amines, N-allylpiperidine, N-2-methylallylpiperidine and diethyl-2-methylallylamine, were reduced by sodium and methanol in liquid ammonia to the corresponding saturated amines, while N-crotylpiperidine, N-2-*t*-butylallylpiperidine, N-cyclohex-2-enylpiperidine and N-2,3,4,5-tetrahydrobenzylpiperidine were unaffected by the same reagent. In no case was a non-terminal olefin reduced.

The successful reduction of 1-hexene invalidates the generally held opinion that isolated carbon–carbon double bonds are inert in metal–liquid ammonia systems. Failure to obtain reduction of 2-hexene is consistent with King's observation[6] that reduction of non-conjugated olefins under these conditions is confined to terminal double bonds. A satisfactory interpretation of these results must await further experimental data.

The reduction of 2-cyclopropyl-1-pentene by sodium and methanol in liquid ammonia does not appear to proceed more readily than the similar reduction of 1-hexene and gives no ring-opening products. The reduction of the cyclopropyl olefin would thus indicate that the conjugation between the cyclopropyl group and the ethylenic linkage is not a first-order conjugation. This result is in agreement with considerable spectroscopic evidence that the conjugation of the cyclopropyl group with an unsaturated center is a second-order conjugation, that is, hyperconjugation.[7]

Acknowledgment.—We wish to express our appreciation to Vernon A. Slabey and Paul H. Wise of the Lewis Flight Propulsion Laboratory of the National Advisory Committee for Aeronautics for a sample of 2-cyclopropyl-1-pentene and for an infrared spectrum of 2-cyclopropylpentane, and to John A. Queiser for the determination of infrared spectra.

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(7) For leading references, see R. P. Mariella and R. R. Raube, THIS JOURNAL, **74**, 518 (1952).

BRUCETON, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Reaction of Propylene Oxide with Hydrogen Halides

BY C. A. STEWART AND CALVIN A. VANDERWERF

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Extent of attack on the secondary carbon by halide ion on propylene oxide in ring-opening reactions with hydrogen chloride, hydrogen bromide and with hydrogen iodide has been found to decrease in the order Cl > Br > I and to increase with increase in temperature. Entropies and enthalpies of activation have been calculated and the differences are rationalized by consideration of transition state structures. Significant solvent effects in the reactions also have been observed. Addition of positive halogen 3,5-dinitrobenzoates to propylene has been found to afford largely the secondary ester, with an increase in primary ester formation accompanying an increase in temperature. Analysis of isomeric content of reaction products was accomplished largely by infrared spectrophotometric methods.

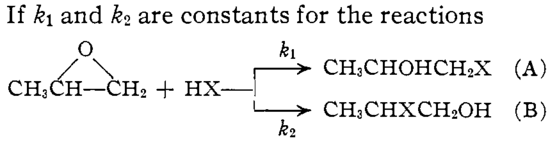
As part of a general study of factors affecting the direction of ring opening in unsymmetrically substituted ethylene oxides, a comparison has been made of the reactions of the simplest of these compounds, propylene oxide, with hydrochloric, with hydrobromic and with hydriodic acid. The choice of propylene oxide as a substrate for such a study was dictated by the following considerations: (1) the reaction of propylene oxide with hydrochloric acid is known[1] to give a mixture of isomers; (2) from the data of Levene and Walti,[2] it may be assumed that reaction at either carbon takes place with Walden inversion and that the kinetics for both reactions are presumably the same; (3) the smaller the molecule, the greater are the expected differences in the properties of the primary and secondary alcohol products, since the functional group is a correspondingly greater part of the molecule; and (4) the propylene chlorohydrins have already been prepared and characterized.[3]

Smith and Skyle[1] reported that both hydrochloric and hydrobromic acids gave 90% of attack of halogen at the primary carbon of glycidol, while 1,2-epoxybutane has been found[4] to give increasingly greater attack in the primary position as the size of the halogen increases. In this connection, it is significant that Swain[5] has provided quantitative evidence for the long accepted generalization that the base strengths toward carbon of the halide ions are in the same order as the size of the ions, that is, chloride < bromide < iodide.

From the theory of absolute reaction rates, the relative rates of formation of two isomers from the same reactants may be related by the equation[6]

$$\ln\frac{k_1}{k_2} = \frac{\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}}{R} - \frac{\Delta H_1^{\ddagger} - \Delta H_2^{\ddagger}}{RT} \qquad (1)$$

If k_1 and k_2 are constants for the reactions



then from a plot of the reciprocal temperature *versus* the logarithmic ratio of product A to product B obtained in the reaction, it should be possible to evaluate the differences in entropy and enthalpy of activation from the intercept and slope of the straight line predicted from the equation 1. If the differences between chloride, bromide, and iodide are due only to steric effects, one might expect that the en-

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(1) L. Smith and S. Skyle, *Acta Chem. Scand.*, **5**, 1415 (1951).

