[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Stereochemistry of the Primary Carbon. IV. The Decomposition of Optically Active 1-Butyl-1-*d* Chlorosulfite[1,2]

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RECEIVED JULY 23, 1956

The thermal decomposition of undistilled optically active 1-butyl-1-*d* chlorosulfite either alone or in dioxane solution yields 1-butyl-1-*d* chloride with ~90% inversion of configuration. The decomposition of distilled 1-butyl-1-*d* chlorosulfite in dioxane yields a more racemized product which is attributed to partial reaction *via* a primary carbonium ion–chlorosulfite ion ion-pair intermediate.

The relatively low carbonium ion stability and relative unimportance of steric hindrance effects in unbranched primary systems prompted a limited examination of the stereochemistry of some reactions of optically active 1-butyl-1-*d* chlorosulfite which was prepared by the reaction of thionyl chloride and optically active 1-butanol-1-*d*.[1] Thermal decomposition without solvent of the chlorosulfite prepared from 1-butanol-1-*d* having $\alpha^{25}\text{D}$ $-0.142 \pm 0.004°$ (l 4) gave a 45% yield of 1-butyl-1-*d* chloride having $\alpha^{25}\text{D}$ $+0.147 \pm 0.003°$ (l 2). Part of this chloride was allowed to react with tetramethylammonium acetate in acetone solution to yield 1-butyl-1-*d* acetate having $\alpha^{25}\text{D}$ $+0.182 \pm 0.004°$ (l 2). The conditions of this reaction are those of a direct displacement and to a high degree of probability the reaction was accompanied by a complete inversion of configuration.[4] The 1-butyl-1-*d* acetate prepared directly from the 1-butanol-1-*d* with acetyl chloride in pyridine had $\alpha^{25}\text{D}$ $+0.200 \pm 0.004°$ (l 2). Hence the chloride was formed from the decomposition of 1-butyl-1-*d* chlorosulfite with 91 ± 3% inversion of configuration. With these assumptions the ratio of the rotations of 1-chlorobutane-1-*d* and 1-butanol-1-*d* of the same configuration and the same optical purity is 2.28.[5]

When 1-butyl-1-*d* chlorosulfite, which was not purified by distillation, was decomposed in dioxane solution at 83° for 20 hours the 1-butyl-1-*d* chloride obtained had $\alpha^{25}\text{D}$ $+0.140 \pm 0.003°$ (l 2), corresponding to 86.5 ± 4% inversion of configuration. The marked evolution of sulfur dioxide in this reaction indicated that this decomposition proceeded considerably faster than that of a redistilled sample of *n*-butyl chlorosulfite. Furthermore, when 1-butyl-1-*d* chlorosulfite from 1-butanol-1-*d* having $\alpha^{25}\text{D}$ $+0.145 \pm 0.005°$ (l 2) was purified by vacuum distillation and then decomposed in dioxane solution at 84° for 42 hours, the resulting 1-butyl-1-*d* chloride had $\alpha^{25}\text{D}$ $-0.055 \pm 0.004°$ (l 2). Using the relative rotations for chloride and alcohol established above, this value corresponds to 33 ± 3% inversion of configuration and 67% racemization, or, alternatively, 66.5% inversion of configuration and 33.5% retention. The greater control of purity used in this experiment led to an effective *decrease* in the degree of net inversion of configuration obtained.

Discussion

The original "SNi" mechanism[7] for the decomposition of alkyl chlorosulfites has required an extensive modification on the basis of recent experimental results. The stereochemical data of Lewis and Boozer[8] were best rationalized in terms of an intermediate carbonium ion–chlorosulfite ion ion-pair. In a solvent which cannot form a stable compound with the carbonium ion the only course open to the system productive of further reaction other than elimination is a decomposition of the chlorosulfite ion into chloride ion and sulfur dioxide and "internal return"[9] of the chloride ion to yield the alkyl chloride. The reaction of optically active secondary carbinyl chlorosulfites in dioxane, a solvent which can effectively solvate the rear of a carbonium ion,[10] causes the formation of alkyl chloride of retained configuration. The "ion-pair" formulation of the reaction was also used by Cram[11] to interpret his results in the 3-phenyl-2-butyl system. Consequently, the chlorosulfite decomposition bears a strong resemblance to solvolytic displacement reactions.[10c] "Thus the SNi reaction differs from the SN1 reaction only in the sense that the departing group is complex. . . ."[11] This point of view is supported by the acetolysis of 2-octyl chlorosulfite which yields 2-octyl acetate with 40% inversion and 60% racemization. This

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[1] Part III, A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **78**, 5597 (1956).

