene oxide was used.[3] **Ferric chloride–propylene oxide** (1:4) catalyst[19] was used at about 1% based on monomer.

Polymer separation was accomplished by dissolving polymer containing 0.25% of 2,6-di-*tert*-butyl-*p*-cresol in acetone (200 ml/g) and cooling the solution to −30°. A typical crystalline isotactic fraction from the (−)-(*S*) monomer showed [α]^{27}D +26.3° (c = 4.6 g/dl (benzene)), mp 67° by DSC (lit.[20] 62° by DTA).

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(13) A. R. Sexton and E. C. Britton, *J. Amer. Chem. Soc.*, **75**, 4357 (1953).

(14) A. L. Tumolo, Ph.D. Dissertation, University of Pennsylvania, 1963.

(15) P. Vieles, *Ann. Chim.*, [11] **3**, 143 (1935).

(16) P. Vieles and M. Godchot, *Bull. Soc. Chim. Fr.*, [5] **4**, 937 (1937).

(17) P. Levene and A. Walti, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 545.

(18) P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).

(19) See C. C. Price and M. Osgan, *J. Amer. Chem. Soc.*, **78**, 4787 (1956).

(20) R. J. Valles, *Makromol. Chem.*, **113**, 147 (1968).

The soluble amorphous fraction showed $[\alpha]^{27}D$ +13.9° (*c* 18.2 g/dl (benzene)). The results are summarized in Table I.

Polymer degradation by *n*-butyllithium was carried out essentially as reported by Vandenberg[3] using 2.7 mmol of polymer and 1.5 mmol of 2 *M n*-BuLi in hexane in 10 ml of benzene. After standing overnight and then heating 4 hr at 55°, the mixture was added to 150 ml of 96% ethanol, neutralized with HCl, and deionized with Amberlite MB-1. Evaporation of ethanol to 5 ml and azeotroping with benzene was repeated until a clear solution in benzene was obtained, which was then used for glc analysis. For those experiments where 2°,2°-glycol (VI) was to be collected from the degradation, the quantities above were increased by five- to ninefold. Results are summarized in Table I.

Dimer degradations were studied by heating 120 mg of dimer glycol and usually 2.6 ml of 2 *M n*-BuLi in hexane in 10 ml of benzene to 70° for 10 hr. The products were prepared for glc as above and the results are summarized in Table II.

The **column** for these separations was 500 cm × 6 mm packed with Carbowax 20M on Varaport 38.[21] The operating conditions were column 190–195°, injection 300–310°, detector 310–320°, collector 280–290°, He flow 75 ml/min, filament current 165–175 mA. This column, estimated to have *ca.* 3000 theoretical plates, gave clean separation of four dimer glycol peaks: *meso*- and *rac*-VI, 21 min; *erythro*- and *threo*-IV, 26.5 min; *rac*-V, 30 min; *meso*-V, 34.5 min.

Dimer Glycol VI Analysis. Since these diastereoisomers could not be separated, analysis was based on the observation of differences in the crystalline ir spectra (Nujol mulls) for the bis-*p*-nitrobenzoate esters. Both the meso and racemic forms had a band at 8.69 μ while only the meso had a band at 8.51 μ. By using the former as an internal standard, and preparing a calibration plot of A_{851}/A_{869} *vs.* composition for mixtures of the separately prepared diesters, estimates of composition of the 2°,2°-dimer glycol were possible and are included in Table I. For this purpose, about 10–20 mg of the 2°,2°-dimer glycol fraction from 1 g of polymer was obtained by preparative glc. In a typical esterification, 13.3 mg of IV, 66 mg of *p*-nitrobenzoyl chloride, 2.5 ml of toluene. and 110 μl of pyridine were refluxed gently (protected by Drierite) for 1 hr. After evaporation at 50–60°, 5 ml of acetone was added. After evaporation to *ca.* 2 ml, 8 ml of water was added and the precipitated diester washed with 5% aqueous sodium carbonate at 40° and with water and dried to yield 31.8 mg (74%) of diester.