(2) P. A. Levene and A. Walti, *J. Biol. Chem.*, **73**, 263 (1926).

(3) (a) W. A. Raimond, Ph.D. Dissertation, Rutgers University, 1942; (b) W. Fickett, H. K. Garner and H. J. Lucas, THIS JOURNAL, **73**, 5063 (1951).

(4) B. I. Halperin, H. B. Donahoe, J. Kleinberg and C. A. VanderWerf, *J. Org. Chem.*, **17**, 623 (1952).

(5) C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 118–124.

TABLE I

PHYSICAL PROPERTIES OF PROPYLENE HALOHYDRINS

	Compound	B.p. °C.	Mm.	$n^{30}D$	d^{30}_4	Molar refraction	Neut. equiv.
I	1-Chloro-2-propanol	50.6-50.8	30	1.4352	1.1005	22.43^a	94.6^b
II	2-Chloro-1-propanol	53.0-53.6	29	1.4356	1.0903	22.56^a	94.9^b
III	1-Bromo-2-propanol	62.0-62.2	26	1.4762	1.5585	25.17^c	138.9^d
IV	2-Bromo-1-propanol	62.8-64.0	24	1.4785	1.5551	25.32^c	138.9^d
V	1-Iodo-2-propanol	59.0-63.0	9	1.5365	1.8999	30.54^e	185.2^f
VI	2-Iodo-1-propanol	74.0-79.0	20	1.5392	1.8902	30.83^e	181.5^f

Calculated: [a] 22.45; [b] 94.6; [c] 25.35; [d] 139.0; [e] 30.36; [f] 186.0.

thalpy term should be relatively constant, whereas if they result only from differences in base strength, or electronic character, the entropy term should be nearly constant.

Results

The isomeric propylene chlorohydrins and bromohydrins have been synthesized by lithium aluminum hydride reduction of the corresponding haloketones and haloacid halides. The iodohydrins have been synthesized by exchange between the bromohydrins and sodium iodide in acetone. The physical properties of the halohydrins are recorded in Table I.

Infrared spectra of these compounds (see Figs. 3 and 4 for spectra of the chlorohydrins) show that each of the three secondary alcohols gives an absorption peak at about 935 cm.$^{-1}$, and that each of the primary alcohols gives a peak at about 980 cm.$^{-1}$. From the relative heights of these peaks, satisfactory analytical methods have been devised for binary mixtures of each pair of isomers. The ratio of isomers obtained from propylene oxide in water and ether solutions has been determined as a function of temperature and the results plotted by equation 1 in Figs. 1 and 2. The differences in entropy and enthalpy of activation calculated from these lines are given in Table II.

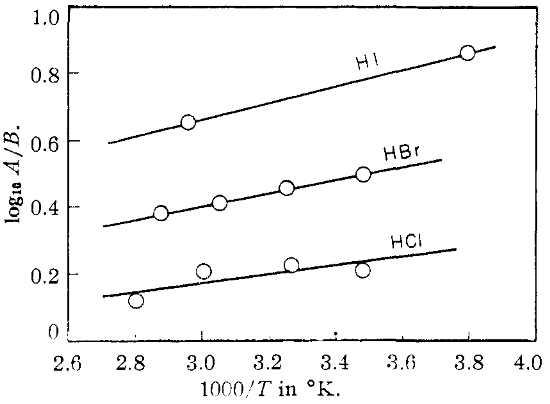

Fig. 1.—van't Hoff plot, propylene oxide + HX, aqueous.

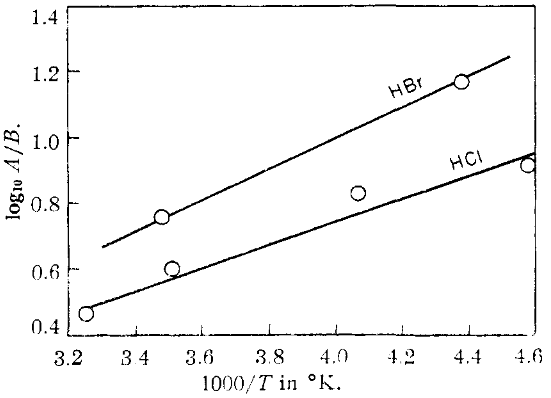

Fig. 2.—van't Hoff plot, propylene + HX, ether.

