termined by potentiometric titration of aliquots. The methoxide solution after completion of the reaction contained methyl propyl ether (74%) and methanol (26%). Neither propylene nor 1-propanol was present, which indicates that the methanol detected by gc was present in the original sodium methoxide. Had methanol been formed by methoxide hydrolysis, the hydroxide ion also produced would have yielded 1-propanol with propyl tosylate.

Values of the solvent activity coefficient differences between methanol and DMSO (${}^{M}\gamma^{D}{}_{Y^-}$) for anions have been published.[1] Values of ${}^{M}\gamma^{D}{}_{PrOTs}$ and the rates of reaction of *n*-propyl tosylate with nucleophilies in methanol are not available but have been estimated from Parker's data[1] for methyl tosylate. The uncertainties of these estimates are probably no greater than that for the anions (±0.3 log units[1]). Log ${}^{M}\gamma^{D}$ was estimated in the following way: $\log {}^{M}\gamma^{DMF}{}_{MeOTs} = -0.6$; $\log {}^{M}\gamma^{DMF}{}_{MeCl} - \log {}^{M}\gamma^{DMF}{}_{t\text{-}BuCl} = +0.2$, and $\log {}^{M}\gamma^{DMF}{}_{MeBr} - \log {}^{M}\gamma^{DMF}{}_{n\text{-}BuBr} = +0.2$; $\log {}^{DMF}\gamma^{D} = 0.0$ to $+0.2$ (MeI, *n*-BuBr, *t*-BuCl). We have therefore made corrections of +0.2 for the larger alkyl group of *n*-PrOTs, and +0.1 for the DMF to DMSO transfer, to give an estimated value of $\log {}^{M}\gamma^{D}{}_{PrOTs} = -0.3$.

From our unpublished rate data for the reactions of MeOTs with Cl^-, Br^-, and I^- in aqueous DMSO (70, 80, and 85% DMSO by volume), we have estimated $\log k_{MeOTs} - \log k_{PrOTs} = 1.4$ (a comparison of values[1] for MeX and *n*-BuX with five nucleophiles in MeOH affords an average value of 1.1). Transfer values for some of the anions in Table I, or appropriate rates in methanol, are not available; these have been omitted from Table II.

TABLE I

RATES OF TOSYLATE DISPLACEMENT IN DMSO

Nucleophile	Tosylate	Temp, °C	$10^5 k_{obsd}$ l. mol^{-1} sec^{-1}	Corrections[a]	Est $10^5 k_2$ PrOTs, 25°
$S_2O_3^{2-}$	Pr	20	5.60×10^4	t_1	9.4×10^4
OH^-	Pr	20	3.67×10^4	t_1, p_1	2.9×10^4
CH_3O^-	Pr	20	1.63×10^4	t_1	2.7×10^4
F^-	Hex	−4.5	7.34×10^2	t_2, s[b]	2.0×10^4
$C_6H_5O^-$	Pr	20	1.57×10^3	t_1	2.6×10^3
N_3^-	Pr	30	3.89×10^2	t_4	2.7×10^2
Cl^-	Pr	20	5.68×10		
	Pr	30	1.37×10^2	t_4	9.5×10
	Pr	40	3.54×10^2		
	Hex	20	4.64×10		
	Hex	−4.5	3.54	*b*	
	Pr	60	3.03×10^3	*b*	
	Pr	60	2.90×10^3		
Br^-	Pr	30	5.26×10	t_4	4.1×10
	Pr	50	4.88×10^2	(Bu_4NBr)	
	Pr	50	4.78×10^2	(KBr)	
I^-	Pr	40	4.33×10	t_3	1.2×10
SCN^-	Pr	40	1.26×10	t_3	3.4
C_6H_5NHMe	Pr	40	1.20×10	t_3	3.2

[a] Temperature: t_1, $k_{25}/k_{20} = 1.67$; t_2, $k_{25}/k_{-4.5} = 22.0$; t_3, $k_{25}/k_{40} = 0.268$; t_4, $k_{25}/k_{30} = 0.692$; k_{25}, obtained from Arrhenius plot for PrOTs with chloride ion. Product (fraction of total rate leaing to expected substitution product): p_1, $k_S/(k_T + k_E) = 0.48$. Substrate(s), $k_{Pr}/k_{Hex} = 1.22$. [b] At higher concentration in 45% DMSO–55% tetramethylene sulfoxide (v/v) (see text). All rates are the average of two or more determinations.