***tert*-Butylethylene oxide** was prepared from pinacolone by bromination, reduction, and base,[22] or preferably from *tert*-butylethylene. The olefin (143.5 g), 291 g of *N*-bromosuccinimide, and 720 ml of water were stirred in a 2-l. flask cooled by a water bath. After the bromoimide was consumed, the layers were separated and the aqueous layer extracted once with ether. The combined organic layers were dried and distilled to yield 260 g (72%) of **1-bromo-3,3-dimethyl-2-butanol**, bp 35.5–36.5° (0.5 mm) (lit.[22] 45–46° (4 mm)). Dropwise addition of 181 g of bromohydrin to 560 g of KOH and 70 ml of water in a 1-l. flask with a distilling head, heated at 165° over 150 min, produced a distillate which was washed four times with 20% NaCl and dried over KOH pellets. After further drying with calcium hydride, 99 g (59%) of *tert*-BuEO distilled at 96.5–97.5° (lit.[22] 97°). The ir spectrum showed a carbonyl band at 1725 cm^{-1}, presumably due to some pinacolone from rearrangement. Fractional distillation from a spinning band column at a 15:1 reflux ratio gave product free of ketone by ir.

Poly(*tert*-butylethylene oxide). A. By Coordination Catalyst. Diethyl zinc–water was used as a catalyst[6] to give an 84% conversion to polymer of which 90% was crystalline polymer, mp ~150°, and 10% was amorphous (soluble in benzene), mol wt 1100 (vpc in benzene).

B. By *tert*-BuOK. A mixture of 1 g of *tert*-BuEO and 1.5 mg of *tert*-BuOK was sealed and heated at 90° for 21 days.[6] The polymer was extracted from the tube with cyclohexane, washed, dried, and freeze-dried, yielding 0.97 g of polymer, mp 47–54°, mol wt 2040 (vpc in benzene).

C. By *tert*-BuOK in DMSO or HMPT. A solution of 13.4 g of *tert*-BuEO and 0.3 g of *tert*-BuOK in 20 ml of dry DMSO was heated in a pressure bottle for 1 week at 60°. The base was neutralized by adding Dry Ice and the polymer was extracted with cyclohexane. After washing and drying, evaporation left 12.7 g (95%) of liquid polymer, mol wt 1000–1300. A similar polymerization in HMPT gave a polymer of 1900 molecular weight.

D. By *tert*-BuOK–Dicyclohexyl-18-crown-6.[23] A mixture of 6.5 g of *tert*-BuEO, 56 mg of *tert*-BuOK, and 185 mg of the crown ether was heated at 80° for 14 days. The polymer produced in 93% yield after purification by treatment with 1 *N* KCl solution and aqueous methanol to remove the crown ether and traces of monomer, respectively, was a viscous amorphous liquid, mol wt 2500 (vpc in benzene). Its nmr spectrum was similar to that of polymer prepared in DMSO.[6]

Degradation of Poly(*tert*-BuEO). The polymer (0.1 g, 1.0 mmol) was dissolved in 10–50 ml of benzene in a pressure vessel and treated with 0.46 ml of a 22% solution of *n*-butyllithium (1.10 mequiv) in hexane. After 12–16 hr at 25° the mixture was heated to 95–100° for 4–6 hr. After cooling, 10 ml of ethanol was added and the mixture was neutralized with hydrochloric acid, and washed with water. The water layer was extracted with ether and the combined organic layers dried and evaporated, leaving a viscous yellow mixture of crude glycols in 47–71% yield.

Dimer glycol separation was effected by a 6 mm × 500 cm aluminum column in an Aerograph Model A-90P packed with Carbowax 20M on Chromosorb W regular 60–80 mesh which had been silanized with dichlorodimethylsilane. Optimum resolution of the dimer glycols was observed at a column temperature of 195°, He flow rate of 100 ml/min, filament current 190 mA, injection port at 305°, and detector block at 335°. The results are summarized in Tables IV, V, and VI.

Dimer Glycol Synthesis. Disecondary Glycol VIII. *tert*-Butylethylene glycol was prepared by hydrolysis of 10 g of *tert*-BuEO (I), bp 97.5–98°,[5,22] in 30 ml of water containing 2 drops of sulfuric acid. After stirring overnight at 35°, the organic layer was washed, dried, and distilled to yield 6.5 g (50%) of crude glycol, bp 52–69° (0.2 mm). Sublimation at 25° (0.05 mm) produced a white crystalline solid, mp 45–48° (lit.[24] mp 48–49°).

This glycol (2.7 g) was heated at its melting point with 30 mg of sodium and then 2.3 g of *tert*-BuEO was added dropwise at 125°. After stirring at 125° for 3 hr, the separated aqueous phase was washed with ether and the combined organic layers dried and distilled to yield 0.80 g of starting glycol, bp 54–64° (0.4 mm), and 0.36 g of dimer glycol VIII bp 87° (0.4 mm). Sublimation at 25° and 0.05 mm gave a 6.9% yield of white VIII, mp 67–69.5°.

