The Acetolysis of 3-Phenyl-2-butylsulfoxonium Ions[1a-d]

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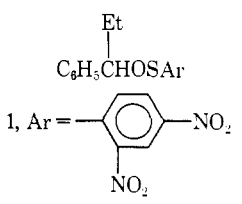
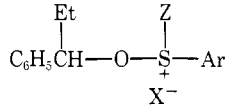
Abstract: The enantiomeric and racemic *threo*- and *erythro*-3-phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenates have been subjected to chlorination in acetic acid solution. Under a variety of reaction conditions the chloride, acetate, and alcohol products of phenyl, methyl, and hydrogen migration have been identified and their yields determined. The results can be explained with 3-phenyl-2-butyl carbonium ions with very slightly restricted rotation about the C_α—C_β bond which can undergo phenyl, methyl, or hydrogen migration, or can collapse to 3-phenyl-2-butyl product. Previously, the 3-phenyl-2-butyl carbonium ions formed in the acetolysis of the tosylates exhibited no response to added $LiClO_4$. We have shown here in the corresponding sulfoxonium ion acetolysis that small amounts of added $LiClO_4$ not only severely reduced *threo* $\rightleftharpoons$ *erythro* "leakage" and influenced the proportions of acetates and chlorides produced, but also depressed the fractions of products arising from methyl and hydrogen migration. We interpret this to signify occurrence of several ground-state sulfoxonium ion pairs giving rise to the corresponding carbonium ion pairs upon rupture of the $\geq$C—O– bond. We attribute the effect of added lithium perchlorate to an increase in the fraction of product formed from external ion pairs and separated ions. Thus, the observed stereospecificity is to be correlated with the incidence of carbonium ion pairs highly stabilized by solvation.

In our earlier studies[2] on the chlorination, in acetic acid, of 1-phenylpropyl 2,4-dinitrobenzenesulfenate (**1**) we demonstrated the intervention of several sulfoxonium ion pairs, **2**. It appeared that the initially



1, Ar =



2, Z and X = Cl^- or AcO^-

formed ground-state ion pairs control the destinies of carbonium ions they produce. The respective solvent structures organized about the sulfoxonium cations are transferred in their essential features to the developing carbonium ions. For example, a carbonium ion inheriting the solvent structure of an external sulfoxonium ion pair cation behaves like an external carbonium ion.

In our present study of the 3-phenyl-2-butyl system, we examined a complex carbonium ion whose ion pairing behavior has been extensively characterized by means of the $LiClO_4$ special salt effect criterion.[3] It has been reported,[4] for example, that only in acetolyses which lead to ion pairs with long half-lives can the multiplicity of ion pairing relationships be perceived with the $LiClO_4$ rate response.

In our earlier work,[2] too, it was demonstrated that the special salt effect on reaction rate could be correlated with a corresponding effect on product composition. The concentration of lithium perchlorate controls the proportion of acetate and chloride produced through its influence on return from external to internal ground-state sulfoxonium ion pairs like **2** (and consequently on the carbonium ion pairs resulting from them).

The aim of the present study is to determine in what respects the 3-phenyl-2-butylsulfoxonium ions arising in the chlorination of the sulfenate ester in anhydrous acetic acid media differ from the sulfonate ester substrate with respect to the stereochemistry and composition of the products they yield. Furthermore, the ability of the 3-phenyl-2-butyl cation to rearrange introduces a variable for investigation in connection with the transfer of solvent structure from the monodentate sulfoxonium cation.

Experimental Section

Most of the radioactivity analyses were done by liquid scintillation counting in a Packard Tricarb scintillation counter, Model 314 EX, using vials purchased from the Packard Instrument Co. Iodoform and its precursors were analyzed by the dry-combustion method using an ionization chamber[5] in conjunction with an Applied Physics Corp. Model 31 vibrating reed electrometer.[6]

Melting points were obtained with the help of a Kofler hot bench. Optical rotation measurements were made with a Hilger standard polarimeter using a sodium source and a 5-cm Rudolph polarimeter cell. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Gas–liquid partition chromatography was performed on a Kromo-Tog, Model K-1, supplied by Burell Corp., Pittsburgh, Pa. Analytical and preparative columns were made of Pyrex glass 8 ft in length with diameters of 0.25 in. for the analytical columns and 0.5 in. for the preparative columns; the exit portal was maintained between 100 and 120°. The columns used in this study were prepared from materials supplied by F & M Scientific Corp., Avondale, Pa. Three columns were used: column I, 20% Carbowax 20M on 30–60 mesh Diatoport P; column II, 20% Carbowax 20M on 60–80

(1) (a) Preliminary communication: H. Kwart, E. N. Givens, and C. J. Collins, *J. Am. Chem. Soc.*, 90, 7162 (1968). (b) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp. (c) This paper is No. XXV in the Molecular Rearrangement series; paper XXIV: C. J. Collins and M. H. Lietzke, *J. Am. Chem. Soc.*, **89**, 6565 (1967). (d) Throughout this paper we use the convenient but incorrect name 3-phenyl-2-butyl for the group properly named 2-phenyl-1-methylpropyl because we believe the first name has been commonly applied before and readily conveys the appropriate structural information to the reader. (e) Predoctoral Fellow of the Oak Ridge National Laboratory, 1962–1964, from the University of Delaware.

(2) H. Kwart and P. S. Strilko, *Chem. Commun.*, 767 (1967).

(3) For a review of the evidence for different kinds of ion pairs, including the normal and special salt effect, see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 167–171.

(4) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 78, 2763, 2767 (1956).

(5) B. B. Tolbert, "Ionization Chamber Assay of Radioactive Gases," U. S. Department of Commerce, Report No. UCRL-3499, 1956.

(6) V. F. Raaen, Ph.D. Dissertation, University of Tennessee, Knoxville, Tenn., 1958.

mesh Diatoport W; column III, 20% diethylene glycol succinate on 60–80 mesh Diatoport W.

Quantitative infrared analyses were made with a Beckman infrared spectrophotometer, Model IR-9, using neat liquid films in a microcell with 0.025-mm path length. The optical densities of the various pure alcohols less the base line were determined between 750 and 1300 cm^{-1} at 13 selected wavelengths. The various optical densities of a known composition, approximating the acetate product from run 4, were measured; the amounts of each component were calculated by a series of equations using a combined least-squares program on a computer.[7] The alcohol concentrations for the known, the concentrations computed for the known, and the concentrations computed for the reduced unknown (in mole per cent) for run 4 are, respectively: *threo*-3-phenyl-2-butanol, 59.4, 52.9 ± 3.2, 55.9 ± 6.7; *erythro*-3-phenyl-2-butanol, 9.7, 13.2 ± 2.7, 7.9 ± 5.8; 2-methyl-1-phenyl-1-propanol, 22.3, 22.5 ± 1.3, 19.4 ± 2.7; 2-phenyl-2-butanol, 8.6, 7.7 ± 2.7, 7.9 ± 5.8.

Nmr spectra of samples in carbon tetrachloride solutions containing tetramethylsilane as an internal reference were made with a Varian nmr spectrometer, Model A-60. Quantitative measurements were obtained from integral ratios of tertiary hydrogen resonances. Chemical shifts in cycles per second downfield from reference of tetramethylsilane of the tertiary hydrogen resonances where X is chloride, acetate, and alcohol are, respectively: $(CH_3)_2CHC(H)XC_6H_5$, 274, 326, 256 (doublets); $CH_3CH(C_6H_5)C(H)XCH_3$, 242, 299, 224 (multiplets, *erythro* and *threo* superimposed); $CH_3C(H)(C_6H_5)CHXCH_3$, 169, 167, 156 (multiplets, *erythro* and *threo* superimposed).

