

cating a capacity of 4.78–5.58 meq./g. of polymer. This polymer has relative viscosities in pyridine of 1.140 (0.126 g./100 ml.); 1.08 (0.063 g./100 ml.) and 1.04 (0.032 g./100 ml.).

Viscosity Measurements.—The polymers were dissolved in J. T. Baker C.P. pyridine or in 0.094 *N* sodium hydroxide

and the solutions filtered. The viscosities were measured in Ostwald viscometers at 30° at successive dilutions starting with solutions of 0.4–0.6 g. per 100 ml. of solvent in most determinations.

LOUISVILLE, KY.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Stereochemistry of the Formation and Decomposition of Dimethyl- α -phenethylsulfonium Bromide^{1,2}

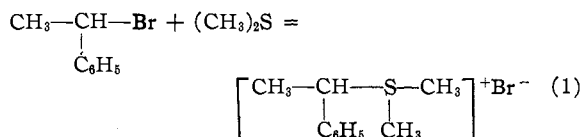
BY SAMUEL SIEGEL³ AND ALLEN F. GRAEFE

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The formation of dimethyl- α -phenethylsulfonium bromide from methyl sulfide and α -phenethyl bromide, and its decomposition, proceed with the predominant inversion of the asymmetric carbon atom. The reaction takes place in a medium of low polarity, the liquid reactants, at 23°. Kinetic evidence points to a homogeneous reaction although the salt has a low solubility in the reaction medium. The significance of these results for the theory of the displacement reaction is discussed.

Although the displacement of a halide ion from an alkyl halide in a polar solvent, by reagents such as sodium iodide, is clearly accompanied by inversion of configuration,⁴ it is not so evident that all one-stage displacement reactions must occur with this steric result.⁵ In particular, a displacement reaction between two reactants of such a type that a large separation of charge must appear in the transition state, is one which might take place with retention of configuration. However, the thermal decomposition of D-(+)-N,N,N-trimethyl- α -phenethylammonium acetate yields a product with an inverted configuration⁶ as does the decomposition of 1-piperityltrimethylammonium hydroxide.⁷ These observations have been cited in support of a quantum mechanical argument for a nearly linear arrangement of the reaction centers in the transition state of all displacement reactions.⁸ But the argument is weakened by the fact that the decomposition occurs in a fused salt, a medium equivalent to one with a high dielectric constant, and one which would certainly tend to minimize electrostatic effects.

It appeared to us that if electrostatic interactions could influence the course of a displacement reaction from one of inversion of configuration (the usual result) to retention of configuration, then such an effect would be most pronounced if the reaction occurred in a solvent having a low dielectric constant. A suitable reaction appeared to be that of α -phenethyl bromide with methyl sulfide to form a sulfonium salt, or the reverse process.



The reactants on the left are low in polarity and can themselves provide the appropriate medium. By the use of the principle of microscopic reversibility, one may conclude that if the formation of the sulfonium salt proceeds with inversion of configuration then the reverse process should likewise proceed with inversion, the converse being equally true.

The conditions for the formation of this salt from the above reagents and, alternatively, from methyl α -phenethyl sulfide and methyl bromide were studied systematically. Substantially pure dimethyl- α -phenethylsulfonium bromide was isolated and characterized, and information to guide the subsequent studies with the optically active reagents was collected.

The stereochemistry of the forward reaction was studied directly by the isolation of the active salt from active α -phenethyl bromide and methyl sulfide and the stereochemistry of the reverse reaction was studied indirectly by allowing the salt, formed from active methyl α -phenethyl sulfide and methyl bromide, to decompose in the presence of an excess of the latter. These conditions served to drive the reaction in the desired direction by the removal of methyl sulfide as the insoluble trimethylsulfonium bromide.

Experimental⁹

α -Phenethylsulfonium Bromide.—A mixture of α -phenethyl bromide¹⁰ (137.0 g.), thiourea (56.4 g.) and 95% ethyl alcohol (375 ml.) was refluxed for six hours. The solvent was removed by distillation under reduced pressure. An equal volume of anhydrous benzene was added to the hot residue, and the mixture was swirled until crystallization had begun and finally chilled to 0°. The solid was filtered and washed repeatedly with absolute ether until the washings were colorless, and dried at 70°; yield 177.6 g. (91.8%), m.p. 153–157°. A small sample of the material

(1) From the dissertation of Allen F. Graefe, submitted in partial fulfillment of the requirements for the Ph.D. degree at Illinois Institute of Technology, February, 1952.