TABLE II

DIFFERENCES IN ENTROPY AND ENTHALPY OF ACTIVATION

Halide	Solvent	$\Delta(\Delta S^{\ddagger})$, cal./mole/deg.	$\Delta(\Delta H^{\ddagger})$, kcal./mole
Cl	Water	−0.85	−0.55
Br	Water	−0.70	−0.85
I	Water	-0.32^a	-1.12^a
Cl	Ether	−2.8	−1.54
Br	Ether	−2.0	-1.56^a

[a] Data from two determinations only.

The reactions of propylene oxide with sodium bromide, ammonium bromide and magnesium bromide etherate also have been studied, and the orientation of ring opening determined. With ammonium and magnesium bromides, the orientation was only slightly more toward the primary carbon than for the corresponding reaction with hydrogen bromide. With sodium bromide, however, orientation was almost totally (95%) toward the primary carbon whereas hydrogen bromide under the same conditions gave 25% of the isomer corresponding to secondary attack.

The addition of halogen(I) 3,5-dinitrobenzoates[4] to propylene to form the esters of the halohydrins also has been studied. At Dry Ice temperature, only the "normal" or Markownikoff product was obtained, while at 0°, mixtures containing small amounts of the primary alcohol were formed in the reaction. The addition of catalytic amounts of benzoyl peroxide appeared to have no effect on the reaction.

Experimental

1-Chloro-2-propanol (I).—To an ice-cold slurry of 50.0 g. (1.28 moles) of lithium aluminum hydride in one liter of ether, 330 g. (3.60 moles) of chloroacetone was added over a period of one hour. The reaction mixture was allowed to stand for half an hour before decomposition of the excess hydride with water. Sufficient sulfuric acid (4 N) was then added to give a separable mixture. The ether layer was decanted and the aqueous layer extracted with three 300-ml. portions of ether. The combined ether layers were dried, first over sodium sulfate, then over magnesium sulfate. The ether was removed on a steam-bath, and the remaining liquid was distilled at reduced pressure to give 150 g. (44%) of crude material boiling at 50.6–50.8° at 30 mm. when fractionated through a 100-cm. glass-bead column.

I was prepared also by the sulfuric acid-catalyzed hydration of allyl chloride by the procedure of Dewael.[7] No trace of isomeric chlorohydrin could be detected.

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[7] A. Dewael, *Bull. soc. chim. Belg.*, **39**, 87 (1930).

TABLE III

3,5-DINITROBENZOATE ESTERS

Propanols	Ester	Yield, %	M.p., °C.	Analyses, % Carbon Calcd.[a]	Carbon Found	Hydrogen Calcd.[a]	Hydrogen Found	Halogen Calcd.[a]	Halogen Found	Nitrogen Calcd.[a]	Nitrogen Found
1-Chloro-2	VII	72	82.8– 83.8[b]								
2-Chloro-1	VIII	88	77.0– 77.9[c]								
1-Bromo-2	IX	69	92.4– 92.9	36.0	36.3	2.7	2.6	24.0	23.9	8.4	8.5
2-Bromo-1	X	66	78.2– 79.2	36.0	35.9	2.7	2.6	24.0	23.9	8.4	8.2
1-Iodo-2	XI	88	81.6– 83.8	31.5	31.8	2.4	2.3	33.4	33.1	7.4	7.5
2-Iodo-1	XII	82	99.4–100.5	31.5	32.1	2.4	2.3	33.4	33.3	7.4	7.4

[a] For $C_{10}H_9N_2O_6X$. [b] Reported[3a] 83.6–84.7°. [c] Reported[3b] 78.0–78.3°.

2-Chloro-1-propanol (II).—II was prepared by lithium aluminum hydride reduction of α-chloropropionyl chloride by the procedure of Fickett, Garner and Lucas.[3] An 82% yield of product, b.p. 53.0–53.6° at 29 mm., was obtained.

Bromopropanols.—1-Bromo-2-propanol (III), b.p. 62.0–62.2° at 26 mm., and 2-bromo-1-propanol (IV), b.p. 62.8–64.0° at 24 mm., were prepared in 29 and 84% yields, respectively, by lithium aluminum hydride reduction of bromoacetone and α-bromopropionyl bromide. III was also prepared by sulfuric acid-catalyzed hydration of allyl bromide, following the procedure for the chloro compound. Infrared analysis by the method described below indicated that the product, which was obtained in 11% yield, contained 91% of III and 9% of the isomeric IV.

