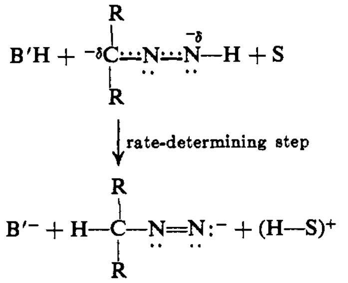
Kishner reaction involves a more-or-less concerted formation of a carbon–hydrogen bond and the breaking of the nitrogen–hydrogen bond in the hydrazone anion



$$\mathrm{B'H} + {}^{-\delta}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\cdots\ddot{\mathrm{N}}\cdots\overset{-\delta}{\ddot{\mathrm{N}}}\mathrm{—H} + \mathrm{S} \xrightarrow{\text{rate-determining step}} \mathrm{B'}^- + \mathrm{H—}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\mathrm{—}\ddot{\mathrm{N}}\mathrm{=}\ddot{\mathrm{N}}\mathrm{:}^- + (\mathrm{H—S})^+$$

where B′–H is a protic solvent such as butyl carbitol, and where S is a hydrogen-acceptor solvent. It is reasonable to expect that DMSO is a superior hydrogen-acceptor solvent than butyl carbitol, and thus we can understand why the presence of DMSO in a mixture of DMSO and alcohol accelerates the WK reaction until the total concentration of the latter becomes so low that it is depleted from the activated complex and the C–H bond formation process begins to suffer. In absolute DMSO at 100° the WK reaction occurs[9] nearly two magnitudes slower than when a relatively low concentration (0.12 *M*) of hydroxylic solvent is present, but it is still approximately 30 times faster than the rate calculated from the temperature dependence of the reaction in pure butyl carbitol.[3] Thus, we may conclude that in absolute DMSO, this normally aprotic solvent is forced into the role of a proton donor[14] and that the reaction rate suffers accordingly, but, in spite of this, the reaction is still faster than in pure butyl carbitol because of the superiority of DMSO, when compared to butyl carbitol, in the role of the hydrogen-bond acceptor.

Since the product of the rate-determining step postulated above is the anion of a diimide,[15] it is to be expected that this anion suffers a rapid elimination of nitrogen, and that the resulting carbanion and the nearby HS^+ species collapse to the final WK product.

Acknowledgment. We wish to thank Mr. H. Poussin for technical assistance in carrying out some of the experiments.

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(14) This point of view will be developed more fully in a future publication.

(15) The first diimide to be studied in detail is that reported recently by E. M. Kosower and P. C. Huang, *J. Am. Chem. Soc.*, **87**, 4645 (1965), and it is shown that the ionization of phenyldiimide under basic conditions is extremely rapid.

Reactions of Epoxides in Dimethyl Sulfoxide Catalyzed by Potassium *t*-Butoxide

Charles C. Price and Donald D. Carmelite[1]

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104. Received April 18, 1966

Abstract: The polymerization of ethylene oxide proceeded to completion in DMSO giving a polymer with a molecular weight calculated from the ratio of the monomer to the *t*-butoxide initiator. Propylene oxide gives a polymer with a limiting molecular weight of about 1200, limited by the usual chain-transfer process to the monomer. No detectable sulfoxide end group was observed by infrared in either case, indicating that the methyl hydrogens of propylene oxide are at least 1000 times more readily abstracted by alkoxide groups on growing polymer chains than are hydrogens in DMSO. Substitution of deuterium for the methyl hydrogens of propylene oxide led to an increase in molecular weight and a decrease in allyl unsaturation, as expected for a chain-transfer process involving this methyl group. The reaction of tetramethylethylene oxide with *t*-butoxide in DMSO proceeds solely by attack at methyl, producing α,α,β-trimethylallyl alcohol in 98% yield. Trimethylethylene oxide similarly produces a good yield of two isomeric alcohols, α,α-dimethylallyl alcohol (80%) and α,β-dimethylallyl alcohol (15%). *t*-Butylethylene oxide shows no evidence of chain transfer but is remarkably less reactive to polymerization than propylene oxide.

Earlier studies of epoxide polymerization by strong bases, such as KOH,[2–7] have involved problems of interpretation due to insolubility of the catalyst in the polymerization medium. This has led to the suggestion[2] that the reaction is heterogeneous for powdered KOH in the monomer or in monomer solutions, although it may only be the initial reaction of KOH with an epoxide to generate a glycolate ion which is indeed heterogeneous.[3]

Because of the recognition of the value of DMSO solutions of potassium *t*-butoxide for reactions initiated by base,[8,9] we have now investigated this medium for homogeneous base-catalyzed reactions with epoxides.

For ethylene oxide, polymerization proceeded readily

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(1) From a Ph.D. Dissertation by D. D. Carmelite, 1966; supported in part by a grant from the General Tire and Rubber Co.

(2) L. E. St. Pierre and C. C. Price, *J. Am. Chem. Soc.*, **78**, 3432 (1956).

(3) E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *ibid.*, **86**, 4678 (1964).

(4) G. J. Dege, R. L. Harris, and J. S. MacKenzie, *ibid.*, **81**, 3374 (1959).

(5) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

(6) G. Gee, W. C. E. Higginson, P. Levesley, and K. J. Taylor, *J. Chem. Soc.*, 1338 (1959).

(7) W. H. Snyder, Ph.D. Dissertation, University of Pennsylvania, 1961; W. H. Snyder, K. J. Taylor, N. S. Chu, and C. C. Price, *Trans. N. Y. Acad. Sci.*, **24**, 341 (1962).

(8) (a) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960); (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(9) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961).