The relative nucleophilicities of anions toward alkyl tosylates are reasonably consistent among protonic solvents, and among aprotic solvents, but not between the two groups. The orders of decreasing nucleophilicity follow: EtOTs in H_2O,[4] $S_2O_3^{2-} > N_3^- > OH^- > SCN^1 \sim I^-$; MeOTs in MeOH,[1] $N_3^- > I^- > SCN^- > Br^- > Cl^-$; MeOTs in DMF,[1] $N_3^- \sim Cl^- > I^- > SCN$; PrOTs in DMSO (Table I), $S_2O_3^{2-} > OH^- \sim CH_3O^- \sim F^- > C_6H_5O^- > N_3^- > Cl^- > Br^- > I^- > SCN^-$. In both aprotic solvents the now familiar order of halide reactivity is observed. In DMSO azide ion is distinctly more nucleophilic than chloride. Thiosulfate is most nucleophilic in water and in DMSO. However, if OH^-, CH_3O^-, and F^- were free of hydroxylic solvation and ion association in DMSO, it is probable that these anions would be more reactive than thiosulfate. There is a tendency for the small basic anions to be highly nucleophilic in DMSO, whereas strong hydrogen bonding greatly decreases the relative reactivity of these ions in protonic solvents. Larger more polarizable anions undergo relatively small changes in solvation in the transfer from aprotic to protic solvents.[1,5] The slightly increased solvation of propyl tosylate and the decreased solvation of the transition states in DMSO (relative to methanol) both have a rate decreasing effect. But the more important factor (in this system) of anion desolvation leads to the observed rate increases, which are most striking for small nucleophiles.

TABLE II

SN2 REACTIONS OF ANIONS AND *n*-PROPYL TOSYLATE AT 25° IN METHANOL AND DIMETHYL SULFOXIDE

						MeOTs,[d]
Nu^-	Log $k^{D}{}_{PrOTs}$[a]	Log k^D/k^M[b]	Log ${}^{M}\gamma^{D}{}_{PrOTs}$	Log ${}^{M}\gamma^{D}{}_{Y^-}$	Log ${}^{M}\gamma^{D}{}_{\ddagger}$[c]	Log ${}^{M}\gamma^{DMF}{}_{\ddagger}$
N_3^-	−2.6	2.1	−0.3	3.5	1.1	2.3
Cl^-	−3.0	3.5	−0.3	5.5	1.7	2.1
Br^-	−3.4	2.6	−0.3	3.6	0.7	1.2
I^-	−3.9	0.9	−0.3	1.3	0.1	0.6
SCN^-	−4.5	0.8	−0.3	1.4	0.3	1.3

[a] Rate of reaction of *n*-PrOTs in DMSO at 25° with indicated nucelophile. [b] Relative rates in DMSO *vs.* MeOH. [c] Change in solvent activity coefficient of the SN2 transition state upon transfer from MeOH to DMSO. [d] Change in γ for the transition state of the $CH_3OTs + Nu^-$ reaction upon transfer from MeOH to dimethylformamide (ref 1).

Registry No.—*n*-Propyl tosylate, 599-91-7.

Acknowledgment.—This work was supported by the Robert A. Welch Foundation (Grant E-136).

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[5] R. Fuchs, J. L. Bear, and R. F. Rodewald, *ibid.*, **91**, 5797 (1969).

Neighboring-Group Participation in Free-Radical Reactions of Halohydrins and Hydroxy Sulfides[1]

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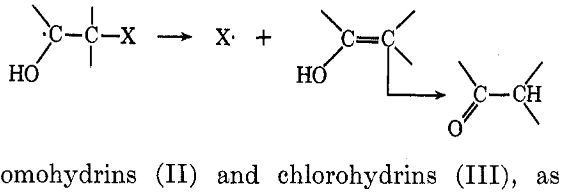
Peroxide-induced decomposition reactions of β-hydroxy sulfides (I) yielding mercaptans and ketones proceed by the free-radical chain sequence 1 and 2.[2]

(1)

I, X = RS
II, X = Cl
III, X = Br



(2)

Bromohydrins (II) and chlorohydrins (III), as expected, decompose by a similar chain sequence (see Experimental Section) since halogen atoms are both good hydrogen atom abstractors and undergo β elimi-