1-Iodo-2-propanol (V).—A mixture of 26.8 g. (0.200 mole) of 1-bromo-2-propanol (III), 30.5 g. (0.200 mole) of sodium iodide and 150 ml. of anhydrous acetone was refluxed for ten hours. After removal of the acetone under reduced pressure, the halohydrin was dissolved in 75 ml. of ether, filtered to remove sodium bromide, and distilled. Approximately 27.5 g. (74%) of pure material, b.p. 59–63° at 9 mm., and an additional 4.5 g. (12%) of less pure fore and end fractions were obtained.

2-Iodo-1-propanol (VI).—By the procedure described for V, but with a 40-hr. reflux period for the less reactive secondary halide, 25.0 g. (67%) of product boiling at 74–79° at 20 mm. was obtained. Redistillation at 9 mm. produced slight decomposition and was not effective in removing the small amount of free iodine present.

Dinitrobenzoate Esters.—Each halohydrin was esterified by heating of 0.01–0.015 mole of the alcohol with a 5–10% excess of 3,5-dinitrobenzoyl chloride (recrystallized Eastman Kodak product) for a period of 1–4 hr. The reaction mixture was taken up in chloroform, washed with sodium carbonate solution, and the chloroform evaporated under a stream of dry air. The crude material thus obtained was recrystallized several times from technical heptane which had been purified by shaking with sulfuric acid and distillation over sodium. The yields and melting points of the dinitrobenzoates are reported in Table III.

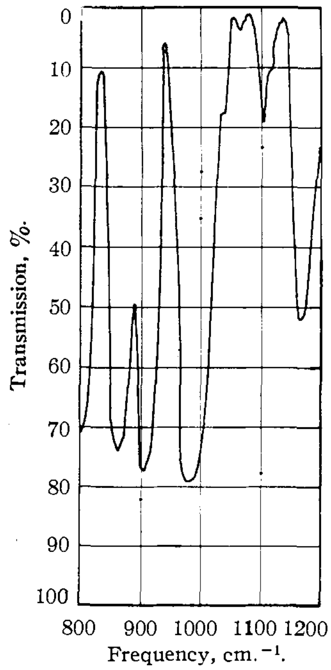


Fig. 3.—Portion of infrared spectrum of 1-chloro-2-propanol.

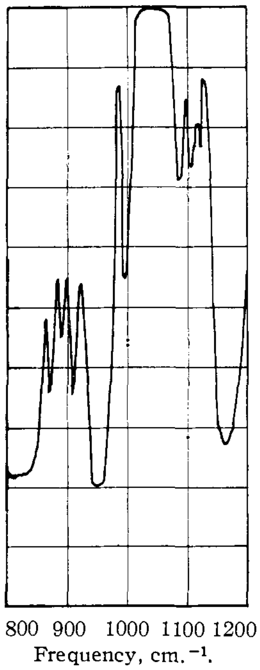


Fig. 4.—Portion of infrared spectrum of 2-chloro-1-propanol.

Infrared Spectra and Analysis.—The spectrum of each of the compounds was determined by means of a Perkin-Elmer Model 21 Infrared Spectrophotometer. The spectra of the halohydrins were taken on the pure liquids in 0.025-mm. sodium chloride cells, and those of the dinitrobenzoates on solutions of 150 mg. of solid per ml. of chloroform in 0.05-mm. cells. Portions of the chlorohydrin spectra are shown in Figs. 3 and 4.

Isomeric mixtures of the halohydrins were analyzed from the peaks occurring at 925 to 940 cm.$^{-1}$ for the secondary alcohols and at 970–985 cm.$^{-1}$ for the primary alcohols. The ratio of the heights of these peaks measured in percentage transmission from the minimum between them is shown as a function of composition for synthetic mixtures of the pure isomers in Figs. 5, 6 and 7.

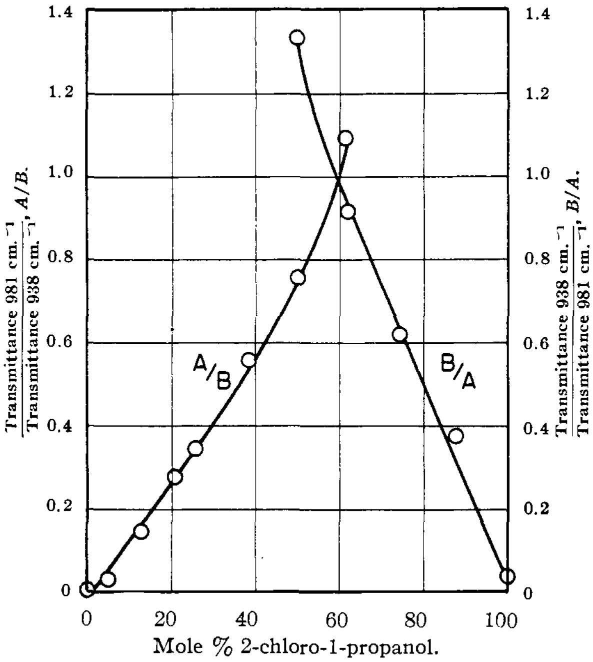


Fig. 5.—Calibration curves for infrared analysis of mixtures of 1-chloro-2-propanol and 2-chloro-1-propanol.