(2) Presented at the 121st National Meeting of the American Chemical Society, Milwaukee, Wis., March 31, 1952.

(3) Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

(4) E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185, 202 (1938).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 159–160; N. Meer and M. Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

(6) H. R. Snyder and J. H. Brewster, *THIS JOURNAL*, **71**, 291 (1949).

(7) J. Read and J. Walker, *J. Chem. Soc.*, 308 (1934).

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

(9) Elementary analyses were done by the Micro-Tech Laboratories, Skokie, Illinois.

(10) H. Rupe and W. Tomi, *Ber.*, **47**, 3064 (1914).

was recrystallized three times from 95% ethyl alcohol to a constant melting point of 158–159°.

Anal. Calcd. for $C_9H_{13}N_2SBr$: N, 10.73; S, 12.27; Br, 30.60. Found: N, 10.83; S, 12.42; Br, 31.23.

The picrate¹¹ was prepared in alcohol from which it separated on dilution with water. After it was recrystallized three times from an alcohol–water mixture it melted at 165–166° (lit.¹¹ 167°).

α -Phenethyl Mercaptan.—Fifty-three grams of α -phenethylisothiuronium bromide was dissolved in 118 ml. of 95% ethyl alcohol, and 125 ml. of dilute sodium hydroxide (1 g. of solid per 10 ml. of water) was added. The remaining operations were usual¹² and the product was distilled *in vacuo*; yield 23.0 g. (83%), b.p. 71–72° (4 mm.), lit. b.p. 82–83° (10 mm.).¹³

Methyl α -Phenethyl Sulfide.—A solution of sodium ethoxide (prepared from 12.1 g. of sodium) in 200 ml. of absolute ethyl alcohol was added to α -phenethyl mercaptan (73.2 g.) which was cooled by a salt-ice-bath.¹⁴ Methyl iodide (71 g.) was added to the cold solution. The mixture was allowed to warm slowly to room temperature and then heated for two hours on a steam-bath. The cooled mixture was diluted with water, acidified, and the organic material separated by extraction with benzene. The extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed by a flash distillation from potassium carbonate, and the residue was distilled from metallic sodium *in vacuo*; yield 72.0 g. (91.1%, based upon the methyl iodide used), b.p. 84–85° (2 mm.). A portion of this material was redistilled from sodium a second time and a middle cut from the distillate was analyzed.

Anal. Calcd. for $C_9H_{12}S$: C, 71.00; H, 7.95; S, 21.06. Found: C, 70.68; H, 8.16; S, 20.47.

Studies in the Formation of Dimethyl- α -phenethylsulfonium Bromide from Methyl Bromide and Methyl α -Phenethyl Sulfide.—To establish optimum conditions for the isolation of dimethyl- α -phenethylsulfonium bromide, the effect of the variables of temperature, composition and time of reaction upon the yield and purity of the salts which are formed was studied.

Mixtures of methyl α -phenethyl sulfide and methyl bromide (obtained in cylinders from the Matheson Company, East Rutherford, N. J.) were sealed into ampoules. The methyl bromide was passed successively through a tube packed with calcium chloride, and through a bubble tower containing concentrated sulfuric acid before it was condensed in the ampoule at -80° .

The following data (Table I) were obtained for each experiment: the weight of dry salt isolated; a halogen (Volhard) analysis of the salt; the weight of dimethyl- α -phenethylsulfonium picrate formed from a weighed sample of the salt; and the melting point of the salt. The reaction mixtures were kept at room temperature ($23 \pm 2^\circ$) except where noted in the table.

At the appropriate time the ampoules were cooled to -80° , opened, allowed to warm to room temperature so that most of the excess methyl bromide was driven out, and then transferred to a dry box in which further operations were performed. The salt was filtered, washed with dry ether and dried on the filter. Portions were transferred to tared flasks for the necessary analyses and a sample was sealed in a long capillary tube for the determination of its melting point.

In experiments 10A and 11A, the non-volatile liquid, which remained after filtration and removal of excess methyl bromide by volatilization in a current of dry air, was identified as α -phenethyl bromide from its elementary analysis and physical properties.

The salt isolated in each experiment was colorless. The purest sample of dimethyl- α -phenethylsulfonium bromide which was obtained melted at 76–80°. It forms a picrate, m.p. 120–121°, with an aqueous solution of sodium picrate.

Anal. Calcd. for $C_{18}H_{17}N_3O_7S$: N, 10.63. Found: N, 10.65.

(11) E. L. Brown and N. Campbell, *J. Chem. Soc.*, 1699 (1937).