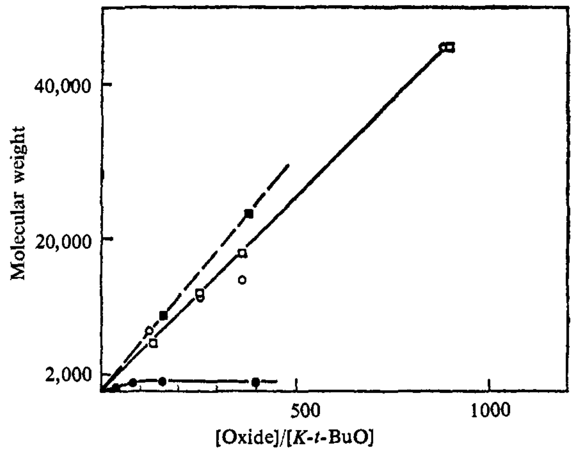


Figure 1. Molecular weights of poly(ethylene oxide) and poly(propylene oxide); theory (without chain transfer), □, ■; experimental, ○, ●.

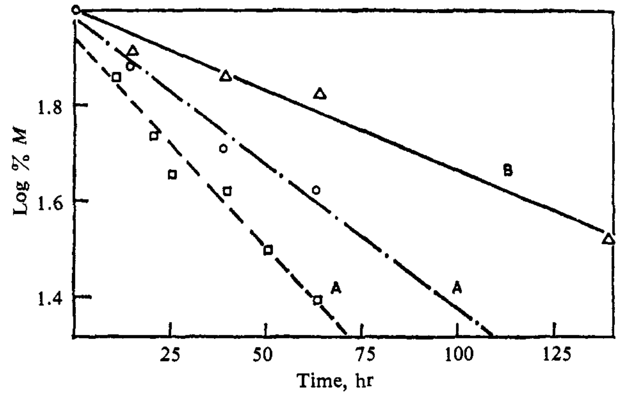


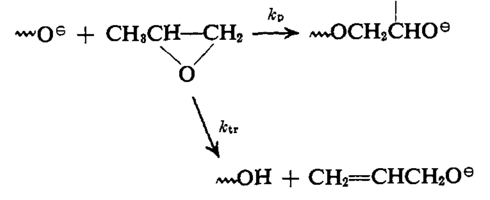
Figure 2. Rates of polymerization of propylene oxide (A) and the 3,3,3-trideuterio analog (B): □, A, [t-BuO$^-$] = 0.0208 M, $k_2 = 2.8 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$; ○, A, [$t$-BuO$^-$] = 0.0167 M, $k_2 = 2.3 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$; △, B, [$t$-BuO$^-$] = 0.0167 M, $k_2 = 1.2 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$.

at room temperature to produce the polymer in good yield with a molecular weight inversely proportional to the monomer–base ratio. The data, summarized in Figure 1, clearly indicate there is no complication of chain transfer to DMSO under these conditions. In other words, growing alkoxide groups react with the monomer at a rate which must be at least 10,000 times the rate of alkoxide abstraction of a proton from DMSO to give dimsyl anion, although the low basicity of DMSO (pK_a = ~31)[8b] indicates an insignificant concentration of dimsyl ion even at equilibrium.

For propylene oxide, the plot of molecular weight against 1/[t-BuO$^-$] reaches a maximum of about 1200 (see Figure 1) indicating a ratio of $k_p : k_{tr} = 20$ in DMSO. This ratio is appreciably smaller than in more inert solvents,[3] *e.g.*, $k_p : k_{tr} \simeq 50$ in the monomer,[2] indicating that the base attack on hydrogen is relatively more favored in DMSO by a factor of approximately 2.5.

There are two reports in the literature on the polymerization of 3,3,3-trideuteriopropylene oxide by powdered KOH in glyme (dimethyl ether of ethylene glycol).[3,7] Synder[7] found almost identical terminal unsaturation from the normal and deuterated monomer while the deuterated monomer surprisingly gave a lower molecular weight polymer. Steiner, Pelletier, and Trucks[3] found lower unsaturation from the deuterated monomer and a lower rate of reaction, but gave no information on the molecular weights.

The results reported herein for the homogeneous system are indeed in complete accord with transfer to the methyl group of the monomer, since the molecular weight for the deuterated polymer was about twice that of normal and the unsaturation about one-half. These observations, summarized in Table III, are in accord



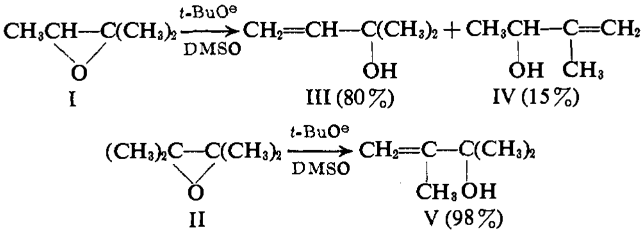
$$\sim\!O^\ominus + \underset{\diagdown O \diagup}{CH_3CH\!-\!CH_2} \xrightarrow{k_p} \sim\!OCH_2\overset{\overset{CH_3}{|}}{C}HO^\ominus \qquad (1)$$

$$\xrightarrow{k_{tr}} \sim\!OH + CH_2{=}CHCH_2O^\ominus \qquad (2)$$

with this scheme with $k_{trH} : k_{trD} \simeq 2$.

The rate of polymerization of propylene oxide was found to be pseudo first order (Figure 2). The second-order rate constant at 30° for the normal monomer, $k_{2(H)} = 2.5 \times 10^{-4}$ l. mole^{-1} sec^{-1}, was appreciably larger than for the deuterated monomer, $k_{2(D)} = 1.2 \times 10^{-4}$ l. mole^{-1} sec^{-1}.[10] Snyder[7] actually found the deuterated polymer gave greater yields than normal; we have no explanation to offer for this apparent difference in rates since we would have expected only extremely small secondary isotope effects on k_p, and there appears to be no evidence for a reaction destroying base catalyst. In this case, unlike the studies with solid KOH present,[3] there is no change to explain an increase in rate as due to increased solubilization of base as increased alkoxide arising from chain transfer to monomer.