[2] Taken in part from the dissertation of W. D. Schaeffer in partial fulfillment of the requirements for the Ph.D. degree, University of California, June, 1956.

[3] General Electric Fellow, 1955–1956.

[4] J. Steigman and L. P. Hammett, THIS JOURNAL, **59**, 2536 (1937).

[5] The question arises as to the extent of racemization of 1-butyl-1-*d* chloride by the tetramethylammonium chloride formed during the reaction with tetramethylammonium acetate. The solubility of tetramethylammonium chloride in acetone is very limited. The resulting solution is less than 0.005 *M* in chloride ion. Since the specific rate constant for reaction of *n*-butyl chloride with chloride ion in boiling acetone is approximately 1×10^{-5} l. mole^{-1} sec.$^{-1}$[6] the half-life for the racemization under our conditions is greater than 3000 hours. Since the reaction was stopped after 21 hours no appreciable amount of racemization can be due to this cause. However, the possibility of some slight racemization by a heterogeneous reaction with the precipitated tetramethylammonium chloride is not ruled out.

[6] P. B. D. de la Mare, *J. Chem. Soc.*, 3169 (1955).

[7] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. O. Scott, *ibid.*, 1252 (1937).

[8] (a) E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 308 (1952); (b) C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953); **76**, 794 (1954).

[9] W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951).

[10] (a) W. E. Doering and A. Streitwieser, Jr., unpublished results; (b) A. Streitwieser, Jr., and W. D. Schaeffer, Abstracts of papers presented at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956, p. 52N; (c) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

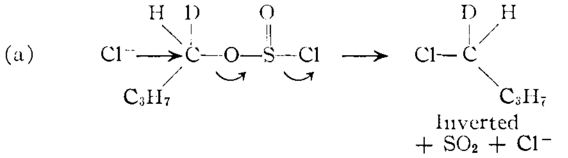
[11] D. J. Cram, THIS JOURNAL, **75**, 332 (1953). This paper includes many references to the earlier literature.

behavior is rather analogous to the acetolyses of secondary alkyl tosylates.[12]

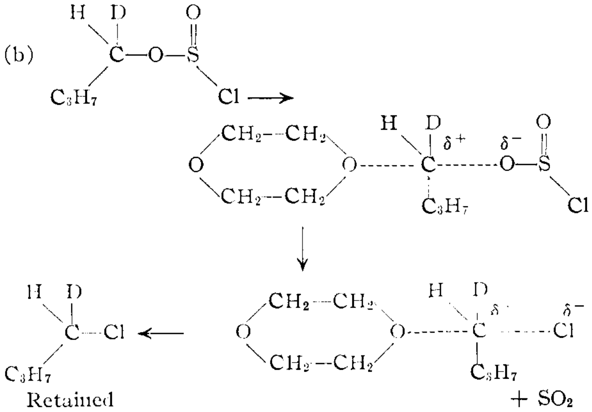
The presence of pyridine in dioxane changes the steric course of the reaction and produces an extensively inverted product.[8b] Lewis and Coppinger[13] have found that the chlorosulfite decomposition is catalyzed by chloride ion. For example, 10^{-4} M chloride ion doubles the rate of decomposition of isopropyl chlorosulfite. This result is explained as a competing direct displacement reaction by chloride ion which would yield an inverted product. Cram[11] has postulated a similar displacement.

In the case of primary systems carbonium ion stability is relatively low; the rate of formation of the carbonium ion–chlorosulfite ion ion-pair which would lead to retention in dioxane should be rather slow. On the other hand, direct displacement reactions are much faster on primary compounds than on secondary,[10c] and the chloride ion catalysis which would lead to inversion should be facilitated. The largely inverted product obtained from the relatively rapid decomposition of unpurified 1-butyl-1-*d* chlorosulfite undoubtedly results from the chloride ion catalyzed decomposition (reaction a). The fact that purified chlorosulfite resulted in *less* inversion of configuration strongly suggests that in this experiment the carbonium ion ion-pair mechanism (reaction b) was almost as important as the chloride ion displacement. To the extent that this argument is valid these results constitute stereochemical evidence for the existence of primary carbonium ions or their equivalent as intermediates in this reaction.