Ring Opening Reactions of Propylene Oxide.—Propylene oxide was treated under the reaction conditions listed. Results of infrared analysis of the products are given in Table IV.

(a) Fifty ml. (0.715 mole) of propylene oxide was added to 400 ml. of a solution 2.5 *M* in sodium chloride and 6 *M* in hydrochoric acid, held at a specified temperature. The

TABLE IV

RING OPENING REACTIONS OF PROPYLENE OXIDE

Reagent	Solvent and procedure	Temp., °C.	Yield, %	$n^{30}D$	Neut. equiv.[a]	Products A	Products B	% A	% B
HCl	Ether(b)	-55	95	1.4350	94.5	I	II	89	11
	Ether (b)	-27	89	1.4350	95.0	I	II	87	13
	Ether(b)	12	87	1.4349	95.9	I	II	80	20
	Ether(b)	35	85	1.4352	95.5	I	II	74	26
	Water(a)	15	61	1.4352	94.9	I	II	62	38
	Water(a)	33	64	1.4350	94.8	I	II	63	37
	Water(a)	60	64	1.4352	95.0	I	II	62	38
	Water(a)	83	59	1.4352	94.5	I	II	56	44
	Acetone(b)	10	87	1.4350	94.8	I	II	84	16
HBr	Ether(c)	-45	98	1.4830	[b]	III	IV	92	8
	Ether(c)	15	100	1.4816	[b]	III	IV	85	15
	Water(d)	15	77	1.4772	138.4	III	IV	76	24
	Water(d)	35	84	1.4767	138.4	III	IV	74	26
	Water(d)	55	77	1.4765	139.0	III	IV	72	28
	Water(d)	75	76	1.4765	139.7	III	IV	71	29
$MgBr_2$	Ether(g)	35	60	1.4764	139.3	III	IV	84	16
NH_4Br	Water(f)	30	71	1.4756	...	III	IV	77	23
NaBr	Water(h)	22	62	1.4754	139.2	III	IV	95	5
HI	Water(e)	-10	75	[b]	[b]	V	VI	88	12
HI	Water(e)	65	75	[b]	[b]	V	VI	82	18

[a] Calcd. for C_3H_7ClO, 94.5; C_3H_7BrO, 139.0; C_3H_7IO, 186.0. [b] Impure products ($C_3H_6Br_2$ or iodine).

reaction mixture was extracted with ether and the extract dried, heated on a steam-bath to remove ether, and distilled through a 100-cm. Vigreux column.

(b) Fifty ml. of propylene oxide and anhydrous hydrogen chloride were added simultaneously to 400 ml. of ether containing a small amount of thymol blue. The rates of addition were adjusted so that the solution was near the color change from yellow to red (*p*H 2–3 in water). The solution was connected to an aspirator to remove solvent, and the mixture was distilled as in (a).

(c) Fifty ml. of propylene oxide and anhydrous hydrogen bromide were allowed to react as in (b). The excess hydrogen bromide and ether were removed on a steam-bath; the resulting bromohydrin contained difficultly separable impurities, probably the dibromide.

(d) Fifty ml. of propylene oxide was added slowly to 125 ml. of concentrated hydrobromic acid. The bromohydrin was isolated as in (a).

(e) Propylene oxide (29 g., 0.50 mole) was added to a

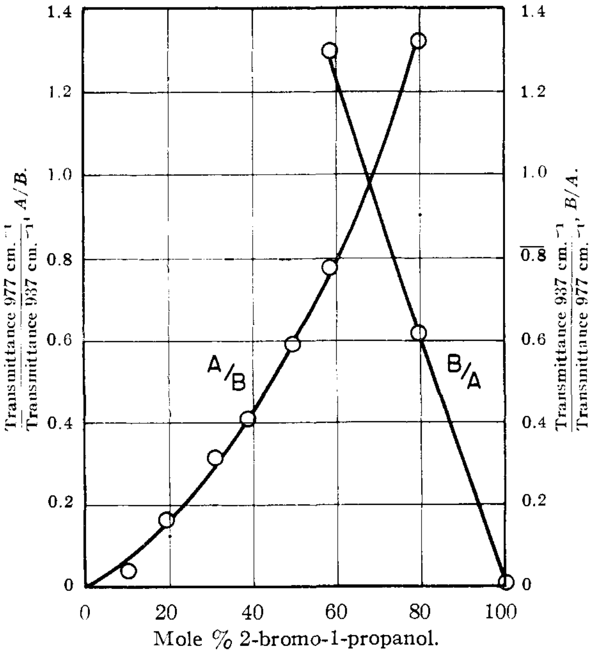


Fig. 6.—Calibration curves for infrared analysis of mixtures of 1-bromo-2-propanol and 2-bromo-1-propanol.