Alcohols. 3-Phenyl-2-butanol-1-^{14}C was prepared by addition of methylmagnesium-^{14}C iodide to hydratropic aldehyde.[8] Hydratropic aldehyde obtained from Matheson Coleman and Bell was distilled at 34° (0.5 mm) prior to use. The distilled alcohol, bp 77–78° (1.2 mm), was separated into its racemic diastereoisomeric forms and further into their respective enantiomers by known methods.[9] 2-Methyl-1-phenyl-1-propanol was prepared by the addition of isopropylmagnesium bromide to benzaldehyde, bp 75–77° (1.2 mm).[10] 2-Phenyl-2-butanol was prepared by addition of methylmagnesium iodide to propiophenone, bp 63° (0.8 mm), $n^{24}D$ 1.5152.[11] Nmr, infrared, and glpc data verified the structures and purities of the expected products.

Acetates. The action of acetic anhydride in pyridine on the respective racemic alcohols afforded the corresponding acetates as follows: *erythro*- and *threo*-3-phenyl-2-butyl acetate,[12] 2-methyl-1-phenyl-1-propyl acetate, bp 74–75° (1.0 mm),[12] and 2-phenyl-2-butyl acetate.[11] Nmr, infrared, and glpc determinations verified the structures and expected purities of these products.

Chlorides. 2-Chloro-3-phenylbutane was prepared from a mixture of *threo*- and *erythro*-3-phenyl-2-butanol and thionyl chloride.[13] The nmr spectrum of the distilled product showed that there was no 1-chloro-2-methyl-1-phenylpropane in the mixture. Gas–liquid partition chromatography gives the same *erythro*/*threo* ratio for the chloride product as for the alcohol reactant, which confirms the results of Cram.[13] Hydrogen migration during this reaction can occur only in trace amounts as determined by the absence of significant quantities of olefin.

1-Chloro-2-methyl-1-phenylpropane was prepared from the alcohol and thionyl chloride.[14] In a 50-ml flask equipped with reflux condenser, magnetic stirrer, and dropping funnel, 20 ml of thionyl chloride was slowly added to 5.0 g of 2-methyl-1-phenyl-1-propanol. The reaction mixture was refluxed on the steam bath for 1 hr, then some of the excess thionyl chloride was distilled. The residue was stirred with ice and extracted with hexane. The hexane layer was washed with water, with sodium carbonate solution, and again with water. The hexane was dried, the solvent was evaporated under aspirator pressure through a 1-ft Vigreux column, and the oil was distilled: bp 53° (0.6 mm), $n^{23}D$ 1.5126. The nmr spectrum verified the structure of the chloride; one peak was obtained on glpc analysis (column II).

2-Chloro-2-phenylbutane was prepared by treating the corresponding alcohol with dry hydrogen chloride.[15,16] Nmr analysis verified the structure.

3-Phenyl-2-butyl 2,4-Dinitrobenzenesulfenates. D-(−)-*erythro*-3-Phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate was prepared according to the method of Kharasch.[17] D-(−)-*erythro*-3-Phenyl-2-butanol (bp 67–68° (7 mm), $\alpha^{24}D$ −0.68°, *l*, 1 dm, neat)[9] was prepared from the hydrolysis of D-(+)-*erythro*-3-phenyl-2-butyl acid 3-nitrophthalate ($[\alpha]^{23}D$ +34.6°, *l*, 1 dm, 3% C_2H_5OH)[7] in 85% yield.

To a solution of 8.44 g (0.036 mole) of 2,4-dinitrobenzenesulfenyl chloride[18] in 80 ml of ethylene chloride was added 6.04 g (0.040 mole) of D-(−)-*erythro*-3-phenyl-2-butanol followed by 8 ml of pyridine. The flask was stoppered and kept at room temperature for 2 hr. The precipitate was separated by filtration, the filtrate was next evaporated under aspirator pressure, and finally water was mixed with the oil to react with any excess sulfenyl chloride. The oil was crystallized and recrystallized from ethanol (mp 64°, yield 65%, $[\alpha]^{23}D$ −49.1°, *l*, 1 dm, 3% $CHCl_3$).

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63. Found: C, 55.83; H, 4.70.

L-(+)-*erythro*-3-Phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate (mp 64°, $[\alpha]^{24}D$ +42.8°, *l*, 1 dm, 3% $CHCl_3$) was prepared by the preceding method. The acid 3-nitrophthalate (mp 158°, $[\alpha]^{24}D$ −32.5°, *l*, 1 dm, 3% C_2H_5OH)[9] was hydrolyzed to the corresponding L-(+)-*erythro*-3-phenyl-2-butanol ($\alpha^{24}D$ +0.658°, *l*, 1 dm, neat)[19] from which the sulfenate ester was prepared.

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63. Found: C, 55.08; H, 4.65.

L-(+)-*threo*-3-Phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate was prepared by the above method from L-(+)-*threo*-3-phenyl-2-butanol (bp 71° (1 mm), $\alpha^{24}D$ +30.88°, *l*, 1 dm, neat).[7,20] The alcohol was prepared by hydrolysis of the corresponding acid phthalate ester ($[\alpha]^{24}D$ +26.4°, *l*, 1 dm, 3% C_2H_5OH).[9] The isolated sulfenate ester, mp 104°, was twice recrystallized from ethanol (mp 106°, 64% yield, $[\alpha]^{24}D$ +50.6, *l*, 1 dm, 3% $CHCl_3$).

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.53. Found: C, 54.59; H, 4.68.

D-(−)-*threo*-3-Phenyl-2-butanol-1-^{14}C ($\alpha^{24}D$ −31.37°, *l*, 1 dm, neat)[20] was converted to D-(−)-*threo*-3-phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate (mp 107°, $[\alpha]^{24}D$ −50.4°, *l*, 1 dm, 3% $CHCl_3$).

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63. Found: C, 55.27; H, 4.61.

Racemic *threo*-3-phenyl-2-butanol-1-^{14}C was obtained by hydrolyzing the racemic *threo*-acid phthalate ester, mp 131°.[9] The purity of the alcohol was checked by gas–liquid partition chromatography on column II. *threo*-3-Phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate was prepared as above, mp 116°, 62% yield.

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63. Found: C, 55.30; H, 4.75.

Pure *erythro*-3-phenyl-2-butanol-1-^{14}C, obtained from the hydrolysis of the acid 3-nitrophthalate, mp 158°,[9] was converted to *erythro*-3-phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate in the usual way, mp 77°.

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63. Found: C, 55.15; H, 4.84.

Pyridine Salts of 4-Substituted 2-Nitrobenzenesulfonic Acids. Attempts to isolate either the sulfinyl chlorides or their ethyl or methyl esters as products from the chlorination of several different sulfenate esters were unsuccessful. The pyridine salts of the corresponding sulfonic acids were isolated. The procedure is illustrated by the following example. To 4.0 g (0.0115 mole) of *t*-butyl 2,4-dinitrobenzenesulfenate, mp 118°,[17] in 40 ml of acetic acid was slowly added 0.71 ml (0.0115 mole) of chlorine. The solvent was evaporated under aspirator pressure at a maximum water bath temperature of 40°. The resulting oil could not be induced to crystallize. The oil was divided into two portions. One portion was dissolved in hot absolute ethanol, the second in hot absolute

(7) We wish to thank Dr. L. Scroggie of the Analytical Division, Oak Ridge National Laboratory, for assistance in obtaining the infrared spectra.

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(13) D. J. Cram, *ibid.*, 75, 332 (1953).

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(20) D. J. Cram, *ibid.*, 74, 2129 (1952).

Table I. Configurations and Molecular Rotations of Alkyl-Substituted Benzyl Alcohols and Chlorides

R	$RCHXC_6H_5$ X = OH[a]	X = Cl[a]
CH_3	−52.5°	−78.8°[b]
C_2H_5	−39.4°	−48.8°
n-C_3H_7	−34.9°	−82.3°
i-C_3H_7	−31.4°	
	(−68.4°[c])	(−54.3°)[d]
n-C_4H_9	−28.2	−96.6°

[a] $M^{25}D$ (*l*, 1 dm, neat). [b] MD −63°, see ref 26. [c] MD (*l*, 1 dm, 6.8% in ether). [d] MD (*l*, 1 dm, 9.9% in ether).