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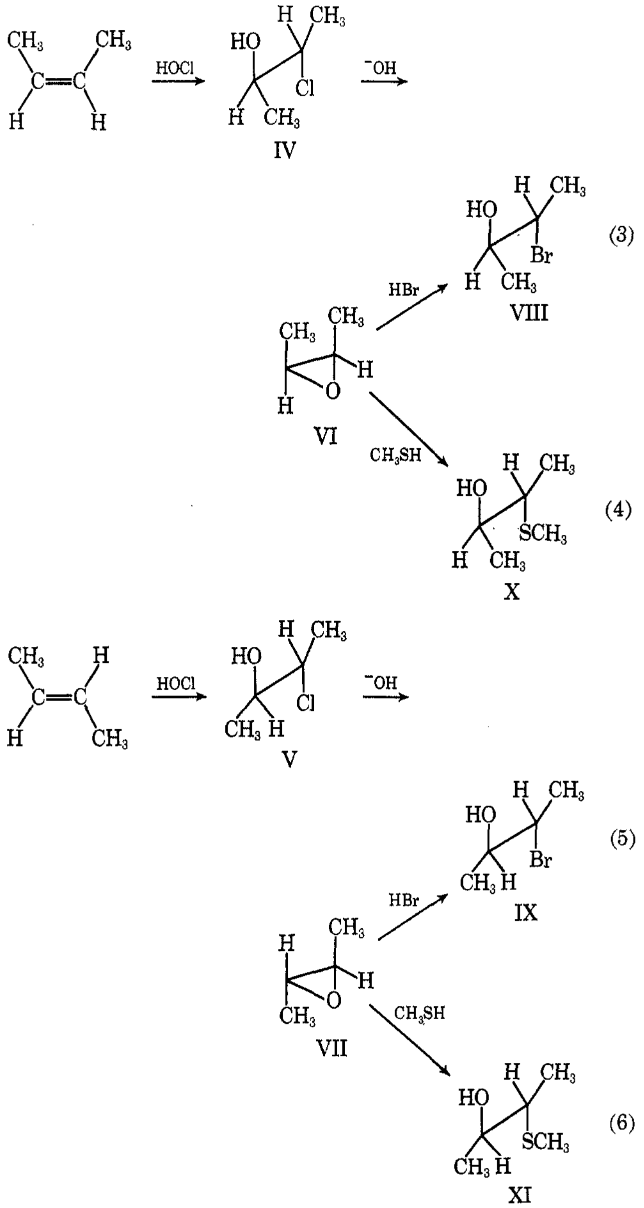
[1] This work was supported by a grant (GP-8578) from the National Science Foundation.

[2] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **31**, 3366 (1966).

nation readily.[3] The stereochemical aspects of the hydrogen atom abstraction reaction in the chain sequence described here indicate participation of a bridged radical species in the transition state of the reaction.

The stereoisomeric *threo*- and *erythro*-3-chloro-2-butanols (IV and V, respectively) were prepared by addition of hypochlorous acid to *cis*- and *trans*-2-butene, respectively. *cis*- and *trans*-2,3-epoxybutanes (VI and VII) were obtained by reaction of IV and V, respectively, with base. Reaction of VI and VII with hydrobromic acid or sodium methyl sulfide in alcohol yielded the stereoisomeric bromohydrins VIII and IX and hydroxy sulfides X and XI.



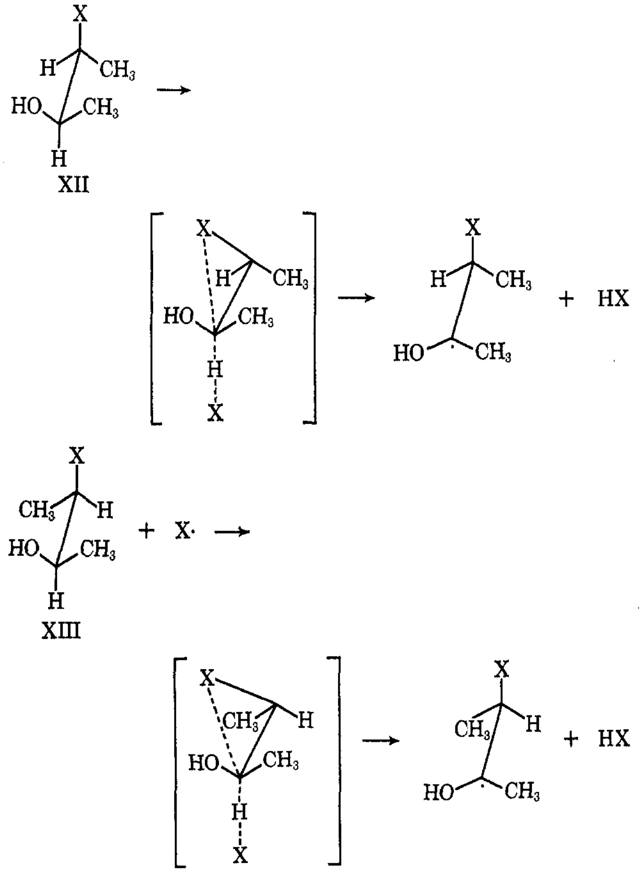
Competition reactions of the stereoisomeric pairs serve to measure the relative rates at which the hydrogen abstraction reaction from the two isomers occurs. The results of these competition studies are given in Table I.