(a)



(b)



Experimental

Decomposition of *n*-Butyl Chlorosulfite in Dioxane.—To a 500-ml. flask immersed in an ice-bath and arranged for magnetic stirring was added 140 ml. of pentane and 48.2 g. (0.405 mole) of specially distilled thionyl chloride. Twenty grams (0.27 mole) of *n*-butyl alcohol diluted with 40 ml. of pentane was added slowly dropwise. After stirring for 1 hour at room temperature the pentane and excess thionyl chloride were removed under reduced pressure at room temperature. The residue was distilled through a small Vigreux column; 31.5 g. (75% yield) of *n*-butyl chlorosulfite was collected, b.p. 65–72° (15 mm.).

A mixture of 35 ml. of dioxane[14] and 3.5 g. of *n*-butyl chlorosulfite was maintained at 84° and periodically 1-ml. aliquots were withdrawn and the infrared spectra taken in a 0.1-mm. cell using pure dioxane in the reference cell. The rate of disappearance of *n*-butyl chlorosulfite with time was calculated from the characteristic absorption band at 1220 cm.$^{-1}$. The results of these measurements are given in Table I. The resulting rate constant should be considered a maximum for the unimolecular decomposition of the chlorosulfite because the extent of direct displacement by any traces of chloride ion present was not determined. Nevertheless, the rate found is 1/42 as fast as that of 2-pentyl chlorosulfite under the same conditions.[8a]

TABLE I

DECOMPOSITION OF *n*-BUTYL CHLOROSULFITE IN DIOXANE AT 84°

Time, sec.	Reaction, %	$10^5 k$, sec.$^{-1}$
7,200	20.5	3.1
16,200	36.5	2.8
21,600	47.5	3.0
64,800	89.1	3.4
	Average	3.1 ± 0.2

Thermal Decomposition of Optically Active 1-Butyl-1-*d* Chlorosulfite.—To an ice-cold mixture of 100 ml. of pentane and 35.7 g. (0.30 m.) of specially distilled thionyl chloride there was slowly added dropwise, with stirring, 15.0 g. (0.20 m.) of optically active 1-butanol-1-*d* having $\alpha^{25}\text{D}$ −0.142 ± 0.004° (l 4),[1] diluted with 25 ml. of pentane. The addition was made over a period of 1 hour and the mixture was stirred at room temperature for an additional hour. The pentane and excess thionyl chloride were removed at room temperature by reduced pressure. During an attempted vacuum distillation of the residue a vigorous reaction took place in the flask. In a few minutes the pot became almost dry but no distillate was collected. The product from the reaction, optically active 1-butyl-1-*d* chloride, was obtained from the Dry Ice trap. Distillation through a small glass spiral column gave 8.5 g. (45% yield) of 1-butyl-1-*d* chloride, b.p. 76.5–77.5°, having $\alpha^{25}\text{D}$ +0.147 ± 0.004° (l 2).

Reaction of Tetramethylammonium Acetate with Optically Active 1-Butyl-1-*d* Chloride in Acetone.—In a reflux system protected by a calcium chloride drying tube 30.0 g. (0.23 mole) of tetramethylammonium acetate[15] was refluxed with 120 ml. of dry acetone. When solution was complete, 3.4 g. (0.036 mole) of the optically active 1-butyl-1-*d* chloride prepared above was added. After about 2 hours solid tetramethylammonium chloride began to separate. After refluxing for 21 hours the reaction mixture was cooled with running water and was poured into 150 ml. of ice and water. The mixture was extracted 3 times with 60-ml. portions of pentane. The combined pentane extracts were dried with anhydrous sodium sulfate. After distillation of the pentane the residue was distilled through a small glass spiral column to give 4.0 ml. of material, b.p. 110–126°. Redistillation of this material through the same column gave 2.5 ml. of 1-butyl-1-*d* acetate, b.p. 124–125°, having $\alpha^{25}\text{D}$ +0.182 ± 0.004° (l 2).