Anal. Calcd for $C_{12}H_{26}O_3 \cdot {}^1/_3H_2O$: C, 64.28; H, 11.96; mol wt 218. Found: C, 64.32; H, 11.77; mol wt 215 (vpo in methyl ethyl ketone).

The ir band for primary hydroxyl appearing at 1050 cm^{-1} for VIIe and VIIt is missing in VIII, there being only a complex C–O stretching band from 1075 to 1115 cm^{-1}. The nmr spectrum in CCl_4 showed bands at δ 0.91 (18 H), 3.15–3.65 (6 H), and 3.8 ppm (2 H). The latter disappeared on exchange with D_2O. The main features of the complex from δ 3.15 to 3.65 ppm can be ascribed to the expected triplet at 3.55 and doublet at 3.35 ppm, with J = 5.5 Hz.

Primary–Secondary Glycols, VIIe and VIIt. 1-Bromo-2-hydroxy-3,3-dimethylbutane (137 g) was added dropwise to a solution of 52.4 g of sodium in 340 ml of methanol. After refluxing overnight, excess methanol was distilled and the residue washed and distilled to give 60 g (58%) of **1-methoxy-2-hydroxy-3,3-dimethylbutane**, bp 61.5–62.5° (25 mm), $n^{25}D$ 1.3146.

Anal. Calcd for $C_7H_{16}O_2$: C, 63.61; H, 12.19. Found: C, 63.81; H, 11.97.

The nmr spectrum in CCl_4 had bands at δ 0.90 (18 H) and 3.15–3.55 (7.3 H). In the complex from δ 3.15 to 3.55 ppm, the methoxyl was a sharp singlet at 3.35 ppm.

The methyl ether above (66.6 g) was treated with 10 g of sodium and the product was dissolved in 150 ml of dry diglyme. The solution was placed in two pressure bottles, 16.8 g of *tert*-BuEO was added to each, and they were sealed under nitrogen and heated to 130–150° for 48 hr. After washing with water and drying, the solvent was removed by distillation and the residue was distilled at 0.05 mm, bp 52.4–54°, to yield 12.1 g (16%) of a pale yellow liquid.

Anal. Calcd for $C_{13}H_{28}O_3$: C, 67.20; H, 12.15. Found: C, 67.39; H, 11.89.

The nmr in CCl_4 showed bands at δ 0.90 (18 H) and 2.9–3.85 ppm (10 H). There was about 1 H from δ 2.9 to 3.15 ppm.

Cleavage to VIIe and VIIt was accomplished by refluxing 12.1 g of the above dimer methyl ether with 13.2 g of 48% aqueous hydro-

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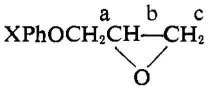
[21] H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography," Consolidated Printers, Berkeley, Calif., 1968, p 67.

[22] S. J. Hurst and J. M. Bruce, *J. Chem. Soc.*, 1321 (1963).

[23] The sample of crown ether[11] was kindly supplied through the courtesy of Dr. H. K. Frensdorff, E. I. duPont deNemours and Co.

[24] H. Adkins and H. R. Billica, *J. Amer. Chem. Soc.*, 70, 3121 (1948).

Table VIII. Major Characteristics of the Nmr Spectra of Substituted Phenyl Glycidyl Ethers[a]



$\overset{a}{XPhOCH_2}\overset{b}{CH}—\overset{c}{CH_2}$ (with O bridging CH and CH$_2$)

Subst X	H_X	H_{Ph}	H_a	$H_{a'}$	H_b	H_c	$H_{c'}$	$J_{aa'}$	J_{ab}	$J_{a'b}$	J_{bc}	$J_{bc'}$	$J_{cc'}$
H		~7.0	3.70	4.08	3.17	2.70	2.54	11	5.4	3.0	4	3.5	5.5
p-Cl		7.18, 6.75[b]	3.67	4.12	3.22	2.75	2.60	11	6.0	2.8	4	2.6	5.0
p-CH_3O	3.75	7.00, 6.70[b]	3.87	4.17	3.30	2.86	2.70	11	6.0	3.0	4	2.6	5.0
p-CH_3	2.18	7.00, 6.70[b]	3.65	4.00	3.12	2.62	2.48	11.5	6.0	3.0	4.5	3.2	5.7
2,6-$(CH_3)_2$	2.18	6.84	3.42	3.82	3.08	2.56	2.40	11	6.0	3.0	4.0	2.5	5.0
2,4,6-$(CH_3)_3$	2.24	6.78	3.68	3.98	3.30	2.80	2.64	11.5	5.5	3.5	4.0	2.5	5.0

[a] δ in ppm; *J* values in Hz. [b] $J = 9.0$ Hz.

bromic acid until evolution of methyl bromide ceased. The organic layer was washed and distilled. A viscous liquid (0.7 g) distilled at 80–85° (0.1 mm) leaving 3.2 g of solid residue. The latter was purified by sublimation at 35° (0.05 mm) to give dimer glycol VIIt, mp 58–60.5°.