The transfer reaction (2) above was found to be the dominant reaction for tri- and tetramethylethylene oxides (I and II). These results support earlier reports



$$\underset{\text{I}}{\underset{\diagdown O \diagup}{CH_3CH\!-\!C(CH_3)_2}} \xrightarrow[\text{DMSO}]{t\text{-BuO}^\ominus} \underset{\text{III (80\%)}}{CH_2{=}CH\!-\!\underset{OH}{C}(CH_3)_2} + \underset{\text{IV (15\%)}}{CH_3\underset{OH}{CH}\!-\!\underset{CH_3}{C}{=}CH_2}$$

$$\underset{\text{II}}{\underset{\diagdown O \diagup}{(CH_3)_2C\!-\!C(CH_3)_2}} \xrightarrow[\text{DMSO}]{t\text{-BuO}^\ominus} \underset{\text{V (98\%)}}{CH_2{=}\underset{CH_3}{C}\!-\!\underset{OH}{C}(CH_3)_2}$$

of rearrangements of epoxides to allylic alcohols.[11–13]

As an additional test of the importance of the methyl hydrogen in chain transfer, t-butylethylene oxide was treated with potassium t-butoxide in DMSO. In 2 weeks at room temperature, the monomer was recovered nearly quatitatively (propylene oxide gives over 90% of the polymer under the same conditions). At 60°, a 1:1 ratio of oxide and t-butoxide gave a good conversion to the adduct (VII).

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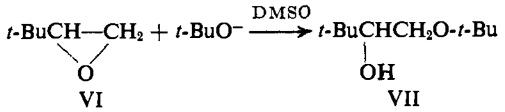
(10) These rate constants are in reasonable agreement with the rate reported[3] earlier, $k_a = 1.2 \times 10^{-4}$ mole^{-1} sec^{-1} for propagation in monomer as solvent and KOH as catalyst.

(11) R. L. Letsinger, J. G. Traynham, and E. Bobko, *J. Am. Chem. Soc.*, **74**, 399 (1952).

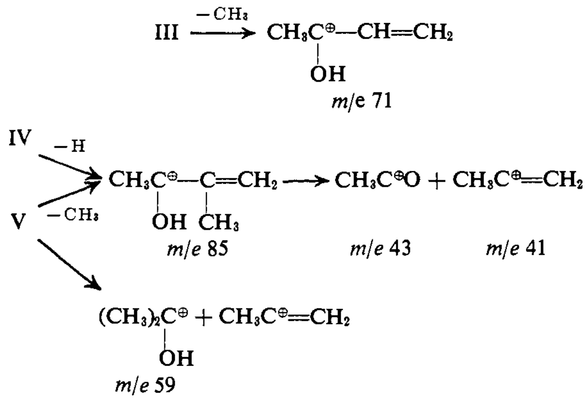
(12) H. F. Fife and F. H. Roberts, British Patent 601,608 (1948); Olin Matheson Chemical Corp., British Patent 902,953 (1962); *Chem. Abstr.*, **58**, 13794 (1963).

(13) T. L. Jacobs, D. Dankner, and H. R. Dankner, *J. Am. Chem. Soc.*, **80**, 864 (1958); L. T. Haynes, I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1583 (1947); D. M. Burness, *J. Org. Chem.*, **29**, 1862 (1964); G. W. Fowler and J. T. Fitzpatrick, U. S. Patent 2,426,264 (1947).

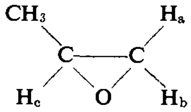


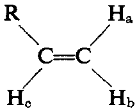
At a ratio of 20:1, a 90% yield of oily polymer, DP = 11, was obtained. With solid KOH at 130° for 2 weeks, a 53% yield of solid polymer, mp 44°, was obtained. These data suggest that the alkoxide derived from VI, which is a neopentyl alkoxide, adds very reluctantly to VI.

Incidental to this investigation, the mass spectra of the allylic alcohols were determined. The results, in Tables VI, VII, and VIII, show principal peaks all readily explained by splitting to produce reasonably stable cation fragments as follows.



The nmr spectrum of propylene oxide can be interpreted as follows. The methylene hydrogens, H_a and H_b, appear at τ 7.75 and 7.4, respectively, splitting each other by $J = 5.5$ cps and split by the methine hydrogen, H_c, τ 7.2, by $J = 3.5$ (*cis*) and 2.6 cps (*trans*). The methyl hydrogens (τ 8.85, $J = 6.0$ cps) split the methine quartet further into a broad complex multiplet.[14] In the trideuterio analog, the methine hydrogen is split by deuterium, $J = 0.6$ cps.





III

Alcohol III shows nmr peaks at τ 5.05 and 5.2, H_a and H_b, splitting each other by $J = 2.2$ cps and split by H_c, $J = 10.4$ (*cis*) and 19 cps (*trans*), with H_c split into two doublets by $J = 10.4$ and 19 cps.

Experimental Section[15]

Dimethyl sulfoxide was purified by refluxing with calcium hydride for 4 hr, followed by distillation through a 2-ft column of glass helices at a reflux ratio of 10:1. After a second redistillation, the center 60% fraction was collected over calcium hydride and sealed with a serum cap. It was 99+% pure by vpc.

Propylene oxide was dried over KOH and redistilled, 99+% pure by vpc.