When a sample of the same 1-butanol-1-*d* used for the preparation of the chlorosulfite was allowed to react with acetyl chloride in pyridine, the 1-butyl-1-*d* acetate produced had $\alpha^{25}\text{D}$ +0.200 ± 0.004° (l 2).

When 25 mg. of finely divided tetramethylammonium chloride was refluxed with 50 ml. of acetone for several hours, some remained undissolved. Hence the resulting solution was less than 0.005 M in tetramethylammonium chloride.

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(12) J. Kenyon, H. Phillips and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(13) E. S. Lewis and G. M. Coppinger, THIS JOURNAL, **76**, 796 (1954).

(14) The dioxane was purified by the method given by L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 2nd ed., 1941, p. 368.

(15) H. L. Goering, T. D. Nevitt and E. F. Silversmith, THIS JOURNAL, **77**, 4042 (1955).

Decomposition of Unpurified Optically Active 1-Butyl-1-*d* Chlorosulfite in Dioxane.—The chlorosulfite prepared as above from 11.9 g. (0.10 mole) of thionyl chloride and 4.0 g. (0.053 mole) of 1-butanol-1-*d* having $\alpha^{25}\text{D}$ −0.142 ± 0.004° (*l* 4)[1] was dissolved in 25 ml. of dioxane[14] and maintained at 84°. A marked evolution of sulfur dioxide began immediately. After heating for 20 hours the reaction was cooled to room temperature and distilled through a small glass spiral column, collecting 6.1 ml. of 1-butyl-1-*d* chloride, b.p. 78-90°. The distillate was mixed with 5 ml. of pentane and was washed with 4 ml. of water. The organic phase was dried with anhydrous sodium sulfate and distilled through a small column, collecting 3.0 ml. of 1-butyl-1-*d* chloride, b.p. 78-79°, having $\alpha^{25}\text{D}$ +0.140 ± 0.003° (*l* 2).

Decomposition of Distilled Optically Active 1-Butyl-1-*d* Chlorosulfite in Dioxane.—The chlorosulfite was prepared as above from 16.0 g. (0.133 mole) of freshly distilled thionyl chloride and 7.5 g. (0.10 mole) of 1-butanol-1-*d* having $\alpha^{25}\text{D}$ +0.145 ± 0.005° (*l* 4).[16] Distillation through a small Vigreux column gave 12.0 g. (77% yield) of optically active 1-butyl-1-*d* chlorosulfite, b.p. 65-71° (15 mm.).

This material was dissolved in 50 ml. of dioxane[14] and was maintained at 84° for 42 hours. The mixture was distilled through a small glass spiral column and 4.5 ml. of material was collected, b.p. 76-89°. Redistillation of this material through the same column gave 3.0 ml. of 1-butyl-1-*d* chloride, b.p. 77.5-78.5°, having $\alpha^{25}\text{D}$ −0.055 ± 0.004° (*l* 2).

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[16] This material was the product of a separate preparation to be described in a later paper.

BERKELEY, CALIFORNIA

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

Base-induced Rearrangements. Action of Iodide Ion on Certain 1,3-Dihalides

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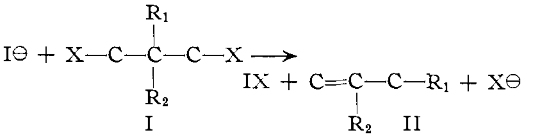
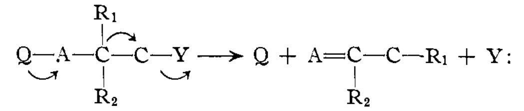
Eight 1,3-dihalides of type I were treated with sodium iodide in dimethylformamide or acetamide at temperatures ranging from 120 to 170°. Six of these dihalides showed the rearrangement-elimination reaction of equation 1, giving moderate yields of either the olefin II, or of an olefin readily obtained by isomerization of II. Both alkyl and hydrogen migration was accomplished, but phenyl migration was not. Qualitative evidence indicates that the rearrangement is "base-induced," with the primary force being an electron "push" on the carbon atom carrying the migrating group.