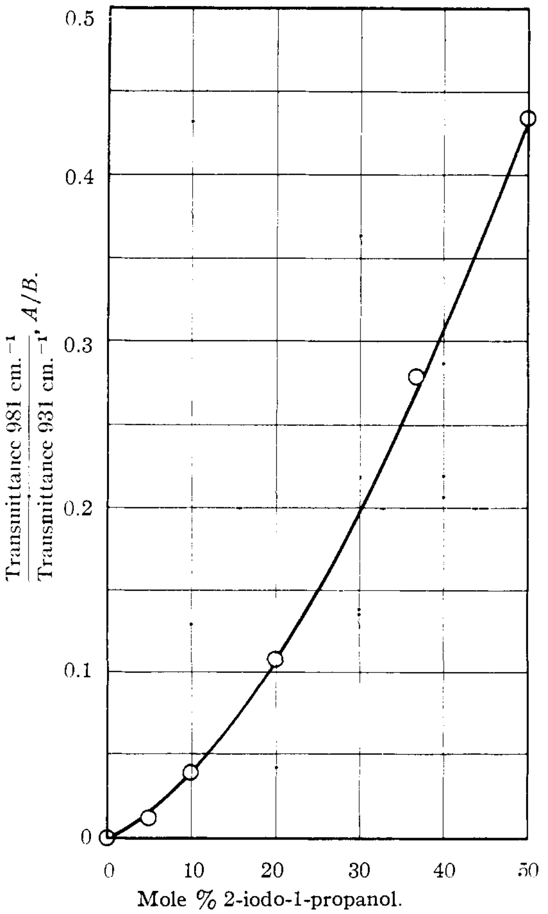


Fig. 7.—Calibration curve for infrared analysis of 1-iodo-2-propanol and 2-iodo-1-propanol.

solution of 100 ml. of concentrated hydriodic acid in 100 ml. of water. The product was isolated as in (a).

(f) To a solution containing 145 g. (1.5 moles) of ammonium bromide, 50 ml. of propylene oxide and a trace of methyl orange in 300 ml. of water, concentrated hydrobromic acid was added at such a rate as to maintain the solution at the indicator change. The product was isolated as in (a).

(g) To the two-phase mixture resulting from the reaction between 15 g. (0.615 mole) of magnesium and 80 g. (0.50 mole) of bromine in 400 ml. of dry ether was added 70.0 ml. (1.0 mole) of propylene oxide. The precipitate was filtered, pressed dry and hydrolyzed with 500 ml. of 2 *N* sulfuric acid. The reaction mixture was worked up as in (a).

(h) To a solution containing 400 g. of sodium bromide, 50.0 ml. of propylene oxide and a trace of thymol blue in 600 ml. of water, aqueous acetic acid (40%) was added at such a rate as to keep the solution at the color change (*p*H 8) of the indicator. The product was isolated as in (a).

The yields in some of the reactions, particularly those of propylene oxide with hydrogen chloride in water, were rather low. This was shown to be largely the result of difficulties in isolation, rather than to incomplete reaction, as synthetic mixtures of the products, added to solutions corresponding to those in which the reactions were run, were isolated in percentages very nearly equal to the reported yields. More significant, the ratio of isomers was not significantly altered in the isolation procedure.

Commercial propylene chlorohydrin (Eastman Kodak Co., 75% I) or bromohydrin (Eastman Kodak Co., 85% III), substituted for propylene oxide in each of the above reactions, was recovered unchanged. Heating with sodium bromide or potassium bisulfate likewise produced no change in composition.

Addition of Halogen (I) 3,5-Dinitrobenzoates to Propene.—To 16.0 g. (0.050 mole) of silver 3,5-dinitrobenzoate[4] in 200 ml. of anhydrous solvent in either a Dry Ice–chloroform or ice-bath, the desired quantity of halogen was added. After a 10-minute shaking period, commercial propene was bubbled in until the halogen disappeared. The reaction mixture was allowed to warm to room temperature, filtered, and the solvent evaporated. The resulting solid was taken up in chloroform and again evaporated to dryness in order to remove 3,5-dinitrobenzoic acid, which is insoluble in chloroform. Infrared spectra of this product and of the material obtained upon recrystallization from heptane were determined and compared to the spectra of the pure isomers. Recrystallization did not appear to change the isomeric composition of the mixtures. The results are given in Table V.