Viscosity molecular weights[16] were determined for poly(ethylene oxide) in water at 35°, using the relation $[\eta] = (6.4 \times 10^{-5})\bar{M}_v^{0.82}$. A Model 301A Mechrolab vapor osmometer was also used, standardized by phenanthrene in benzene. Unsaturation was measured by bromine titration,[3] infrared on a Perkin-Elmer Model 421, nmr on a Varian HR-60, mass spectra on a Consolidated Model 21-130, and vpc on a Burrell Kromo-Tog Model K-1: (a) 20% Carbowax 20M on Fluoropak 80 (20% C/F), (b) 10% silicone oil (Dow 550) on Fluoropak 80 (10% S/F), or (c) 10% silicone oil (Dow 550) on Chromosorb W (10% S/C).

1,1,2,2,-Tetramethylethylene oxide was prepared by dropwise addition of 1 mole of peracetic acid (40% in acetic acid) to a vigorously stirred suspension of 150 g of anhydrous sodium carbonate in 1 mole of 1,1,2,2-tetramethylethylene in 150 ml of methylene chloride; essentially the procedure of Sorenson and Campbell.[17a] After addition of 250 ml of water, the reaction mixture was extracted with 600 ml of methylene chloride, in three equal portions. The solvent was removed by distillation through a well-insulated, 1 × 24 in. column packed with glass helices. The crude yield of 1,1,2,2-tetramethylethylene oxide was 81.4 g (81.4%), bp 89–91°. Redistillation at a reflux ratio of 20:1 afforded 37.4 g of pure olefin oxide, bp 90.5–91°, n^{20}_{D} 1.4016 (lit.[17b] bp 90–90.5°, n^{20}_{D} 1.4010).

The infrared spectrum (cm^{-1}) shows absorption (% transmission) useful for confirming the structure of 1,1,2,2-tetramethylethylene oxide at 2960 (59%, methyl, asymmetric stretching), 1460 (45%, methyl, asymmetric bending), a doublet at 1380 (32 and 73%, *gem*-dimethyl, symmetric bending), 1160 (66%, C–O, antisymmetrical stretching), and 840 (52%, epoxide ring, stretching). The nmr spectrum shows a single intense peak at τ 8.7 corresponding to the single type methyl hydrogen, and mass spectral analysis shows a parent peak at *m/e* 100.

1,1,2-Trimethylethylene oxide was prepared by the same procedure used for 1,1,2,2-tetramethylethylene oxide. The crude yield of 1,1,2-trimethylethylene oxide, bp 74–76°, was 58.5 g (68.1%). Fractional distillation afforded 22.1 g of pure 1,1,2-trimethylethylene oxide, bp 76–76.5°, n^{20}_{D} 1.3846 (lit.[18] bp 74–76°, n^{20}_{D} 1.3838).

The infrared spectrum (cm^{-1}) shows bands (% transmission) useful for confirming the structure of 1,1,2-trimethylethylene oxide at 3000 (48%), 2960 (62%), 1460 (53%), doublet 1380 (46 and 75%), 1250 (31%), 1120 (57%), 960 (31%), 850 (72%). The nmr spectrum shows a multiplet at τ 8.9 and a quartet at τ 7.2 in the expected ratio of 9:1 (CH_3:CH). Mass spectral analysis shows the parent peak at *m/e* 86.

***t*-Butylethylene Oxide.** The acetate of *t*-butylmethylcarbinol was prepared in 84.5% yield by treatment of 2 moles of the alcohol with a 10% excess of acetic anhydride and 15.0 g of anhydrous sodium acetate. The reaction mixture was refluxed for 5 hr to give a nearly quantitative yield of the acetate. The acetate was converted in good yield to *t*-butylethylene by pyrolysis of the acetate at 500 ± 50°. The reaction technique was suggested by procedure of Whitmore and Rothrock.[19]

Fractional distillation of crude pyrolysate gave 66.3 g (71%) of *t*-butylethylene, 99% pure by vpc, bp 41–41.5°, n^{20}_{D} 1.3771 (lit.[19] bp 40.2–40.3°, n^{20}_{D} 1.3760).

The synthesis of *t*-butylethylene oxide was attempted using the same procedure as used to synthesize the 1,1,2,2-tetramethylethylene oxide, the treatment of the corresponding olefin with peracetic acid. To 42.0 g (0.5 mole) of *t*-butylethylene in 75 ml of methylene chloride and a suspension of 75 g of sodium carbonate was added, with stirring, 0.5 mole of peracetic acid (40% in acetic acid), dropwise, over a 6-hr period. The reaction was maintained at 0 ± 5° with an ice bath. The absence of a marked heat of reaction allowed maintaining the temperature at 0° with much less difficulty than in the previous cases. A peroxide test with acidic potassium iodide and 1 ml of the reaction mixture revealed that the peracetic acid had not reacted appreciably. The reaction mixture was stored for 2 weeks in a refrigerator (at a temperature of 14–18°). At the end of this time, 100 ml of water was added, and the resultant mixture was extracted with 600 ml of methylene chloride, in three equal portions. The methylene chloride extract was washed with ferrous sulfate solution until it no longer gave a positive peroxide test. Fractional distillation afforded 11.3 g (19.4%) of *t*-butylethylene oxide, bp 89–90.5°, n^{20}_{D} 1.3998 (lit.[20] bp 86°, n^{20}_{D} 1.3977).

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(14) Similar values have been recently reported by G. Allen, D. J. Blears, and K. H. Webb, *J. Chem. Soc.*, 810 (1965).

(15) Elementary analyses by Galbraith Laboratories, Knoxville, Tenn., and by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim, West Germany.

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(18) A. Z. Alizade, *Azerb. Khim. Zh.*, **4**, 63 (1960); *Chem. Abstr.* 18573*b* (1961).

(19) F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **55**, 1108 (1933).

(20) I. N. Rozhkov and S. M. Makin, *Zh. Obshch. Khim.*, **34**, 59 (1964).

Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.07. Found: C, 71.66; H, 11.89.