(12) G. G. Urquhart, J. W. Gates and R. Conner, *Org. Syntheses*, **21**, 36 (1941).

(13) B. Holmberg, *Arkiv Kemi. Mineral. Geol.*, **13A**, No. 8, 9 (1939); *C. A.* **33**, 6278 (1939).

(14) W. R. Waldron and E. E. Reid, *This Journal*, **45**, 2406 (1923).

TABLE I
THE REACTION OF METHYL BROMIDE WITH METHYL α -PHENETHYL SULFIDE

Expt. no.	Mole ratio ^a	Time, hr.	Salt isolated per gram of sulfide, g.	Bromine in salt, %	Dimethyl- α -phenethylsulfonium bromide, %	
					A ^b , c	B ^d
1A	10	312	1.28	44.44	41.1	27
2A	10	192	1.28	39.92	63.1	64
3A	10	69	0.93	35.51	84.6	88
4A	1	69	.84	33.09	96.3	95
5A	0.5	69	.55	33.42	94.7	100
6A	1	24	.28	32.90	97.2	95
7A	0.5	24	.21	32.89	97.3	95
8A	1	4	.16	31.75	103.0	100
9A	0.5	4	.02	32.86	97.4	...
10A ^e	10	888	1.12	49.13	18.4	0–3 ^g
11A ^e	10	360	1.16	48.83	19.7	0–2 ^g

^a The ratio of methyl bromide to methyl α -phenethyl sulfide. ^b These data were calculated from the data in column 5 and on the basis that the salts isolated consisted entirely of mixtures of dimethyl- α -phenethylsulfonium bromide and trimethylsulfonium bromide. ^c The melting point of the picrate isolated in expt. 1–8 was 119–120°. The melting point of trimethylsulfonium monopicrate is 199°; that of the dipicrate is 70–75°; F. E. Ray and G. J. Szasz, *J. Org. Chem.*, **8**, 121 (1943). ^d These data were calculated from the weights of derived dimethyl- α -phenethylsulfonium picrate, corrected for its solubility in water. Trimethylsulfonium picrate is quite soluble in water. ^e This reaction was conducted at 34.7°. ^f The amount of salt isolated was insufficient for the isolation of a picrate. ^g No picrate formed on adding aqueous sodium picrate to this sample.

The picrate is identical to the one obtained from the treatment of an aqueous solution of dimethyl- α -phenethylsulfonium methosulfate with sodium picrate. The picrate resulted from a mixture of methyl α -phenethyl sulfide (1.0 g.), methyl sulfate (0.83 g.) and 1 ml. of dry benzene which separated into two layers in about five hours (the salt was not obtained in a crystalline form), but was allowed to stand at room temperature for a week before it was converted to the picrate (2.33 g., m.p. 107–118°). The weight of purified picrate was 1.91 g., m.p. 119–120°.

Studies in the Formation of Dimethyl- α -phenethylsulfonium Bromide from Methyl Sulfide and α -Phenethyl Bromide.—In a like manner the optimum conditions for the isolation of dimethyl- α -phenethylsulfonium bromide from methyl sulfide and α -phenethyl bromide was investigated. Because the reagents boil above room temperature they were allowed to react in tubes which were tightly corked. The operations involved in isolating the salt were performed in a dry box. The data are compiled in Table II.

TABLE II
THE REACTION OF METHYL SULFIDE WITH α -PHENETHYL BROMIDE

Expt. no.	Mole ratio ^a	Time, hr.	Salt isolated per gram of sulfide, g.	Bromine in salt, %	Dimethyl- α -phenethylsulfonium bromide, %	
					A ^b	B ^c
1B	10	384	0.49	36.14	81.5	82.4
2B	1	240	.51	33.50	94.3	90.3
3B	0.5	240	.45	32.91	97.2	97.2
4B	10	240	.31	34.60	88.9	91.6
5B	1	120	.31	31.99	101.7	97.6
6B	0.5	120	.30	32.70	98.1	96.2
7B	1	24	.12	32.45	99.4	100.0
8B	0.5	24	.06	32.40	99.6	99.4
9B ^d	10	888	.71	50.04	14.0	0–3 ^e
10B ^d	10	360	.48	49.48	16.7	0–5 ^e

^a The ratio of methyl sulfide to α -phenethyl bromide. ^b See footnote b, Table I. ^c See footnote d, Table I. ^d This reaction was conducted at 34.7°. ^e No picrate formed on adding aqueous sodium picrate to this sample.