Into 10.0 g (0.0288 mole) of sulfenate ester ($[\alpha]^{24}D$ −49.1°, *l*, 1 dm, 3% $CHCl_3$) in 288 ml of dry acetic acid (0.10 *M* in ester) was slowly bubbled 2.6 ml (0.047 mole) of dry chlorine through an inlet tube extending beneath the surface of the reaction solution. Chlorine had previously been collected after bubbling through concentrated sulfuric acid into a measured test tube maintained at Dry Ice–acetone temperatures. The reaction vessel was maintained at 20 ± 1° throughout the period of the reaction. The addition of chlorine required approximately 30 min; the reaction mixture was vigorously stirred for an additional 30 min. Precautions were taken to exclude light during the period of reaction. An intense yellow-orange ester color changed to a lightly tinted greenish solution after addition of 1.3 ml of chlorine which indicates complete reaction of ester. Further addition of chlorine resulted in the usual chlorine–acetic acid color. The reaction mixture was poured into 1500 ml of water with immediate formation of a precipitate. The aqueous layer was extracted with 250 ml of pure pentane; then the 2,4-dinitrobenzenesulfonyl chloride was separated by filtration: yield, 5.72 g (75%); mp 102°. The pentane layer was separated and the aqueous layer was extracted with two additional 300-ml portions of pure pentane. The combined pentane extracts were washed with 10% sodium bicarbonate solution until neutral to pH paper. The pentane layer was dried over anhydrous magnesium sulfate and the solvent evaporated to an oil under aspirator pressure using a 1-ft Vigreux column with a maximum water bath temperature of 35°. The oil was divided into equal portions and chromatographed on separate Fisher alumina columns prepared in pentane and eluted with 700 ml of pentane. First fractions contained primarily olefin with small amounts of chloride; later fractions contained pure chlorides. Acetates were eluted with 1000 ml of 1:1 benzene–hexane mixtures; alcohols were eluted with 700 ml of dry ether. The various fractions were evaporated to oils under aspirator pressure through a 1-ft Vigreux column using a maximum water bath temperature of 40°. Oil weights and radioactivity analyses gave the yields of each group of compounds These groups were then analyzed separately. Data are shown in Table II. Optical rotations of various fractions are shown in Table III.

Table II. Products from the Chlorination of 3-Phenyl-2-butyl 2,4-Dinitrobenzenesulfenate in Acetic Acid at 20°

				Chlorides			Acetates				Alcohols				Total	
				threo-	*erythro-*		*threo-*	*erythro-*			*threo-*	*erythro-*			DN-	leakage,[f]
Run	Ester[a]	Yield[c]	Olefin	I[e]	I[e]	II[e]	I[e]	I[e]	II[e]	III[e]	I[e]	I[e]	II[e]	III[e]	BS[d]	%
1	D-(−)-*erythro*	99	1	3.4	47.9	5.7	2.9	18.7	1.7	0.7		4.3		13.7	75	6.3
2	L-(+)-*erythro*	88	3	4.1	48.1	5.8	2.8	19.8	2.0	0.5		4.3		9.7	75	6.9
3	*eythro*[b]	87	12	2.0	31.0		1.3	42.7				7.2		2.8	71	3.3
4	L-(+)-*threo*	90	1	41.2	4.1	12.8	15.7	3.2	6.8	0.8	0.9		2.0	12.0	65	7.3
5	*threo*[b]	93	7	26.9	1.0	6.1	37.5	2.8	5.5		8.4	0.3	0.9	3.2	75	4.1

[a] 0.10 *M* ester concentration. [b] Contained 0.080 *M* $LiClO_4$ in acetic acid. [c] Mole per cent based on recovered C-14 from starting sulfenate ester. [d] 2,4-Dinitrobenzenesulfonyl chloride (DNBS) yield based on weight of recovered sulfonyl chloride. [e] I, 3-phenyl-2-butyl; II, 1-phenylisobutyl; III, 2-phenyl-2-butyl. [f] We define "leakage" as the per cent of total *threo* products formed from *erythro* reactant, or of *erythro* product formed from *threo* reactant. See C. J. Collins, B. M. Benjamin, and M. H. Lietzke, *Ann.*, **687**, 150 (1965). When considering only the acetate product, the leakage amounts to as much as 17% for the *threo* and 13% for the *erythro*. When considering the chloride, *threo* gives 9% leakage and *erythro* gives 7%.

The chloride fraction from the chromatogram above was distilled through a short-path still: bp 55–75° (1 mm); $\alpha^{24}D$ −8.50° (*l*, 1 dm, neat). In column II the amount of *threo*-chloride in the mixture was found to be 6%. Nmr of the mixture showed 10% 1-chloro-2-methyl-1-phenylpropane present; the tertiary chloride, 2-chloro-2-phenylbutane, was not detected since it decomposed completely to olefin in the chromatograph. The *erythro*-chloride was present to the extent of 84% in the mixture. In column II, *threo*-chloride was removed from the mixture. The mixture of *erythro*-chloride and 1-chloro-2-methyl-1-phenylpropane was distilled and analyzed by nmr as above to give 89% *erythro*-chloride and 11% 1-chloro-2-methyl-1-phenylpropane, $\alpha^{24}D$ −8.50° (*l*, 1 dm, neat). Pure *erythro*-chloride was collected by removing the benzylic chloride by selective decomposition on column I. The *erythro*-chloride was distilled, $\alpha^{25}D$ −8.34° (*l*, 1 dm, neat).

The acetate fraction from the alumina column was distilled, bp 60–90° (1.0 mm), through a short-path still, $\alpha^{25}D$ +27.00° (*l*, 1 dm, neat). On column III the mixture showed 5% 2-methyl-1-phenyl-1-propyl acetate, and with nmr this acetate was found to be 9% of the mixture; the 2-phenyl-2-butyl acetate was not detected. The acetate mixture was reduced to alcohol with lithium aluminum hy-

methanol. To both 2 ml of dry pyridine was added and the resulting precipitate was separated by filtration and recrystallized twice from absolute ethanol, mp 195°. The solid dissolves in water, shows only aromatic hydrogen bands in the nmr in deuterium oxide, and smells of pyridine in aqueous solution.

Anal. Calcd for $C_{11}H_8N_3O_7S$: C, 40.49; H, 2.47; N, 12.88; S, 9.83. Found: C, 40.00; H, 2.89; N, 12.56; S, 9.83.

In a like manner, methyl 4-methyl-2-nitrobenzenesulfenate (mp 70–71°)[21] produced salt, mp 132–133°.

Anal. Calcd for $C_{12}H_{12}N_2O_5S$: C, 48.63; H, 4.08; O, 27.00; S, 10.82. Found: C, 48.23; H, 4.12; O, 26.4; S, 10.6.

Methyl 2-nitrobenzenesulfenate, mp 48–50° (lit.[22] mp 54°), gave a product, mp 120.5–122°.

Anal. Calcd for $C_{11}H_{10}N_2O_5S$: C, 46.79; H, 3.57. Found: C, 46.44; H, 3.51.

Methyl 4-chloro-2-nitrobenzenesulfenate (mp 110–112°)[23] produced a salt, mp 163–163.5°.

Anal. Calcd for $C_{11}H_9ClN_2O_5S$: C, 41.71; H, 2.86; Cl, 11.19. Found: C, 41.75; H, 2.94; Cl, 10.96.

Absolute Configurations. The various starting materials and products have been related to D-glyceraldehyde[12,13,24,25] except for 1-chloro-2-methyl-1-phenylpropane. It is known that 1-chloro-1-phenylethane and 1-phenylethanol of the same configuration have the same sign of rotation.[26]

The rotational data of Levene, Makeska, and Marker[14] which have been used previously by Cram to assign the configuration of 2-methyl-1-phenyl-1-propanol[27] can be used in like manner to assign the configuration of 1-chloro-2-methyl-1-phenylpropane. The configuration of the chloride is the same as the alcohol with the analogous orientation of the hydroxyl and chloride groups (Table I).

Chlorination in Acetic Acid of *erythro*-3-Phenyl-2-butyl-1-^{14}C 2,4-Dinitrobenzenesulfenate. Chlorinations in acetic acid followed the general procedure outlined here using D-(−)-*erythro*-3-phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate (run 1) as an example.