The infrared bands (% transmission, assignment) useful in identification are (in cm^{-1}) at 3050 (50%, methylene stretching, terminal epoxy), 3000 (61%, epoxy ring, CH stretching), 2960 and 2860 (83 and 66%, methyl asymmetric and symmetric stretch, respectively), doublet 1460 (80 and 63%, CH_3 bending), doublet 1380 (30 and 79%, *gem*-dimethyl symmetrical bending), 1240 (52%), 930 and 840 (83 and 79%, epoxy ring stretching vibrations). The nmr spectrum showed an intense singlet at τ 9.0 (CH_3) and a multiplet at around τ 6.5 (epoxy ring hydrogens) whose ratio of areas was 3:1. Mass spectral analysis showed the parent peak at *m/e* 100.

Ethylene Oxide Polymerization. Into a pressure bottle containing a dry, oxygen-free atmosphere was placed 0.112 g (0.001 mole) of potassium *t*-butoxide and a solution of 6.2 g (0.141 mole) of ethylene oxide in 25 ml of DMSO. The ethylene oxide–DMSO solution was prepared by pouring ethylene oxide from a freshly opened bottle into a tared 125-ml erlenmeyer flask, containing 25 ml of DMSO and 2 g of calcium hydride. The flask was stoppered with a serum cap wired in place. The weight of ethylene oxide was determined by difference. The solution was transferred by a nitrogen-flushed hyperdermic syringe to a pressure bottle. It was necessary to cool the reaction mixture under a running tap for the first 4 hr of reaction. The reaction mixture was stirred for 2 weeks at room temperature. The color of the reaction mixture changed from pale to golden yellow during the course of the reaction and was visibly thickened by the fourth day of reaction.

The contents of the flask were neutralized with 0.1 *N* hydrochloric acid. The viscous solution was added dropwise into a large erlenmeyer flask containing 2 pt of absolute ether. The polymer precipitated on contact with the ether. The flask was stoppered and placed in a refrigerator overnight. The polymer was collected by suction filtration. A solution of the polymer in benzene was filtered, and a fluffy, white polymer was collected after freeze drying. The polymer was identified as polyethylene oxide by infrared comparison to an authentic sample. The weight of polymer collected was 4.8 g (77.4%). The results are summarized in Table I and Figure 1.

Table I. Polymerization of Ethylene Oxide by Potassium *t*-Butoxide in DMSO[a]

Ethylene oxide, *M*	*t*-BuO⁻, *M*	Yield, %	[η]	$\bar{M}_v$[b]	Calcd, mol wt[c]
5.63	0.0400	77.4	0.115	9,840[d]	6,200
5.93	0.0200	85.5	0.145	12,840	13,050
4.00	0.0100	91.6	0.170	14,500	17,600
6.53	0.0067	98.6	0.305	42,500	43,100

[a] For 2 weeks at room temperature. [b] From $[\eta] = (6.4 \times 10^{-5})\bar{M}_v^{0.82}$.[15] [c] From [ethylene oxide]44/[*t*-BuO⁻]. [d] Perhaps some low molecular weight polymer was lost in this precipitation.

Propylene Oxide Polymerization. A pressure bottle was flushed with dry, oxygen-free nitrogen for 30 min. To the pressure bottle was added 29.0 g (0.500 mole) of propylene oxide, 1.40 g (0.0125 mole) of potassium *t*-butoxide, and 125 ml of DMSO. For the first several hours of reaction, the reaction mixture was cooled under a running tap, and then the pressure bottle was placed on a mechanical shaker at room temperature for 2 weeks. During the course of the reaction, the color of the homogeneous solution changed from yellow to light brown. No thickening of the solution was noted but a 0.25-in. upper layer of yellow oil was noted after 1 week of reaction. After 2 weeks of reaction, the polymerizate was neutralized to a phenolphthalein end point with powdered Dry Ice and 1 ml of water.

The reaction mixture was extracted with 300 ml of cyclohexane in three equal portions. The extracts were combined, dried over magnesium sulfate, and filtered through fluted filter paper. The cyclohexane was removed by distillation at a reduced pressure of 0.5 mm. After removal of solvent by distillation, a yellow oil remained which was transferred to a 50-ml erlenmeyer flask with the aid of 10 ml of hexane. To protect against oxidation of the polymer, 0.1 g of hydroquinone was added. The solution was allowed to stand in a refrigerator overnight. No DMSO crystals were noted (DMSO, mp 18°, crystallizes from cold hexane at 10° even from very dilute solutions). The solution was transferred into a tared 50-ml erlenmeyer flask containing a small magnetic stirring bar. The solvent was removed by distillation at reduced pressure. The distillation to remove solvent was carried out with the aid of stirring and heat from a water bath held at 40–45°. The final traces of hexane were removed by distillation at 0.03 mm. The weight of the polymer obtained was 26.4 g (91.0%), and the $\bar{M}_n$ obtained osmometrically was found to be 648. These results and other similar experiments are summarized in Table II. The polymer was identified as poly(propylene oxide) by infrared comparison with an authentic sample of poly(propylene oxide). Several samples of poly(propylene oxide) prepared in this way showed a sharp band at 1667 cm^{-1}, evidently due to propenyl ether end groups.

Table II. Polymerization of Propylene Oxide by Potassium *t*-Butoxide in DMSO

Propylene oxide, *M*	*t*-BuO⁻, *M*	Yield, %	$\bar{M}_n$
4.00	0.100	91	650
4.00	0.050	78	1200
4.00	0.010	58	1220
4.00	0.0022	3.3	. . .
1.00	0.025	75	640
1.00	0.0125	95	1170
1.00	0.0075	93	975
1.00	0.0025	30	1040

The DMSO–water extraction layers were collected and distilled to dryness at a reduced pressure of 0.1 mm with warming to 50°. No water-insoluble solid remained; however, a trace of polymer did.