TABLE I

COMPETITION REACTIONS OF STEREOISOMERIC 3-HALO- AND 3-METHYLTHIO-2-BUTANOLS

Compd	$k_{threo}/k_{erythro}$	No. of runs	Av dev
3-Chloro-2-butanols (IV and V)	1.02	2	0.01
3-Bromo-2-butanols (VIII and IX)	1.44	5	0.04
3-Methylthio-2-butanols (X and XI)	1.26	3	0.04

Although the isomeric chlorohydrins have essentially the same reactivity, the threo isomers of the bromohydrins and hydroxy sulfides are more reactive than the corresponding erythro isomers toward hydrogen abstraction. The greater reactivity of the threo isomers can be accounted for in terms of anchimeric assistance of the bromine and methanethio group in forming a bridged radical in the transition states of the hydrogen abstraction reaction. In order for the bridged radical to contribute to the transition state, its conformation must be such that the neighboring group is anti to the hydrogen being abstracted. The energy of the transition state of erythro isomers (XII) in this conformation is greater than that of the threo (XIII) owing to the gauche interaction of the two methyl groups in XII.



Bridging of a β bromine with the carbon from which a hydrogen is abstracted by a bromine atom has been suggested to account for the enhanced reactivities of β hydrogens in the brominations of bromoalkanes.[4]

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[3] L. P. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, **71**, 2015 (1949); K. E. Wilzback, F. R. Mayo, and R. Van Meter, *ibid.*, **70**, 4069 (1948); D. H. R. Barton, *J. Chem. Soc.*, **148**, 155 (1949); N. V. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.*, **74**, 4141 (1952); F. Wackhaltz, *Z. Phys. Chem. (Leipzig)*, **126**, 1, (1927).

[4] W. A. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963); P. S. Skell and P. D. Readio, *ibid.*, **85**, 2849 (1963). For an alternative explanation, see D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *ibid.*, **91**, 7398 (1969).

Such neighboring-group participation is a significant factor if the transition state of the reaction involves breaking of the carbon–hydrogen bond and consequently radical formation at the carbon atom allowing for the bridged radical to contribute to lowering the activation energy requirement. The effect is observed in the endothermic hydrogen abstraction by bromine atoms and might be expected in hydrogen atom abstraction by the thiyl radical which is also an endothermic reaction. Contribution of the bridged radical species to the hydrogen abstraction from the chlorohydrins IV and V by a chlorine atom is small. Little carbon–hydrogen bond breaking develops in the transition state of the reaction, and consequently the carbon has little radical character to allow for bridging with the β chlorine. This being the case, no advantage is obtained in the conformational requirement of positioning the chlorine anti to the abstracted hydrogen. The lack of a neighboring-group effect in the chlorohydrin reaction cannot be attributed to the inability of the chlorine, which is isoelectronic with bivalent sulfur, to form bridged radicals since such species have been reported in other systems.[5]

Experimental Section[6]

threo-**3-Chloro-2-butanol (IV)** was prepared from *cis*-2-butene and hypochlorous acid by the general method described by Coleman and Johnstone,[7] bp 24–26° (5 mm) [lit.[8] bp 36.5–40 (14 mm)]. The ir and nmr spectra of the material were consistent with the assigned structure.

erythro-**3-Chloro-2-butanol (V)** was prepared from *trans*-2-butene and hypochlorous acid,[7] bp 55–60° (80 mm) [lit.[8] bp 44–44.5° (16–20 mm)]. The ir and nmr spectra were consistent with the assigned structure.

cis-**2,3-Epoxybutane (VI)**.—This material was prepared both by reaction of *cis*-2-butene with *m*-chloroperbenzoic acid following the procedure of Pasto and Cumbo[9] and by elimination of hydrogen chloride from *threo*-chloro-2-butanol with potassium hydroxide in aqueous solution as described by Wilson and Lucas,[10] bp 58–59° (lit.[10] bp 59.9–60.4°).