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(22) T. Zincke and F. Farr, *ibid.*, **391**, 71 (1912).
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(25) D. J. Cram and J. Allinger, *ibid.*, **76**, 4518 (1954).
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(27) See ref 12, Table II.

Table III. Optical Rotations of Products from Chlorination of 3-Phenyl-2-butyl 2,4-Dinitrobenzenesulfenate[a]

Run	Ester	Chlorides[b]			Acetate mixture	Alcohol mixture	Acetates[b]			Alcohols[b]				
		Mixture	*threo*-I	II			*threo*-I	*erythro*-I[c]	II[c]	Mixture[d]	*threo*-I	*erythro*-I	II	III
1	D-(−)-*erythro*	−8.50		−9.8[e,f]	+27.00	−4.83	−27.6[g]	−0.68[g]	−8.38 ± 2.62[e]	−1.08	Absent	−0.63[g]	Absent	−1.22[e]
2	L-(+)-*erythro*[h]	+7.38		+8.14[e,f]	−24.41	+4.22	+32.0[e]	+0.65[g]	+2.71[e]	+0.73	Absent	+0.63[g]	Absent	+0.77[e]
4	L-(+)-*threo*	+8.17	+1.37	+(19–32)[e]	− 7.92	+1.91	+3.32	+0.70 ± 0.19[e]	−2.62 ± 0.72[e]	+3.90		Absent		(+)

[a] *l*, 1 dm, neat; values are given in degrees. [b] I, II, III. See footnote *e*, Table II. [c] Rotations are for corresponding alcohols. [d] Obtained directly from the reaction, not from reducing acetate. [e] Calculated. [f] Minimum rotation. [g] Isotope dilution method. [h] 94% optically pure.

Table IV. Distribution of Enantiomeric Products from the Chlorination of *threo*- and *erythro*-3-Phenyl-2-butyl Sulfenate Esters

Run	Diastereomer[a]	Olefins	Chlorides[b]					Acetates[b]						Alcohols[b]					
			threo-I		*erythro*-I		II[c]	*threo*-I		*erythro*-I		II		*erythro*-I			III		
			E	R	E	R		E	R	E	R	E	R	III	*threo*-I	E	R	II	E	R
1	D-(−)-*erythro*	1		3.4[d]	46.5 (−)	1.4	5.7 (−)[e]	2.5 (−)	0.4	18.3 (−)	0.4	0.7 (−)	1.0	0.7[d]		3.9 (−)	0.4		0.8 (−)	12.9
2	L-(+)-*erythro*[f]	3		4.1[d]	46.7 (+)	1.4	5.8 (+)[e]	2.8 (+)		19.8 (+)		0.3 (+)	1.7	0.5[d]		4.3 (+)			0.4 (+)	9.3
4	L-(+)-*threo*	1	2.3 (+)	38.9		4.1[d]	12.8 (+)[e]	1.6 (+)	14.1	3.2 (+)		0.8 (−)	6.0	0.8[d]	0.9[d]			2.0[d]	12.0 (+)[e]	

[a] For conditions, see Table I. For definition of structures, see Table I. [b] E, enantiomer; R, racemate; enantiometer indicated by sign of rotation accompanying mole per cent concentration. Where the optical purity is unknown, the enantiometer in excess is indicated by the accompanying sign of rotation. [c] Rotation of optically pure 1-chloro-2-methyl-1-phenylpropane is unknown. [d] Optical rotation unknown. [e] Optical purity unknown. [f] 94% optically pure; calculations are uncorrected.

dride in ether; the resulting oil was distilled: bp 70–90° (0.6 mm); $\alpha^{22}D$ −4.74° (*l*, 1 dm, neat). From the gas–liquid partition chromatographic analysis on column II[28] the mixture of *erythro*-alcohol and 2-methyl-1-phenyl-1-propanol comprised 85% of the total while the mixture of *threo*-alcohol and 2-phenyl-2-butanol comprised the remaining 15%. By use of column II, the two pairs of alcohols described above were separated and each was distilled The mixture of *erythro*-alcohol and 2-methyl-1-phenyl-1-propanol, $\alpha^{23}D$ −1.11° (*l*, 1 dm, neat), was analyzed by nmr to be 92% *erythro*-alcohol and 8% benzylic alcohol. Isotope dilution[29,30] was used to establish the optical activity of the *erythro*-alcohol. A portion (0.08400 g) of the above mixture of *erythro*-alcohol and 2-methyl-1-phenyl-1-propanol (0.5308 mCi/mole) was combined with 0.16490 g of nonradioactive racemic *erythro*-3-phenyl-2-butanol. The corresponding acid 3-nitrophthalate was prepared with 0.266 g of 3-nitrophthalic anhydride in dry pyridine. The mixture was heated on the steam bath for 2 hr, cooled, and poured into benzene. The benzene solution was washed with 5% sulfuric acid, dried, and evaporated to an oil on the steam bath with a stream of dry air. The oil was crystallized from an ethyl acetate–hexane mixture followed by two additional recrystallizations: mp 132–133°, $[\alpha]^{24}D$ 0.0° (*l*, 1 dm, 3% C_2H_5OH, 0.1468 mCi/mole). The *erythro*-alcohol is calculated to be 98% optically pure.

The mixture of *threo*-alcohol and 2-phenyl-2-butanol from the above preparative separation was analyzed on column II at a higher temperature and higher flow rate to effect a slight separation of the tertiary alcohol from the *threo*-alcohol. Analysis showed 74% *threo*-alcohol, 17% 2-phenyl-2-butanol, and a 9% mixture of *erythro*-alcohol and 2-methyl-1-phenyl-1-propanol. By the isotope dilution procedure,[29,30] the optical purity of the *threo*-alcohol was found to be 87%. The iodoform analysis of the above mixture of 92% *erythro*-alcohol and 8% 2-methyl-1-phenyl-1-propanol was performed according to the method of Bonner and Tanner.[8] The radioactivity analysis of D-(−)-*erythro*-3-phenyl-2-butyl 2,4-dinitrobenzenesulfenate was 0.4376 mCi/mole. The starting alcohol produced iodoform that gave a radioactivity analysis of 0.3861 mCi/mole. The alcohol product produced iodoform that analyzed 0.2655 mCi/mole.

The alcohol from the alumina column was distilled, bp 80–95° (0.1 mm), through a short-path still, $\alpha^{24}D$ −1.08° (*l*, 1 dm, neat). Analysis on column II indicated 76% 2-phenyl-2-butanol and 24% *erythro*-alcohol. Nmr verified the presence of these two components. By the described isotope dilution technique,[29,30] the optical purity of the *erythro* isomer was calculated to be 91%.

Chlorination in Acetic Acid of *threo*-3-Phenyl-2-butyl 2,4-Dinitrobenzenesulfenates. Chlorination of L-(+)-*threo*-3-phenyl-2-butyl 2,4-dinitrobenzenesulfenate (run 4) followed the procedure described above for the *erythro* diastereoisomer. Analysis of the chloride, acetate, and alcohol fractions from the alumina column is described below. The chloride fraction was distilled using a short-path still, $\alpha^{22}D$ +8.16 (*l*, 1 dm, neat). Gas–liquid partition chromatography on column II showed 71% *threo*-chloride and 29% of the mixture of *erythro*-chloride and 1-chloro-2-methyl-1-phenylpropane. The nmr analysis showed 7% *erythro*-chloride and 22% of the latter benzylic chloride. Separation of the mixture into the *threo*-chloride and the mixture of *erythro*-chloride and 1-chloro-2-methyl-1-phenylpropane was effected by use of column II. The distilled *threo* fraction, $\alpha^{22}D$ +1.82° (*l*, 1 dm, neat), still retained 5% of the mixture of *erythro*-chloride and benzylic chloride. A second pass through column II produced pure *threo* chloride, $\alpha^{23}D$ +1.37° (*l*, 1 dm, neat). The mixture of *erythro*-chloride and the benzylic chloride separated above was distilled, $\alpha^{22}D$ +10.42° (*l*, 1 dm, neat); gas–liquid partition chromatographic analysis showed 32% *threo*-chloride and 68% of the mixture of *erythro*-chloride and the benzylic chloride. The *threo* and *erythro* concentrations were about equal from observations of the nmr; further gas–liquid partition chromatography measurements using columns I and III likewise set this ratio at approximately 1. Therefore, the composition is approximated as 30% *threo*, 30% *erythro*, and 40% 1-chloro-2-methyl-1-phenylpropane.