The salts were tinged with a violet material which was insoluble in ether but soluble in water. This impurity (present in small amounts) did not appear to interfere with the analyses which were performed. The optimum conditions for the isolation of the desired salt is a mole ratio of 1, at room temperature (23°) and time of approximately 1-5 days.

L-(-)- α -Phenethyl Bromide.¹⁵—This was prepared according to the method of Gerrard¹⁵ from D-(+)- α -phenethyl alcohol (11.2 g.; $\alpha^{23,0D} +32^\circ$, l 1 dm., no solvent), phosphorus tribromide (25 g.) and pyridine (34.5 g.) in the solvent carbon disulfide; yield 5 g.; $\alpha^{23,5D} -67.0^\circ$, l 1 dm., no solvent.

D-(+)- α -Phenethyl Chloride.¹⁶—L-(-)- α -Phenethyl alcohol (32.7 g., $\alpha^{23,5D} -36.8^\circ$) phosphoryl chloride (27.4 g.) and pyridine (42.4 g.) in absolute ethyl ether yielded D-(+)- α -phenethyl chloride: 22.4 g. (80%), b.p. 60-62° (4 mm.), $n^{20D} 1.5273$ (lit.¹⁶ $n^{20D} 1.5262$), $\alpha^{24D} +70.4^\circ$.

The L-(-)- α -Phenethylisothiuronium Chloride.—The method was the same as that described for the preparation of *dl*- α -phenethylisothiuronium bromide except that the time of refluxing was 24 hours. The D-(+)- α -phenethyl chloride described above (22.4 g.), thiourea (12.1 g.) and 80 ml. of 95% ethyl alcohol were used. The yield was 25 g. (73%), m.p. 117-125°. It was purified by solution in acetone and precipitation with ether followed by recrystallization from dioxane; yield 23 g., m.p. 149-151°; $\alpha^{23D} -0.602$, l 0.25 dm., c 5.10 in water; $[\alpha]^{22,0D} -47.2^\circ$.

Anal. Calcd. for $C_9H_{13}N_2SCl$: N, 12.93; S, 14.79. Found: N, 12.90; S, 14.50.

L-(-)- α -Phenethyl Mercaptan.—The optically active thiol was prepared from the above salt in the manner described for the inactive compound. The following amounts of reagents were employed: L-(-)- α -phenethylisothiuronium chloride, 23 g.; 95% ethyl alcohol, 80 ml.; sodium hydroxide solution (10 g. of solid in 100 ml. of water), 86 ml.; yield 10.3 g. (70%), $\alpha^{23,0D} -10.11^\circ$, l 0.25 dm.

L-(-)-Methyl α -Phenethyl Sulfide.—This compound was prepared from the levorotatory mercaptan *via* the method used for obtaining the *dl*-sulfide described previously. The following reagents were employed: L-(-)- α -phenethyl mercaptan, 10 g.; metallic sodium, 1.65 g.; methyl iodide, 7.72 g.; absolute ethyl alcohol, 28 ml.; yield 8 g. (96%, based on the methyl iodide used); $\alpha^{23,0D} -17.93^\circ$, l 0.25 dm.

Anal. Calcd. for $C_9H_{12}S$: C, 71.00; H, 7.95. Found: C, 71.47; H, 8.00.

D-(+)-Methyl α -Phenethyl Sulfide.—The previously described procedure was followed except that the following modifications were effected: the reaction was carried out at room temperature, the addition of the halide required only 15 minutes and the solution was refluxed for four hours. From L-(-)- α -phenethyl chloride, $\alpha^{27D} -24.3^\circ$ (7.8 g.), methylmercaptan (3.1 g.), metallic sodium (1.5 g.) and absolute ethyl alcohol (25 ml.) was obtained the sulfide: 6.4 g.; $\alpha^{23,7D} +10.06^\circ$, l 0.25 dm.

Anal. Calcd. for $C_9H_{12}S$: C, 71.00; H, 7.95; S, 21.06. Found: C, 71.50; H, 7.87; S, 20.55.

Reaction of Methyl Sulfide with L-(-)- α -Phenethyl Bromide.—Three experiments were made with approximately 1 g. of L-(-)- α -phenethyl bromide ($\alpha^{23D} -65.5^\circ$) and 0.4 g. of methyl sulfide, at a mole ratio of unity. The salt was isolated as described previously, weighed on a sintered glass filter, dissolved in a known volume of water, and the optical rotation of the solution measured. The violet color which was formed during the reaction was re-

moved by 0.1 g. of solid $NaHSO_3$. The data are presented in Table III.