trans-**2,3-Epoxybutane (VII)**.—This compound was prepared from *trans*-2-butene and *erythro*-3-chloro-2-butanol, respectively, by methods described in the previous experiment, bp 53.0–54.5° (lit.[10] bp 53.6–54.1°).

threo-**3-Bromo-2-butanol (VIII)**.—*cis*-2,3-Epoxybutane was added dropwise with constant stirring to an excess of 48% hydrobromic acid cooled in an ice bath. The mixture was allowed to stir for 6 hr and then neutralized with sodium bicarbonate and extracted with ether. After the ether solution was dried over anhydrous magnesium sulfate, the solvent was removed leaving a residue which on distillation gave the desired product, bp 35–38° (5.8 mm) [lit.[11] bp 48–50° (12 mm)].

erythro-**3-Bromo-2-butanol (IX)**.—*trans*-2,3-Epoxybutane gave IX when it was allowed to react with hydrobromic acid in the manner described in the previous experiments, bp 41–43° (6.2 mm) [lit.[11] bp 51–53° (12 mm)].

threo-**3-Methylthio-2-butanol (X)**.—*cis*-2,3-Epoxybutane was added dropwise to an alcoholic solution of sodium methyl sulfide (prepared from methanethiol and sodium ethoxide in absolute ethanol) at 0–5°. After the solution was stirred at room temperature for 20 hr, the resulting mixture was taken up in ether and washed repeatedly with sodium bicarbonate and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and, after removal of the ether, distillation of the resulting residue gave the desired product (50% of theory), bp 38–39° (1.45–1.50 mm).

Anal. Calcd for $C_5H_{12}OS$: C, 50.00; H, 10.07; S, 26.70. Found: C, 50.12; H, 10.31; S, 26.12.

erythro-**3-Methylthiol-2-butanol (XI)** was prepared in about 50% yield from *trans*-2,3-epoxybutane by the same procedure, bp 48–51° (1.35–1.50 mm).

Anal. Calcd for $C_5H_{12}OS$: C, 50.00; H, 10.07; S, 26.70. Found: C, 50.34; H, 10.22; S, 26.29.

General Procedures for Competition Reaction.—Solutions consisting of a pair of epimeric alcohols, di-*tert*-butyl peroxide (5–10 mol %), an internal standard for the gas chromatographic analyses (chlorobenzene for the 3-chloro-2-butanols and bromobenzene for 3-bromo-2-butanols and 3-methylthio-2-butanols), and acid scavenger (propylene oxide or cyclohexene oxide) were divided into several Pyrex tubes, sealed, and placed in a constant temperature bath set at 125°. Tubes were removed after several hours, by which time 25–30% of the less reactive isomer had reacted, and then immediately cooled to 0°. The reaction mixtures were analyzed on a F & M Model 5750 gas chromatograph using a 8 ft × $^1/_8$ in. column packed with 15% E600 on Chromosorb W. The peak areas of the epimeric alcohols and the internal standard were used to determine the amount of epimeric alcohols remaining in the sample. The relative reactivity ratios were calculated from the initial quantities and amounts remaining of each epimer using the equation

$$\frac{k_{\text{threo}}}{k_{\text{erythro}}} = \frac{\log\ (\text{threo})_i/(\text{threo})_f}{\log\ (\text{erythro})_i/(\text{erythro})_f}$$

where the subscripts i and f refer to the initial and final amounts, respectively.

Control Experiments.—When heated for several hours at 125° in the absence of *tert*-butyl peroxide, the isomeric halohydrins and hydroxy sulfides did not yield 2-butanone as a reaction product. All of the compounds did show some degree of thermal instability but decomposed at considerably slower rates than the *tert*-butyl peroxide induced reactions yielding 2-butanone. The thermal decomposition products were not identified.

Registry No.—IV, 10325-40-3; V, 10325-41-4; VIII, 19773-41-2; IX, 19773-40-1; X, 27022-36-2; XI, 27022-37-3.

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[6] All boiling points are uncorrected. Elemental analyses performed by Wiler and Straus, Oxford, England.

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On the Reality of Solvent Effects in the Decomposition of *tert*-Butyl Peroxide[1]

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Although the rate of decomposition of *tert*-butyl peroxide was originally described as essentially the same in the gas phase and a variety of solvents,[2] appreciable variations have subsequently been reported. The decomposition rate of the pure liquid peroxide is increased severalfold by an induced decomposition[3]

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[1] Partial support of the work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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[3] E. R. Bell, F. F. Rust, and W. E. Vaughan, *ibid.*, **72**, 337 (1950).