Accounting for the possibility of racemization to 1-chloro-2-methyl-1-phenylpropane in the separation by gas–liquid partition

(28) Y. Gault and H. Felkin, *Bull. Chem. Soc. Fr.*, 742 (1965).
(29) J. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, 81, 4084 (1959).
(30) B. M. Benjamin and C. J. Collins, *ibid.*, 83, 3662 (1961); C. J. Collins, "Advances in Physical Organic Chemistry," Vol. 2, V. Gold, Ed., Academic Press, New York, N. Y., 1964, p 1.

chromatography, the rotation of 1-chloro-2-methyl-1-phenylpropane must be between +19 and +32°.

The distilled acetate fraction from the alumina column, $\alpha^{22}D$ −7.83° (*l*, 1 dm, neat), gave a nmr analysis that showed that 2-methyl-1-phenyl-1-propyl acetate comprised 30% of the mixture; 2-phenyl-2-butyl acetate was not detected. In column III, the 2-methyl-1-phenyl-1-propyl acetate content was estimated at 24%. The acetate fraction was reduced with lithium aluminum hydride to the alcohol and distilled, $\alpha^{22}D$ +1.91 (*l*, 1 dm, neat). Analysis by gas–liquid partition chromatography showed 58% of a mixture of *threo*-alcohol and 2-phenyl-2-butanol; the remaining 42% was a mixture of *erythro*-alcohol and 2-methyl-1-phenyl-1-propanol, which on further analysis was found to be 10% *erythro*-alcohol and 32% 2-methyl-1-phenyl-1-propanol; the infrared analysis was discussed above. With reference to both the gas–liquid partition chromatography and nmr data, the following are approximate concentrations: *threo* 58 ± 4%, *erythro* 12 ± 3%, 2-methyl-1-phenyl-1-propanol 25 ± 3%, 2-phenyl-2-butanol 3 ± 3%.

The alcohol mixture from the reduced acetate was separated on column II into two fractions. The first fraction was distilled, $\alpha^{22}D$ +3.36° (*l*, 1 dm, neat). The nmr spectrum was identical with pure *threo*-alcohol. The analysis of the distilled second fraction, $\alpha^{22}D$ −1.66° (*l*, 1 dm, neat), by gas–liquid partition chromatography revealed 5% *threo*, 25% *erythro*, and 70% 2-methyl-1-phenyl-1-propanol. Solutions were then obtained for a series of simultaneous equations.

The alcohol fraction from the alumina column was distilled, $\alpha^{22}D$ +3.94° (*l*, 1 dm, neat); analysis by infrared showed 80.8% 2-phenyl-2-butanol, 5.7% *threo*, and 12.6% 2-methyl-1-phenyl-1-propanol. Analysis by gas–liquid partition chromatography on column II was in agreement with the infrared results. The rotations of the alcohol components could not be determined.

Reactions in Acetic Acid with Added Lithium Perchlorate. Both of the racemic diastereoisomers were chlorinated in 0.080 *M* lithium perchlorate in dry acetic acid. To 144 ml of dry acetic acid containing 1.22 g (0.0115 mole) of lithium perchlorate was added 4.99 g (0.0143 mole) of racemic *erythro*-3-phenyl-2-butyl 2,4-dinitrobenzenesulfenate, mp 75–76° (run 3). Chlorination was effected by addition of 1.30 ml (0.028 mole) of chlorine by the method described above. A 70% yield (2.69 g) of 2,4-dinitrobenzenesulfonate, mp 102°, was isolated. The oil product was chromatographed as before into chloride, acetate, and alcohol fractions.

The chloride fraction analyzed on column II showed a 94% mixture of *erythro*-chloride and 1-chloro-2-methyl-1-phenylpropane and 6% *threo*-chloride. The nmr analysis of the distilled chloride fraction offered no evidence for the presence of 1-chloro-2-methyl-1-phenylpropane. The acetate fraction was analyzed by gas–liquid partition chromatography on column II. There was no indication of the presence of 2-methyl-1-phenyl-1-propyl acetate in the mixture. The nmr of the distilled acetate fraction showed the *erythro*-acetate as the only compound that could be identified except for about 2–3% of *threo*-acetate. The alcohol fraction from the alumina column when analyzed on column II showed 28% 2-phenyl-2-butanol and 72% *erythro*-alcohol. The nmr gave no evidence of either 2-methyl-1-phenyl-2-propanol or *threo*-alcohol in the mixture.

The chlorination of racemic *threo*-3-phenyl-2-butyl 2,4-dinitrobenzenesulfenate in acetic acid with added 0.080 *M* lithium perchlorate (run 5) was run by the same procedure described above. The sulfonyl chloride that was isolated amounted to a 75% yield. In the acetate analysis, combined nmr and gas–liquid partition chromatography on the alcohol was necessary for a complete analysis. The analysis of the alcohol fraction required an isotope dilution experiment to determine the *threo* content. The results of the above experiments are included in Table II.

Control Experiments. Stability of *threo*- and *erythro*-3-phenyl-2 butyl acetates and alcohols during the lithium aluminum hydride reduction of the former was tested in the following manner. A diastereomeric mixture (*threo*:*erythro* = 1:2) of 3-phenyl-2-butanol-1-^{14}C (0.469 mCi/mole) was converted to acetate by the acetic anhydride–pyridine method.[12] The pure acetate was reduced to the alcohol with lithium aluminum hydride in ether. The starting and recovered alcohols were subjected to the iodoform reaction; isolated iodoform was recrystallized twice from ethanol, mp 121°. Radioactivity analyses of the iodoform from the starting alcohol and from the reduced acetate were 0.471 and 0.457 mCi/mole, respectively. To check alcohol stability during preparative separations by gas–liquid partition chromatography on column II, an approximately equimolar mixture of *threo*- and *erythro*-3-phenyl-2-butanol-1-^{14}C (0.441 mCi/mole) was separated on column II. Two isolated samples, one of pure *threo*-alcohol and the second a mixture of *threo*- and *erythro*-alcohol, were each degraded by the iodoform reaction along with the starting alcohol. The iodoform activities were: starting alcohol, 0.400 mCi/mole; *threo*-sample from glpc, 0.372; *threo–erythro* sample from glpc, 0.386. The *threo* and *erythro–threo* samples show 8 and 4% rearrangement, respectively. The noticeable difference in activity of the starting alcohol and its iodoform product was unexpected. Lack of rearrangement in the reduction of the acetate discussed above confirmed a previous report in which equal radioactivity concentrations were found for starting alcohol and its iodoform degradation product.[8] Further, the discrepancy cannot be accounted for by an isotope effect in the iodoform reaction.[8,31] The source of alcohol used here and that used in the reduction of the acetate clarifies the discrepancy. Alcohol used in the reduction experiment had undergone no further reactions after preparation, whereas alcohol used in the stability examination of the gas–liquid partition chromatography method had been hydrolyzed from recovered acid phthalate and acid 3-nitrophthalate esters present in mother liquors from the resolution of the alcohol. Therefore, some migration must have occurred in the resolution procedure used to resolve the alcohol.[9] Other workers have also reported slight differences under similar circumstances.[32] The extent of racemization of 2-methyl-1-phenyl-1-propanol or 2-phenyl-2-butanol under like conditions was not studied.

To check the stability of *threo*-2-chloro-3-phenylbutane to racemization in preparative separations by gas–liquid partition chromatography, a sample of *threo*-chloride, $\alpha^{25}D$ −0.78° (*l*, 1 dm, neat) (run 7), separated by the same method was passed through column II a second time. The collected fraction was distilled, $\alpha^{24}D$ −0.81° (*l*, 1 dm, neat). Purity of the compound was verified by gas–liquid partition chromatography.