Polymerization of 3,3,3-Trideuteriopropylene Oxide. By similar procedures, 0.3 g of trideuterio monomer (Merck, Canada) in 1.2 ml of DMSO with varying ratios of *t*-butoxide was polymerized for 2 weeks at 30°. The results are summarized in Table III.

Table III. Comparison of Polymerization of Propylene Oxide (A) and the 3,3,3-Trideuterio Analog (B)

Monomer[a]	*t*-BuO⁻, *M*	Yield, %	$\bar{M}_n$	Unsatd, mequiv/g
1A	1.00	95	840	. . .
1B	1.00	95	1170	. . .
2A	0.067	96	1160	4.25
2B	0.067	91	2500	2.71
3A	0.050	92	1100	. . .
3B	0.050	93	1795	. . .
4A	0.020	80	1135	3.85
4B	0.020	78	2085	2.57

[a] Monomer = 3.3 *M*.

Rate of Propylene Oxide Polymerization. In a reaction flask protected from the atmosphere, 58 g (1.0 mole) of monomer and 0.56 g of potassium *t*-butoxide (5.0 mmoles) in 180 ml of DMSO were stirred at 30°. At intervals, 25-ml samples were withdrawn. A vpc assay on 2 μl on 10% S/F at 120° gave the concentration of monomer (retention time 2.4 min) compared to DMSO (10.3 min). The polymer was isolated after acid washing and its molecular weight determined osmometrically. The results are summarized in Table IV and Figure 2.

Rate of 3,3,3-Trideuteriopropylene Oxide Polymerization. A specially constructed 5.0-ml reaction flask was used for the study. This flask consisted of a 5-ml glass bulb joined to a straight-bore 2-mm vacuum stopcock. A 12/30 standard taper glass joint was attached to the top of the stopcock. A 6-in. hypodermic needle passing through the center of the joint would also pass through the bore of the opened stopcock and reach the center bottom of the glass bulb.

The reaction was conducted in these special reactors under a slight positive pressure of nitrogen. Samples were withdrawn for vpc analysis by passing the 6-in. hypodermic needle of a syringe through a serum cap inserted in the male joint and the bore of the

Table IV. Reaction of Propylene Oxide and *t*-BuOK in DMSO

Time, hr	% conversion[a]	Vpc, % conversion[b]	$\bar{M}_n$
3	16	18.7	887
6	24	27.1	800
22	48	45.0	1270
27	50	55.3	1802
40	. . .	58.8	. . .
52	65	67.6	1670
63	74	75.4	. . .
75	98	80.6	1400
720	102	. . .	1516

[a] Based on grams of polymer recovered. [b] Based on unreacted propylene oxide by vpc method.

stopcock. Except when samples of the solution were being withdrawn, the stopcock was closed. The stopcock was held in place by a spring clamp to ensure the absence of leakage. No loss of weight was noted when 0.3 g of propylene oxide in 1.25 ml of DMSO was kept at 30 ± 0.01° for 1 week, nor was there a difference in the ratio of the areas of the propylene oxide to DMSO vpc peaks from the beginning to the end of the week.

The oxide (0.005 mole) was allowed to distil into the reaction bulb on a vacuum manifold, the stopcock was closed, and the weight of the oxide was determined by difference. A serum cap was inserted into the male joint at the top of the reactor and the area between the closed stopcock and the serum cap was flushed with nitrogen introduced through the serum cap with a hyperdermic needle. To the oxide cooled at liquid nitrogen temperature was added, from a nitrogen-flushed syringe, 0.25 ml of 0.1000 *N* potassium *t*-butoxide in DMSO and 1.0 ml of DMSO. The reaction mixture was held at 30°, and samples were removed periodically.

For assay, 2 μl of reaction mixture was injected on the 10% S/F column, at 140.1°, flow rate 44 cc/min. The retention time of the oxide peak was 1.3 min and of the DMSO 7.7 min. The vpc reproducibility of the propylene oxide/DMSO area ratio was established on five successive 2-μl aliquots to have the same value to within ±1%. The data comparing the amount of unreacted oxide for the two monomers are collected in Table V and Figure 2. The $\bar{M}_n$ of the polymers from these reactions are listed in Table III as 4A and 4B.

Table V. Rates of Polymerization for Propylene Oxide *vs.* 3,3,3-Trideuteriopropylene Oxide at 30°

Time, hr	% unreacted propylene oxide	Time, hr	% unreacted 3,3,3-d_3-propylene oxide
0.05	100.0	0.05	100.0
14.27	76.5	14.48	81.6
38.08	53.3	38.40	72.8
63.90	43.1	64.14	64.7
141.08	20.9	140.64	34.0
170.05	19.2	170.40	31.3
215.42	15.2	215.50	23.8

Reaction of *t*-Butylethylene Oxide. (1) A pressure bottle was flushed with nitrogen for 0.5 hr, stoppered, and placed in a drybox. To the pressure bottle was added 2.5 g (0.025 mole) of *t*-butylethylene oxide, 50 ml of DMSO, and 2.80 g (0.025 mole) of potassium *t*-butoxide. The contents of the pressure bottle were allowed to stand for 2 weeks in an oil bath at 60° with occasional shaking. The reaction mixture separated into two layers after 1 week of reaction. The upper layer, 1.9 g of a pale yellow oil, was subjected to vpc analysis (10% S/F, at 140°, flow rate 44 cc/min) showing a single peak shown to be *t*-butyl 2-hydroxyneohexyl ether (retention time 12.3 min). Extraction of the lower layer with 75 ml of cyclohexane gave an additional 0.3 g of oil whose infrared spectrum was identical with that of the oil in the upper layer.