A study of the reaction, equation 1, of iodide ion with 1,3-dihalides of type I was undertaken to determine whether this reaction is an example of the general "base-induced" rearrangement, equation 2, in which the primary force for rearrangement is an electron push on the carbon atom carrying the migrating group.



$$I^{\ominus} + \underset{\text{I}}{X{-}C{-}\overset{R_1}{\underset{R_2}{C}}{-}C{-}X} \longrightarrow IX + \underset{\text{II}}{C{=}\underset{R_2}{C}{-}C{-}R_1} + X^{\ominus} \quad (1)$$

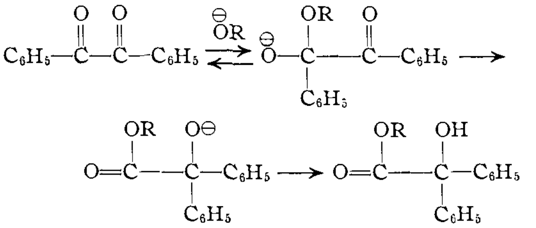


$$Q{-}A{-}\overset{R_1}{\underset{R_2}{C}}{-}C{-}Y \longrightarrow Q + A{=}\underset{R_2}{C}{-}C{-}R_1 + Y{:} \quad (2)$$

In the general equation 2, Q is an electron pair source, Y is a stable entity (*e.g.*, $Br^{\ominus}$, $:NR_3$) and A is carbon or a hetero atom. Our objective is to find examples of the "base-induced" rearrangement which lend themselves to detailed quantitative kinetic studies. A comparison could then be made between factors promoting the "base-induced" rearrangement and those promoting "acid-induced," Wagner-Meerwein type rearrangements, in which the primary force promoting rearrangement is an electron "pull" exerted from an electron deficient site adjacent to the carbon atom carrying the migrating group.

Possible examples of the "base-induced" rearrangement previously described include the benzilic acid rearrangement,[2-5] the Tiffeneau rearrangement of halomagnesium derivatives of halohydrins[6,7] and the reaction of zinc with 1,3-dihalides such as pentaerythrityl tetrabromide.[8-10]

The benzilic acid rearrangement recently has been found to involve general base participation,[2] equation 3, although previously hydroxide ion was considered to be the only effective base promoting the reaction.[3] In this reaction the electron source (Q of equation 2) is an electron pair on the negative oxygen. The relative degree to which the rearrangement is promoted by a "push" of this electron pair as compared to a "pull" by the carbonyl group[5] is uncertain. However, the rearrangement of a phenyl group is retarded by *p*-methyl and facilitated by *p*- or *m*-chlorine,[3,4] indicating perhaps a predominance of "push."



$$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \xrightleftharpoons{OR^{\ominus}} {}^{\ominus}O{-}\overset{OR}{\underset{C_6H_5}{C}}{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5 \longrightarrow O{=}\overset{OR}{C}{-}\overset{O^{\ominus}}{\underset{C_6H_5}{C}}{-}C_6H_5 \longrightarrow O{=}\overset{OR}{C}{-}\overset{OH}{\underset{C_6H_5}{C}}{-}C_6H_5 \quad (3)$$

The Tiffeneau rearrangement may be at least partially base-induced. Geissman and Akawie have proposed a cyclic mechanism for this reaction, equation 4, and believe the rearrangement to be induced by an electrophilic attack of the MgX on the neighboring halogen atoms (*i.e.*, acid-induced).[7]

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[1] Du Pont Fellow, 1954-1955.

[2] W. E. Doering and R. Urban, THIS JOURNAL, **78**, 5938 (1956).

[3] M. T. Clark, E. C. Hendley and O. K. Neville, *ibid.*, **77**, 3280 (1955).

[4] D. G. Ott and G. G. Smith, *ibid.*, **77**, 2325 (1955).

[5] F. H. Westheimer, *ibid.*, **58**, 2209 (1936).

[6] M. Tiffeneau, *Bull. soc. chim.*, [5] **12**, 621 (1945).

[7] T. A. Geissman and R. I. Akawie, THIS JOURNAL, **73**, 1993 (1951).

[8] M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

[9] W. Shand, V. Schomaker and J. R. Fischer, *ibid.*, **66**, 636 (1944).

[10] I. Shokor and N. Slobodin, *J. Gen. Chem. U.S.S.R.*, **21**, 2005 (1951).