The known instability of 2-chloro-2-phenylbutane[15,16] made necessary an investigation of the fate of this chloride in the reaction environment. To 100 ml of 0.0195 *M* (0.0195 mole) chlorine in acetic acid was added 0.583 g (0.00345 mole) of 2-chloro-2-phenylbutane, which by nmr analysis was found to contain approximately 20% olefin. The solution, after remaining at room temperature for 40 min, was poured into 700 ml of water and extracted twice with 125 ml of pure hexane. The combined hexane layers were washed with sodium bicarbonate solution, dried, and evaporated to an oil. Alumina chromatography of the oil gave olefin and alcohol fractions in 45 and 55% yields, respectively. The alcohol was identified as 2-phenyl-2-butanol.

The fate of 2-phenyl-2-butyl acetate in the reaction environment was determined by a similar experiment. To 100 ml of acetic acid with 0.135 mole of chlorine was added 0.556 g (0.0029 mole) of 2-phenyl-2-butyl acetate. After standing at room temperature for 45 min, the solution was poured into 400 ml of water and extracted twice with 150 ml of pure hexane. The hexane layers were washed with 5% sodium bicarbonate, dried, and evaporated to an oil under aspirator pressure using a 1-ft Vigreux column. The product was determined by nmr to be predominantly the starting acetate. An infrared method quantitatively showed the product to be 79% 2-phenyl-2-butyl acetate with absence of any hydroxyl stretching band. Therefore, acetate is not solvolyzed to alcohol under conditions of this reaction.

Results

Both optically active and racemic 3-phenyl-2-butyl-1-^{14}C 2,4-dinitrobenzenesulfenate esters were prepared[17] from the corresponding optically active and racemic 3-phenyl-2-butanol-1-^{14}C[9,20] and 2,4-dinitrobenzenesulfenyl chloride.[18] Each ester was a neatly crystalline material stable to normal laboratory storage for at least several weeks. Analysis of the terminal methyl group in the alcohols by an iodoform degradation procedure[8] showed the label had not remained at the C-1 position but scrambled to the extent of 8% in the *threo* isomer. It presumably had become distributed between the C-1 and C-4 positions by phenyl migration.[32] On the other hand, an analysis of a diastereomeric mixture of *threo*- and *erythro*-alcohols

(31) G. A. Ropp, W. A. Bonner, M. T. Clark, and V. F. Raaen, *J. Am. Chem. Soc.*, 76, 1710 (1954).

(32) W. B. Smith and M. Showalter, *ibid.*, 86, 4136 (1964).

freshly prepared from hydratropic aldehyde and methylmagnesium-^{14}C iodide showed that scrambling had not occurred. Presumably, the resolution procedure caused limited rearrangement to occur in some unknown step.

The reaction of an alkyl arenesulfenate with an equal concentration of chlorine in acetic acid gives alkyl chlorides, alkyl acetates, elimination products, and presumably the sulfinyl chloride. Efforts to isolate 2,4-dinitrobenzenesulfinyl chloride in acetic acid or to trap it as the ester were unsuccessful. Only 2,4-dintrobenzenesulfonyl chloride or the pyridinium salt of the corresponding sulfonic acid could be isolated.

A 2:1 molar ratio of chlorine to sulfenate ester was used during the chlorinations in acetic acid. Extra chlorine caused oxidation of the sulfinyl chloride to sulfonyl chloride. The oxidation probably does not occur until water has been added during the work-up procedure. It is known that 2,4-dinitrobenzenesulfenyl chloride will not react in this medium since acetic acid is too weak a nucleophile.[33] After addition of 1 equiv of chlorine, the intense sulfenate ester color was observed to disappear, leaving an almost colorless solution. The addition of the remaining chlorine left the typically greenish chlorine color suggesting the second portion of chlorine did not react. However, when water was added an immediate precipitate formed with the disappearance of the chlorine color. Although the addition of water may have caused merely a physical change, it may be that water was a necessary reagent (eq 1).

$$\mathrm{ArS(O)Cl} + \mathrm{H_2O} + \mathrm{Cl_2} \longrightarrow \mathrm{ArS(O)Cl} + 2\mathrm{HCl} \qquad (1)$$

The yields of recovered sulfonyl chloride (Table II) are somewhat low because of its partial solution in pentane during the extraction procedure. No effort was made to isolate the additional sulfonyl chloride, although recovery should be possible, either from the pentane or the alumina column that was to separate the reaction mixture.

Yields of olefin, chloride, acetate, and alcohol fractions isolated from the alumina column (see Table II) were calculated from the recovered radioactivities in each fraction. The mole fractions calculated from the weights of each fraction were usually within 1% of the radioactivity values. Total yields were determined by summation of radioactivities in all the fractions.

The procedure for analysis of components within each group is described in the Experimental Section. Precision of these methods varied considerably; for example, measurements by gas–liquid partition chromatography for components that were separated completely from peaks were especially precise; but when two or more peaks overlapped the results were considered only an estimate of the true concentration. The main difficulty in the analysis precedure was the inability to measure accurately concentrations of the *erythro* and 2-methyl-1-phenyl-1-propyl components, a problem common to the chloride, acetate, and alcohol product groups. The infrared and nmr methods alternatively used afforded results which were accurate to within 5% of the correct concentration. Fortunately, however, the effect of these errors on the gross competition is greatly reduced because of the breakdown of the product into smaller fractions for analysis. Runs 1 and 2 especially suggest reproducibility.

Since gas–liquid partition chromatography was used for preparative separations, control experiments were conducted to determine if any change occurred in optical properties during the process of separation. In other mixtures the availability of the isotope dilution method[29,30] made possible an accurate optical purity measurement of one or two components. These independently obtained rotations could then be used to calculate optical purities for other components. For those situations where solution of a series of equations was necessary, a least-squares computer program was used which gave indication of the precision of the method.

In certain situations only the limits of rotation could be determined; for example, in runs 1 and 2 mixtures of *erythro*-chloride and 1-phenylisobutyl chloride were separated from the *threo*-chloride by gas–liquid partition chromatography. Since the rotation of pure *erythro*-chloride is unchanged by the separation procedure, the optical rotation of the 1-phenylisobutyl chloride can be calculated; this rotation is a minimum value, however, because some racemization occurs during the separation procedure.

The small concentrations of 2-phenyl-2-butyl components could have only slight effect on the optical rotations of the acetate or alcohol mixtures. Since the concentrations and specific optical activities of the acetate (αD 1.6°, *l*, 1 dm, neat) and alcohol (αD 17.7°, *l*, 1 dm, neat) are small, they do not make a significant contribution to the total rotation of the mixtures, even if these components were optically pure. The small rotation of the alcohol fraction from the alumina column makes the assignment of rotations to the tertiary alcohol somewhat tentative.

The presence of 2-phenyl-2-butanol in the reaction mixture was traced to the hydrolysis of the corresponding chloride during product isolation. The instability of 2-chloro-2-phenylbutane has been well established.[15,16] From a control experiment, in which the chloride was placed in the sulfenate ester chlorination environment, 2-phenyl-2-butanol and olefin were isolated without any trace of acetate product. An additional control experiment confirmed that 2-phenyl-2-butyl acetate once formed does not hydrolyze to alcohol under similar conditions. Therefore, the yield of 2-phenyl-2-butanol produced in the reaction is considered indicative of the 2-chloro-2-phenylbutane product.

The *erythro*-alcohol obtained in runs 1 and 2 (see Table IV) showed almost complete retention of configuration. The *erythro*-alcohol can possibly arise by cleavage of the sulfur–oxygen bond without rearrangement, a reaction that is known to proceed readily in strong acid media.[34–36] The source of the 1-phenylisobutyl alcohol in run 5 has not been determined, although the hydrolysis of the corresponding chlorine offers a likely route.

(33) E. N. Givens and H. Kwart, *J. Am. Chem. Soc.*, 90, 378, 386 (1968).

(34) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, 39, 269 (1946).

(35) The somewhat greater extent of formation of the products of acid cleavage in the presence of $LiClO_4$ may be due to the acidity caused by this salt in acetic acid.[36]

(36) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, 31, 2719 (1966); I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, 56, 1014 (1934).