The nmr spectrum showed single peaks at τ 9.25 ($(CH_3)_3C$–C) and 9.0 ($(CH_3)_3C$–O) and a multiplet at τ 6.9 ($HOCHCH_2O$) in the ratio of 8.6:8.7:4. The infrared spectrum showed no peaks associated with carbonyl or unsaturated groups. Bands (assignments, vibrational mode) useful in identification occurred at (in cm^{-1}) 3600, 3400 (OH stretching), 2960, 2860 (methyl stretching), 1460 (methyl bending), doublet 1380 (*gem*-dimethyl bending), 1255, 1210, 930 (*t*-butyl, skeletal), 1080 (C–O–C, antisymmetric stretching), 1065 (branched, secondary alcohol, C–O stretching), 895 (*t*-butoxy skeletal).

(2) Two Carius tubes were flushed with dry, oxygen-free nitrogen for 15 min, capped, and placed in a drybox. To each Carius tube was added 2.5 g (0.025 mole) of *t*-butylethylene oxide, 6.25 ml of DMSO, and 0.014 g of potassium *t*-butoxide (0.00125 mole). Both Carious tubes were stoppered, removed, and sealed in an oxygen flame. The first Carius tube was placed on a mechanical shaker for 2 weeks at room temperature.

Complete recovery of starting material by distillation indicated absence of reaction. (Note that propylene oxide polymerizes under these conditions in 90+% yield.)

(3) The second Carius tube was placed in an oil bath at 60° and allowed to stand for 2 weeks with occasional shaking. The polymerizate separated into two layers. The tube was cooled at −78° and opened. The contents of the flask were neutralized to a phenolphthalein end point with anhydrous acidic ion-exchange resin, in DMSO. Analysis by vpc (10% S/F, at 140°, flow rate 44 cc/min) showed no volatile peak whose identity was not known. Extraction of the polymerizate with 75 ml of cyclohexane in three equal portions followed by evaporation of the solvent at 0.05-mm pressure gave 2.3 g (91%) of a yellow oil. The infrared spectrum showed bands (assignment, vibrational mode) used to help identify the product at (in cm^{-1}) 3600, 3400 (hydroxyl end group, –OH stretching), 2960, 2870 (methyl stretching, asymmetric and symmetric), 1460 (methyl asymmetric bending), doublet 1380 (*gem*-dimethyl symmetrical bending), 1255, 1220, and 930 (*t*-butyl, skeletal), and 1100 (C–O, antisymmetric stretching). There was no infrared absorption indicative of unsaturated end groups. The $\bar{M}_n$ of the polymer was determined osmometrically and found to be only 1123 (calculated from monomer: initiator ratio, 2000).

(4) To a Carius tube flushed previously with nitrogen in a drybox was added 1.0 g of *t*-butylethylene oxide and one pellet of powdered potassium hydroxide (previously dried at 100° overnight under nitrogen flow). The Carius tube was placed in an oven at 130° for 2 weeks. A white solid, weighing 0.53 g (53%), mp 44°, was obtained after neutralization with anhydrous acidic ion exchange resin and extraction with hexane followed by evaporation. The infrared spectrum showed the polymer to be chemically the same as the yellow oil obtained previously in reaction 3. The intrinsic viscosity of the polymer was found to be $[\eta] = 0.03$ in toluene at 20°.

Reaction of 1,1,2,2-Tetramethylethylene Oxide with *t*-Butoxide in DMSO. Into a pressure bottle were placed 5.0 g (0.05 mole) of tetramethylethylene oxide, 5.6 g (0.05 mole) of potassium *t*-butoxide, and 100 ml of DMSO. The transfers were made in a drybox free of oxygen, carbon dioxide, and moisture. The reaction mixture was allowed to stand for 2 weeks, with occasional shaking, in an oil bath at 45 ± 1°. The color of the reaction mixture changed from straw yellow to golden brown. After cooling, 1 ml of water was added and sufficient powdered Dry Ice to neutralize the solution to a phenolphthalein end point. The volatile portion of the reaction mixture was distilled at room temperature into a receiving flask cooled in liquid nitrogen.

Analysis by vpc of the volatile portion, 10% S/F, at 140°, flow rate 44 cc/min, indicated peaks for *t*-butyl alcohol (retention time 1.8 min), water (2.0 min), DMSO (7.3 min), 1,1,2,2-tetramethylethylene oxide (3.5 min), and a single unknown X_1 (4.7 min). The relative areas for the X_1 to *t*-butyl alcohol peak were 0.98:1.0, and the area of the 1,1,2,2-tetramethylethylene oxide peak to X_1 peak 0.01:1. This was taken to indicate essentially complete reaction.

The identity of X_1 as 2,3-dimethyl-3-hydroxy-1-butene (V), $n^{20}D$ 1.4312 (lit.[21] $n^{20}D$ 1.4320), was confirmed by spectra. The infrared spectrum showed bands (assignment, vibrational mode) useful in identification at (in cm^{-1}) 3400 (OH stretching), 3090 (vinyl methyl, asymmetric stretching), 1640 (terminal vinyl, stretching), 1460 (methyl, asymmetric bending), doublet 1380 (*gem*-dimethyl, symmetric bending), 1150 (tertiary –OH, C–O, stretching), 960, 910, and 890 (terminal vinyl and terminal methylene, bending).

The nmr spectrum shows a singlet at τ 9.0 (6 H), a singlet at 8.5 (3 H), a singlet at 6.4 (OH), and broadened singlets at 5.4 and 5.7 (1 H each, vinyl methylenes).

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(21) A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964).