TABLE V

ADDITION OF HALOGEN (I) 3,5-DINITROBENZOATES TO PROPENE

Temp., °C.	Solvent	Halogen	Yield, %	Product	%[a]	Product	%[a]
−80	Ether	Cl_2	16.4	VII	100	VIII	0
−80	Ether	Br_2	12	IX	100	X	0
0	Ether	Br_2	17	IX	88	X	12
0	Chloroform	Br_2	54	IX	75	X	25
0	Chloroform	Br_2[b]	36	IX	75	X	25
−80	Ether	I_2	54	XI	100	XII	0

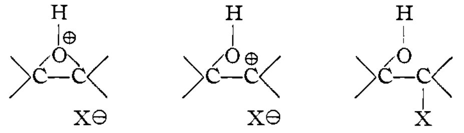
[a] Based on mixture. [b] 0.1 g. benzoyl peroxide added.

Discussion

The significant differences in infrared spectra of the isomers, whose other physical properties are almost identical, constitute further evidence of the value of this rapid and convenient method of studying orientation problems.

From the small differences in entropy and enthalpy of activation in the ring opening of propylene oxide, it seems reasonable to conclude that attack at the primary and attack at the secondary carbon atom occur by the same kinetics, since the differences between first and second order reactions are usually[6] far greater than this. The differences in entropy of activation are consistent with the view that the larger bromide and iodide ions meet with greater steric hindrance than the smaller chloride ion.

The differences in enthalpies of activation are consistent with differences in base strength of the halide ions. The transition state for the reactions of epoxides with the hydrogen halides may be represented as a resonance hybrid of three principal structures, XIII, XIV and XV. The electronic effect of a ring substituent on the direction of ring opening is, on this basis, largely dependent upon the ratio of the contribution to the transition state of structure XV to the contribution of structure XIV (a ratio which in effect represents the relative extent to which bond-making, compared to bond-breaking, has proceeded in the transition state).



XIII XIV XV

If structure XIV makes the major contribution to the transition state, *i.e.*, if bond-breaking has proceeded to a greater extent than bond-making, then an electron-releasing group such as methyl, which stabilizes an adjacent positive charge, favors attack by X^- at the α-position to the methyl group. Conversely, if structure XV makes the major contribution to the transition state, *i.e.*, if bond-making is of pre-eminent importance, then the magnitude of the positive charge on the carbon atom which is attacked is decreased as the reaction proceeds from the initial to the transition state, and an electron-releasing group such as methyl tends to direct attacks of X^- to the unsubstituted carbon atom. Therefore, an increase in the strength of the attacking base, X^-, which brings about an increase in the relative contribution of structure XV to the transition state, for reactions of propylene oxide favors attack away from the methyl.

The relatively high percentage of attack at the primary carbon atom in the reaction with sodium bromide may be explained in similar terms. In the absence of acid catalysis, the type XIV structure shows extremely high charge separation, and its contribution to the transition state is markedly decreased; hence more primary attack is to be expected. The fact that the results with ammonium bromide and magnesium bromide etherate are comparable to those with hydrogen bromide, may be considered as evidence that these Lewis acids are exhibiting a general acid catalysis.[8] The greater tendency for primary attack in ether than in water is consistent with the view that the base strength of the halide ions is decreased by solvation in water, or that the acidity of the hydrogen halides is leveled more extensively by diethyl ether than by water.

The addition of positive halogen salts to propylene may proceed through an open carbonium ion intermediate of the type $CH_3\text{-}\overset{+}{C}H\text{-}CH_2X$, XVI, or,

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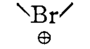
[8] C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951).

for bromine and iodine, preferably a cyclic ion intermediate of the type  $CH_3\text{–}\underset{\overset{\diagdown X \diagup}{\oplus}}{CH\text{–}CH_2}$ (XVII). Intermediate XVI would be preferred to the isomeric primary carbonium ion intermediate and, for this mechanism, predominant formation of the Markownikoff product would be expected. The orientation of ring opening of XVII would be expected to be similar to that for acid-catalyzed ring opening of propylene oxide. Here the transition state structure corresponding to XIV might be expected to have even greater importance than in the acid-catalyzed epoxide reactions, and hence more secondary attack by the incoming base is not unexpected.

Dewael[9] has reported that 1-chloro-2-propanol and 2-chloro-1-propanol react with potassium cyanide to give the same product, 3-hydroxybutyronitrile. Inasmuch as the bromohydrins have now been shown to react with sodium iodide by a normal exchange reaction, the isomerization observed by Dewael was probably due, as he assumed, to preliminary formation of epoxide from the chlorohydrin in the basic medium, followed by opening of the epoxide ring by cyanide ion, and not to a neighboring group effect.