Table V. Migration Characteristics in the Acetolysis of Various 3-Phenyl-2-butyl Substrates

Substrate	Diastereomer[a]	$LiClO_4$, moles/l.	Mole ratio of chloride[b]/ acetate	Migration products[d] Total	Phenyl[c,d] -Cl	Phenyl[c,d] -OAc	Me[d] -Cl	Me[d] -OAc	H[d] -Cl	H[d] -OAc	Ref
Sulfoxonium	D-(−)-*erythro*		2.95	87	53	21	7	2	16	1	Run 1
Sulfoxonium	L-(+)-*erythro*		2.70	85	55	23	7	2	12	1	Run 2
Sulfoxonium	*erythro*	0.080	0.81	77	40	56	0	0	4	0	Run 3
Sulfoxonium	L-(+)-*threo*		2.65	85	46	16	15	8	14	1	Run 4
Sulfoxonium	*threo*	0.080	0.81	79	34	48	8	7	4	0	Run 5
Tosylate	L-(+)-*threo*				85–87			0	11		8, 9
Tosylate	L-(+)-*erythro*				89–94			0	6		8, 9
Diazonium	L-(+)-*threo*				19–25			32	24		9
Diazonium	L-(+)-*erythro*				68			6	20		9

[a] Conditions are shown in Table I. Runs 3 and 5 are based on concentration of diastereomers. Other runs are on the basis of enantiomer concentrations. [b] Includes 2-phenyl-2-butanol concentration in calculating chloride concentration. [c] Phenyl migration in runs 3 and 5 is assumed to occur only in the diastereomer the same as starting material. [d] Normalized on the basis of total migration product.

The effect of added salt on the product distribution was studied in the chlorination of both *erythro*- and *threo*-sulfenate esters (runs 3 and 5). A noticeable change in the chloride–acetate product ratio is shown in Table V. Without added lithium perchlorate the chloride product clearly predominates over acetate product for both *erythro*- and *threo*-sulfenate. However, in the presence of 0.080 *M* lithium perchlorate in acetic acid, the ratio changes sharply. Also, the *erythro*- and *threo*-3-phenyl-2-butyl products increase at the expense of the products of methyl and hydrogen migration. Another observation is a small increase of olefin product in the presence of lithium perchlorate.

Discussion

The decompositions of the sulfoxonium cations generated during the present studies (and of the sulfenate esters previously reported) are unique in that they exhibit behavior similar to *both* the decomposition of diazonium ions[12] and of the acetolysis of the tosylates[9] derived from 3-phenyl-2-butyl precursors.

The optical results show phenyl migration during formation of *threo* products from *threo* reactant, whereas experiments with C-14 demonstrate phenyl migration during formation of *erythro* products from *erythro* reactant. In the absence of lithium perchlorate *erythro* or *threo* "leakage" (runs 1, 2, and 4, Table II) amounts to 7–17%.[37] The presence of 0.08 *M* lithium perchlorate not only eliminates half of the leakage products, but severely reduces the percentages of those products (see Table II) which are formed by methyl and hydrogen migration. From the stereochemistry of the products formed, it is clear that "leakage" from either reactant occurs with inversion about C_α. In principle this inversion could result either (a) by nucleophilic SN2 displacement on C_α or (b) by SN1 attack by solvent or anion on a carbonium ion center. The repression of leakage by lithium perchlorate strongly indicates the latter (SN1 attack) is the mechanism of leakage, since the influence of lithium perchlorate is to prevent return to the intimate ion pairs, and should not affect the SN2 displacement.

These results bear emphasizing by way of comparison with those obtained in deamination and tosylate solvolysis of the *threo*-3-phenyl-2-butyl substrates, where 20–70% of the leakage acetate product was racemic. One must interpret the leakage leading to racemic product as originating in phenyl migration at both C_α and C_β. Thus, the formation of totally active leakage product from both *erythro*- and *threo*-sulfoxonium substrates (as noted here) cannot occur with phenyl migration and only with inversion at C_α.

Hydrogen migration in the 3-phenyl-2-butyl system has been observed in arene- and alkanesulfonate acetolysis[11,20,38] and amine deamination[8,12] (see Table V). Also, since 3-phenyl-2-butyl chloride,[39] alcohol,[38,39] phthalate[39] and *p*-toluenesulfonate[40] produce the methylethylphenylcarbonium ion in strong acid systems such as FSO_3H–SbF_5 at very low temperatures, the presence of the products of hydrogen migration was not unexpected. The concentration of the acetate was quite small and the optical rotation could not be determined. 2-Phenyl-2-butanol that was produced from hydrolysis of the chloride product was very nearly racemic. Therefore, the stereochemistry of the products of hydrogen migration is unknown. Acetolysis of esters of 2-phenyl-2-butanol also gives nearly racemic materials, whereas other solvents often are much more stereospecific.[41]

The presence of the products of methyl migration makes the chlorination of sulfenate esters similar to the deamination reaction, the only other reported reaction in which this product was found. Even in the strong acid systems referred to above,[39] the isopropylphenylcarbonium ion was not formed, although it is quite stable in these systems.[39] The configurational relationship between the isopropylphenylcarbinyl products and the sulfenate ester reactants is known. Thus it is evident that inversion of configuration occurs in the formation of 1-chloro-2-methyl-1-phenylpropane (Table II, runs 1, 2, and 4); the degree of inversion could not be determined since the rotation of the optically pure chloride is unknown. Inversion was also the predominant stereochemical course of the methyl migration reaction in formation of the corresponding acetates from the *erythro*-sulfenate esters (15 and 41%).

An SNi process appears not to operate in this reaction based largely on arguments presented by Cram.[13] If such a reaction occurred L-(+)-*threo*-sulfenate would have given L-(+)-*threo*-chloride completely. If the

(37) See Table II, footnote *f*.

(38) R. S. Bly and R. L. Veasey, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; Abstract S 8.

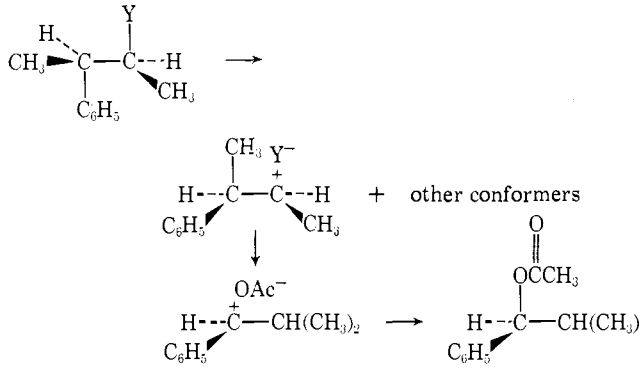
(39) G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 5571 (1966).

(40) M. Brookhart, F. A. L. Anet, D. J. Cram, and S. Winstein, *ibid.*, **88**, 5659 (1966).

(41) L. H. Sommer and F. A. Carey, *J. Org. Chem.*, **32**, 800 (1967).

SNi mechanism had occurred with rearrangement and inversion at both C_α and C_β, D-(−)-*threo*-chloride would have been the only product. Since, however, almost completely racemic chloride was obtained such mechanisms seem very unlikely.

The acetate product of methyl migration from L-*threo*-sulfenate ester (12 ± 3%) exhibited excess retention of configuration. This means the substitution of acetate occurred from the same side of the migration origin occupied by the methyl group, as shown. Al-



though preferential attack by entering group on the opposite side of the carbon from which the migrating group departs is normal, we have observed here a significant exception. Consequently we have demonstrated the presence of the classical isopropylphenylcarbonium ion. We also must conclude, for the same reasons, that hydrogen and methyl migrations take place *via* the open, unbridged, classical 3-phenyl-2-butyl cation.[14] There are two possible extreme modes by which these products can be formed through open carbonium ions: (1) a preferred ground-state may lead to a preferred carbonium ion conformation which can suffer rotation to yield all possible carbonium ion conformers; or (2) several ground-state conformations could yield the carbonium ion conformers directly. Our present data do not allow us to say with confidence whether one or both of these modes are operating. However, a total accounting of the factors determining the nature of the carbonium ions involved must take into consideration the influences of ion pairing.