Table VI. Mass Spectral Analysis,[a] 2,3-Dimethyl-3-hydroxy-1-butene (V) Relative Peak Intensities[b]

m/e	Rel intensity	*m/e*	Rel intensity
18	3.5	51	1.5
26	2.5	52	2.5
27	17.0	53	1.0
28	3.5	54	3.5
29	29.5	55	2.5
31	26.7	56	9.5
37	22.0	57	29.0
38	49.5	58	11.8
39	41.0	59	100.0
40	58.0	60	3.5
41	56.0	65	23.2
42	43.0	67	13.5
43	85.0	69	3.0
44	31.5	82	2.5
45	33.0	85	81.0
50	17.5	86	82.0
		100	2.0

[a] At 20 ev. [b] Relative to largest peak.

The mass spectrum of 2,3-dimethyl-3-hydroxy-1-butene (V), Table VI, shows the parent peak at 100 and major peaks at *m/e* 85, 59, 43, and 41.

Reaction of 1,1,2-Trimethylethylene Oxide with *t*-Butoxide in DMSO. Into a pressure bottle were placed 4.3 g (0.05 mole) of 1,1,2-trimethylethylene oxide, 5.6 g (0.05 mole) of potassium *t*-butoxide, and 100 ml of DMSO. The transfers were made in a drybox free of oxygen, carbon dioxide, and moisture. The reaction mixture was allowed to stand for 2 weeks with occasional shaking in an oil bath at 45°. A color change from straw yellow to brown was noted. The pressure bottle was cooled to room temperature and opened. To the pressure bottle was added 1 ml of water and sufficient powdered Dry Ice to neutralize the solution to a phenolphthalein end point.

The volatile portion of the reaction mixture was trapped at liquid nitrogen temperature, after distillation at 0.05 mm. Analysis by vpc of the volatile portion, 10% S/F, at 140°, flow rate 44 cc/min, showed peaks for water, *t*-butyl alcohol, and DMSO as before, and trace amounts of starting material (retention time 2.8 min). There were also two unidentified peaks, X_2 and X_3. The ratio of the area of *t*-butyl alcohol:($X_2 + X_3$) was approximately 1:0.9, and the ratio of the area of X_2 to X_3 was 6:1 (retention time of X_2 4.1 min, X_3 = 4.7 min). There was insufficient separation even at lower temperature and flow rate to collect pure X_2 and X_3 with this column. However, separation of the peaks for X_2 and X_3 using a more polar vpc column, 20% S/C, at 90°, flow rate 80 cc/min (X_2 retention time 3.9 min; X_3, 6.2 min), allowed collection of sufficient pure material to identify X_2 as 3-methyl-3-hydroxybutene-1 and X_3 as 2-methyl-3-hydroxybutene-1.

The infrared spectrum of 3-methyl-3-hydroxy-1-butene (III) showed bands (assignment, vibrational mode) useful in identification at (in cm^{-1}) 3600 and 3400 (free and polymeric hydroxyl, stretching), 2960, 2870 (terminal vinyl, stretching), 1420 (terminal vinyl, bending), doublet 1380 (*gem*-dimethyl, symmetrical bending), 1150 (tertiary hydroxyl, C–O stretching), 910 (terminal vinyl, bending).

The nmr spectrum (taken in a melting point capillary) shows singlets at τ 8.95 (6 H) and 5.9 (OH), a doublet at 5.2 (J = 10 cps) each split again by J = 2.2 cps (1 H), a doublet at 5.05 (J = 17cps) each also split again by J = 2.2 cps (1 H), and a pair of overlapping doublets at 4.2 (J = 10 and 17 cps, 1 H).

Mass spectral analysis, Table VII, shows parent peak at *m/e* 86 and principal peak at *m/e* 71.

Table VII. Mass Spectral Analysis,[a] 3-Methyl-3-hydroxy-1-butene (III) Relative[b] Peak Intensities

m/e	Rel intensity
18	27.5
27	25.0
29	7.5
31	20.0
39	11.0
40	10.0
41	31.0
42	6.0
51	1.0
53	12.5
58	7.0
59	35.0
60	1.0
67	10.0
68	5.0
71	100.0
72	5.0
73	1.0
86	2.0

[a] At 20 ev. [b] Relative to largest peak.

Table VIII. Mass Spectral Analysis,[a] 2-Methyl-3-hydroxy-1-butene (IV)

m/e	Rel intensity[b]	*m/e*	Rel intensity[b]
18	2.0	45	43.0
19	4.0	50	2.0
26	16.0	51	3.0
27	37.0	54	1.0
28	18.0	55	5.0
29	24.0	57	11.0
31	4.0	58	12.0
37	3.0	59	26.5
38	6.5	65	1.0
39	42.0	67	8.0
40	8.0	68	2.0
41	59.0	69	4.0
42	20.0	71	88.0
43	100.0	72	4.1
44	6.0	85	18.5
		86	9.0

[a] At 20 ev. [b] Relative to largest peak.

The infrared spectrum of 2-methyl-3-hydroxy-1-butene (IV) showed bands (assignment, vibrational mode) useful in identification at (in cm^{-1}) 3600, 3400 (hydroxyl stretching), 3070 (vinyl methylene, asymmetric stretching), 1650 (terminal vinyl, stretching), 1450 (methyl, asymmetric bending), 1430 (terminal vinyl methine, bending), singlet 1370 (methyl symmetrical, bending), 1090 (secondary hydroxyl, C–O stretching), and 940, 950 (terminal vinyl, bending). Note the absence of a doublet at 1370–1380 cm^{-1} which indicates the absence of a *gem*-dimethyl group.[22]

The nmr spectrum (taken in a melting point capillary) shows a doublet at τ 9.0 (J = 7 cps, 3 H), a singlet at 8.5 (3 H), a very broad band at 6.0 (CH), and broadened singlets at 5.2 and 5.4 (1 H each).

Mass spectral analysis data for IV are shown in Table VIII.

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[22] The infrared spectrum was essentially identical with one kindly supplied by Dr. J. D. Roberts, California Institute of Technology, from the Ph.D. Thesis of Eugene Cox for a compound assigned the same structure.