The sulfuric acid-catalyzed hydrations of allyl chloride and of allyl bromide are interesting in that the chloride shows only unrearranged addition whereas the bromide gives a small amount of the rearranged product 2-bromo-1-propanol. This may be explained by the neighboring group effect[10] of the bromine in forming an intermediate cyclic ion of the structure  $CH_3\text{–}\underset{\overset{\diagdown Br \diagup}{\oplus}}{CH\text{–}CH_2}$.

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LAWRENCE, KANSAS

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[9] A. Dewael, *Bull. soc. chim. Belg.*, **33**, 504 (1924).

[10] See S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Ortho Substitution Rearrangement *versus* β-Elimination of Certain Quaternary Ammonium Ions with Sodium Amide. Extension of the Method of Synthesis of Vicinal Alkyl Aromatic Derivatives[1]

BY CHARLES R. HAUSER AND ALFRED J. WEINHEIMER

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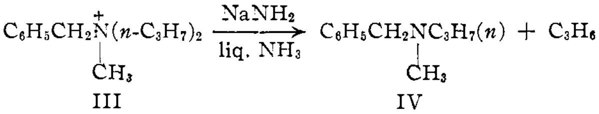
Certain benzyl quaternary ammonium ions having both methyl and higher alkyl groups were found to undergo, with sodium amide in liquid ammonia, both the ortho substitution rearrangement and β-elimination. Quaternary ammonium ion III underwent largely β-elimination, but quaternary ions V and VII exhibited more of the rearrangement than β-elimination. The latter ion formed on rearrangement the ortho ethyl derivative (VIII), the methiodide of which was further rearranged to give the 2,3-methylethyl derivative (X). The methiodide of X was still further rearranged to form the 2,3,4-dimethylethyl derivative (XI). These results support the aromatic nucleophilic displacement mechanism proposed previously.

It has previously been shown[2] that, with sodium amide in liquid ammonia, quaternary ammonium ion I undergoes the ortho substitution rearrangement to form *o*-methylbenzyldimethylamine in 96% yield, whereas quaternary ammonium ion II exhibits exclusively β-elimination to give benzyldi-*n*-propylamine and propylene. The former reaction involves an α-hydrogen of a methyl group, and the latter, a β-hydrogen of a *n*-propyl group. Similarly, certain other quaternary ammonium ions that have only α-hydrogen atoms were shown to exhibit the rearrangement,[2] whereas benzyltri-*n*-butylammonium ion, which has also β-hydrogens, underwent exclusively β-elimination.[2]

$$\underset{\text{I}}{C_6H_5CH_2\overset{+}{N}(CH_3)_3} \qquad \underset{\text{II}}{C_6H_5CH_2\overset{+}{N}(n\text{-}C_3H_7)_3}$$

In the present investigation, certain benzyl quaternary ammonium ions that have both methyl and higher alkyl groups were found to undergo with sodium amide in liquid ammonia both the ortho substitution rearrangement and β-elimination. Thus, benzyl quaternary ammonium ion III, which has one methyl group and two *n*-propyl groups, underwent largely β-elimination to form benzyl methyl-*n*-propylamine (IV) (70%), but a little of the rearrangement also appeared to occur. In this case, the β-elimination furnishes a convenient method for the preparation of tertiary amine IV which, because each of its alkyl groups is different, could presumably not be readily synthesized by the more common methods.



$$\underset{\text{III}}{C_6H_5CH_2\underset{\substack{|\\CH_3}}{\overset{+}{N}}(n\text{-}C_3H_7)_2} \xrightarrow[\text{liq. }NH_3]{NaNH_2} \underset{\text{IV}}{C_6H_5CH_2\underset{\substack{|\\CH_3}}{N}C_3H_7(n)} + C_3H_6$$

On the other hand, benzyl quaternary ammonium ion V, which has two methyl groups and one *n*-propyl group, underwent slightly more rearrangement to form tertiary amine VI (52%) than β-elimination to give benzyldimethylamine (40%). As anticipated, relatively less (30%) of the latter amine from β-elimination was obtained when the reaction was carried out at −70° instead of the usual −33°, although the yield of VI from the rearrangement was only slightly greater (56%). The rearrangement is represented below. The structure of the product VI was established by its oxidation to

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[1] Supported by the Office of Naval Research and the Duke University Research Council.

[2] S. W. Kantor and C. R. Hauser, THIS JOURNAL, **73**, 4122 (1951).