The Influence of Ion Pairing

Table V shows the proportions of chlorides and acetates produced from various substrates and under various reaction conditions. It also shows the distribution of products which results from hydrogen, methyl, or phenyl migration. Listed also for comparison are the results of other workers[9,12,20] obtained in the deamination acetolysis of the corresponding amine and the acetolysis of the tosylate. The extent of product formation through migration in the deamination of the 3-phenyl-2-butylamines as postulated and observed by Cram and McCarty[12] is for *erythro*-amine, phenyl > hydrogen > methyl; for *threo*-amine, methyl > phenyl > hydrogen. The corresponding order derived from the *erythro*-sulfenate chlorination agrees, but the order noted for the *threo*-sulfenate is phenyl > methyl > hydrogen. Thus, the methyl to hydrogen migration ratios for the sulfoxonium ion and diazonium ion cases are *erythro* 0.65 (sulfoxonium), 0.75 (diazonium); *threo* 1.8 (sulfoxonium), 3.2 (diazonium). When we compare (Table V) the different product compositions observed from *threo*- and *erythro*-3-phenyl-2-butyl precursors during (1) the chlorinolysis of the sulfenate esters, (2) the deamination of the amines, and (3) the acetolysis of the tosylates, it seems clear that these differences originate in ion-pairing phenomena, since all three reactions may be looked upon as acetolyses involving 3-phenyl-2-butyl cations.

The influence of added $LiClO_4$ on the product composition is of particular interest in connection with establishing to what degree ion-pairing phenomena control solvolytic behavior in the various 3-phenyl-2-butyl cases considered.

The large increase in the acetate components of the product composition observed for both the *threo*- and *erythro*-sulfoxonium ion substrates in the presence of $LiClO_4$ is consistent with the result[2] obtained in the case of the 1-phenylpropylsulfoxonium ion. Since the net effect of the $LiClO_4$ is to enhance the proportion of external ion pairs, this result was interpreted to indicate that acetate products arise principally from a solvent-separated sulfoxonium ion forming a solvent-separated carbonium ion. Acetate may also be formed from internal ion pair which has returned from external ion pair. This interpretation is shown in Chart I.

We can also assess from the data in Table V the influence of $LiClO_4$ on the proportions of the several migration products. In each case a significant increase in the amount of the product of phenyl migration can be noted; thus the component formed by phenyl migration in *erythro* reactant increased from an average of 75 to 96% and in the *threo* case from 62 to 82%. Furthermore, there is a decrease in the amount of both methyl and hydrogen migration products, though here the extent of the $LiClO_4$ influence is different in each of the diastereoisomers. The methyl migration product in the *erythro* case is wiped out by the $LiClO_4$ and the hydrogen migration is diminished by a factor (approximately 3) greater than the increase in the product of phenyl migration. For the *threo* isomer, the decrease in methyl migration produced by the $LiClO_4$ is quite proportional to the increase in phenyl migration experienced, while the hydrogen migration is diminished by an even greater factor (approximately 4).

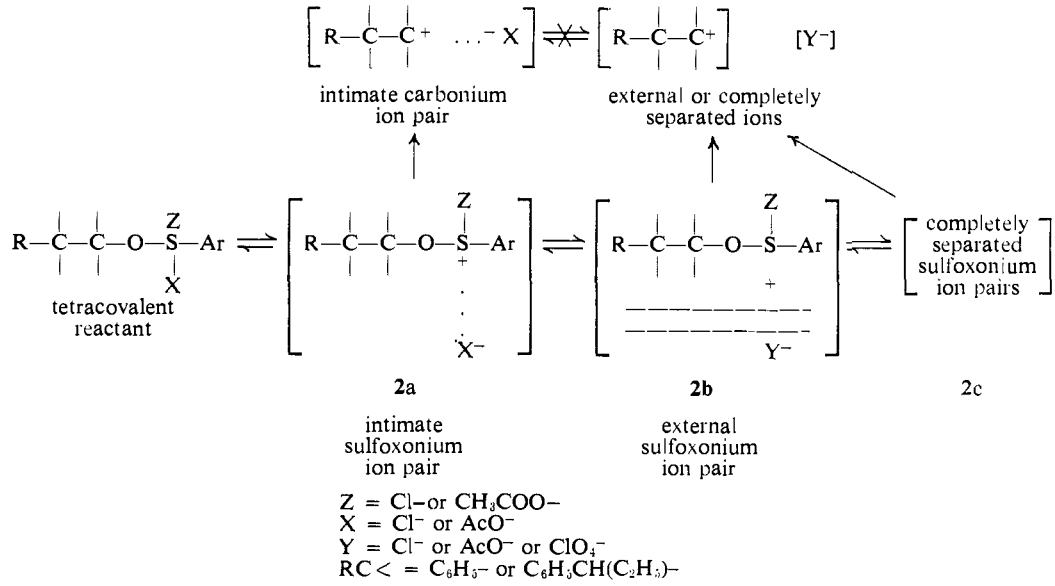
These results enforce the deduction that methyl and hydrogen migrations take place in the intimate ion pair and suggest also the interesting possibility that phenyl migration is more characteristic of the external ion pair.

One somewhat disturbing feature concerning the two runs (runs 3 and 5, Table II) in which $LiClO_4$ was present is the increase in olefin produced. It is evident that the origins of olefin—if all of it comes from the phenylisopropylcarbinyl and 2-phenyl-2-butyl cations—diminish the effect induced by $LiClO_4$ on methyl and hydrogen migration. In no case, however, could the suppression of methyl and hydrogen migration by lithium perchlorate be less than reported in our preliminary communication.[1a,42]

A striking feature of the present data, obvious from Table II, is the fact that in acetolysis solutions 0.08 *M* in lithium perchlorate, the total "leakage" from *threo* reactant to *erythro* products and from *erythro* reactant

(42) In ref 1a, we assumed that olefin was formed only *after* methyl or hydrogen migration (the most pessimistic assumption possible) and included it in the combined percentages of methyl and hydrogen migration.

Chart I



to *threo* products is cut in half. We interpret this result to mean that the stereospecificity is really a function of ion pairing and solvation. Evidence is therefore now at hand establishing that 1,2 shifts can be correlated with the characteristics of the several ion pairs to be encountered in solvents of low ionizing power.

It is of interest also to inquire into the circumstances of rotation about the central C–C bond when the initial carbonium ion center is developing in each of the several sulfoxonium ion precursors, and to compare this situation with the corresponding deamination reaction. Within the transferred solvent structure of the intimate ion pair there is apparently less opportunity available for rotation producing conformational interchange, and thus the *trans* antiparallel requirement for participation is often fulfilled by methyl or hydrogen. However, within the solvent structures of the external ion pairs (as well as the completely separated ions) the more extensive diffusion of positive charge seemingly permits a preference for participation by the group (phenyl) which can create the most stable structure of the carbonium ion. The unstable diazonium ion decomposes almost at the instant of its formation. Little or no solvent structure is consequently transferred to the carbonium ion developed by the departure of nitrogen, This would require more time than is available from the moment of formation of the diazonium ion to the beginnings of the product-forming steps. Under these conditions, the carbonium ion has little opportunity to adjust to the conformational demands for participation of that group in its structure which can render the greatest assistance in distribution of the positive charge so suddenly thrust upon it. Migration results are then chiefly[43] dictated by the conformational preferences in the ground state of the amine precursor.[12] The diazonium ion substrate consequently shows no response of product composition to the addition of small amounts of $LiClO_4$ which has been identified here for the stable sulfoxonium ion substrate (and previously for related species[2]).

(43) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins [*J. Am. Chem. Soc.*, **79**, 6160 (1957)] demonstrated that a migrating phenyl during deamination can attack the migration terminus from *either* direction, leading to inversion or retention of configuration. Collins, *et al.* [*ibid.*, **83**, 3362 (1961); *J. Org. Chem.*, **27**, 3525 (1962)] showed later that aryl migration with retention of configuration can be the preponderant result, quite in contrast to the conclusions of Cram and McCarty (ref 12), who assumed that ground-state control during deaminations could proceed only with backside attack on the migration terminus with complete inversion of configuration.