The liquid distillate was fractionated by glc to give 60% of VIIt (retention time, 52.1 min) and 40% of VIIe, mp 45.5–48° (retention time, 48.8 min). The solid residue was 98% VIIt and 2% VIIe by glc.

Anal. Calcd for $C_{12}H_{26}O_3$: C, 66.01; H, 12.00; mol wt, 218. Found for VIIt: C, 66.26; H. 11.87; mol wt, 215 (vpo). For VIIe: C, 66.23; H, 11.84; mol wt, 215 (vpo).

Both VIIe and VIIt showed an ir band at 1050 cm^{-1}, ascribed to the primary OH C–O stretch, with a more complex C–O stretching band from 1070 to 1120 cm^{-1}. The nmr of VIIe in CCl_4 showed bands at δ 0.93 (18 H), 2.8–3.85 (6 H), and 3.96 (1.8 H). The latter was shown to be OH by deuterium exchange. In the complex, there was a double doublet (1 H) centered at δ 2.95 ppm. The nmr of VIIt in CCl_4 showed bands at δ 0.92 (18 H), 2.85–4.0 (6.4 H), and 4.25 (2.1 H). The latter was shown to be due to OH. In the complex, there was a double doublet (1 H) centered at δ 3.0 ppm.

Diprimary Diglycol (IX, Attempted). In one of several abortive efforts to prepare this glycol, privaldehyde was condensed with acetylene by methods described in the literature.[25] The product, 1,4-di-*tert*-butyl-1,4-dihydroxy-2-butyne, presumably a mixture of DL and meso isomers, showed mp 118–122°, even after repeated recrystallization from *n*-hexane.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.85; H, 11.01.

Repeated efforts to reduce the triple bond to the cis double bond by Lindlar catalyst[26] showed no absorption of hydrogen and starting material was recovered. Use of a Raney nickel catalyst[27] led to absorption of 4 mol of hydrogen and gave a product, mp 178–183°, which showed no double bond in the ir spectrum and no protons below δ 4.22 ppm in the nmr spectrum.

Anal. Calcd for $C_{12}H_{26}O_2$: C, 71.23; H, 12.95. Found: C, 71.19; H, 13.08.

Phenyl glycidyl ether and its *p*-chloro, *p*-methyl, and *p*-methoxyl derivatives were prepared from the phenol and epichlorohydrin as before.[28]

2,6-Dimethylphenyl glycidyl ether was obtained in 70% yield, bp 82° (0.1 mm), purity >99% by glc.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.19; H, 7.86. Found: C, 73.91; H, 7.78.

2,4,6-Trimethylphenyl glycidyl ether was obtained in 65% yield, bp 82° (0.1 mm), purity >99% by glc.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.01; H, 8.37. Found: C, 74.78; H, 8.20.

The nmr spectra of these compounds are summarized in Table VIII.

Polymerizations of PGE. A. Diethylzinc–water. Catalyst solution was prepared by adding exactly 1 equiv of water to 6 ml of 1 *M* diethylzinc in dry benzene under dry nitrogen in a Carius tube. After adding 40 mmol of monomer, the tube was sealed and kept at 60° for 1 day. The polymer was then swollen in hot DMF and poured into excess methanol containing 0.5% HCl. The crude polymer was fractionated by stirring overnight in 100 ml of benzene/g. The benzene-insoluble fraction was collected by centrifugation and the benzene-soluble material by precipitation by pouring into methanol.

B. With Potassium *tert*-Butoxide. Mixtures of 50 mmol of monomer and 0.5 mmol of freshly sublimed catalyst were sealed under nitrogen and kept at 50° for 1 week with occasional shaking. The viscosity increased significantly overnight. The final solid polymer was dissolved in hot THF and precipitated by pouring into 300 ml of 0.05% methanolic HCl. The crude polymers were separated into acetone-soluble and -insoluble fractions by stirring at room temperature with 50 ml of acetone/g. The acetone-insoluble fraction was recovered by centrifugation, the acetone-soluble by precipitation with methanol.

C. With Potassium *tert*-Butoxide in DMSO. These reactions were identical with **B** except that 35 ml of anhydrous DMSO was added.

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