In experiment 1C, the residual α -phenethyl bromide was recovered by removal of the methyl sulfide and ethyl ether at room temperature with the aid of a current of clean air, and a subsequent low pressure distillation. The optical rotation was $\alpha^{24D} -41.8^\circ$.

In experiment 4C the product, obtained after removal of trimethylsulfonium bromide and excess methyl sulfide, was methyl α -phenethyl sulfide. Since only 0.287 g. of the material was available after distillation, this was diluted with 2.50 g. of the pure *dl*-sulfide. The following optical data were then obtained: $\alpha^{24,3D} +0.159^\circ$, l 0.25 dm.; per cent. of solute 11.5, $\alpha^{24,3D} +5.56^\circ$ for the isolated sulfide.

Formation and Decomposition of L-(-)-Dimethyl- α -phenethylsulfonium Bromide: The System Methyl Bromide, L-(-)-Methyl α -Phenethyl Sulfide.—The techniques used in treating the system methyl sulfide, L-(-)- α -phenethyl bromide were also employed here; however, the ampoules used were sealed and permitted to remain under slight pressure, as described previously.

Two experiments were made with L-(-)-methyl α -phenethyl sulfide ($\alpha^{23,0D} -17.93^\circ$, l 0.25 dm., pure liquid). The mole ratio of bromide to sulfide for experiment 1D was 1 and the time was 4 hours. For experiment 2D, the mole ratio was 10 and the time was 360 hours.

Optical data on the salt obtained in experiment 1D are as follows: $\alpha^{24,1D} -0.323^\circ$, l 0.25 dm., c 4.04 g./100 ml., $[\alpha]^{24,3D} -32.0^\circ$. A portion of the above salt was analyzed for halogen using the Volhard method.

Anal. Calcd. for $C_{10}H_{15}SBr$: Br, 32.33. Found: Br, 32.48.

The α -phenethyl bromide isolated from experiment 2D, after filtering the salt, removal of the methyl bromide at room temperature through the use of a current of clean air, followed by a low pressure distillation (1 mm.), had the properties: $\alpha^{23,1D} +3.05^\circ$, l 1 dm., $n^{20D} 1.5609$.

Anal. Calcd. for C_9H_9Br : C, 51.91; H, 4.90; Br, 43.18. Found: C, 52.06; H, 5.00; Br, 43.15.

TABLE III
REACTION OF METHYL SULFIDE AND L-(-)- α -PHENETHYL BROMIDE

Expt. no.	Mole ratio	Time, hr.	Wt. of salt, g.	Optical activity of salt	
				$\alpha^{24,0D}$	Concn., g./100 ml. $[\alpha]^{24,0D}$
1C	1	24	0.105	1.196 ^a	3.28 36.5°
2C	1	120	.239	.337 ^b	7.27 18.5
3C	1	240	.427	.189 ^b	12.21 6.6
4C	10	360	.485	.0	8.51 0.0

^a l 1 dm. ^b l 0.25 dm.

(15) W. Gerrard, *J. Chem. Soc.*, 848 (1945).

(16) W. Gerrard, *ibid.*, 108 (1945).

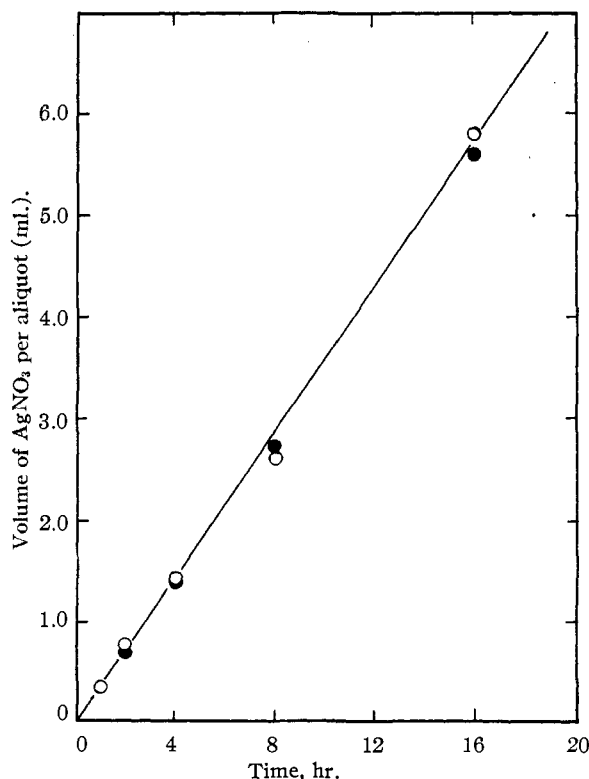


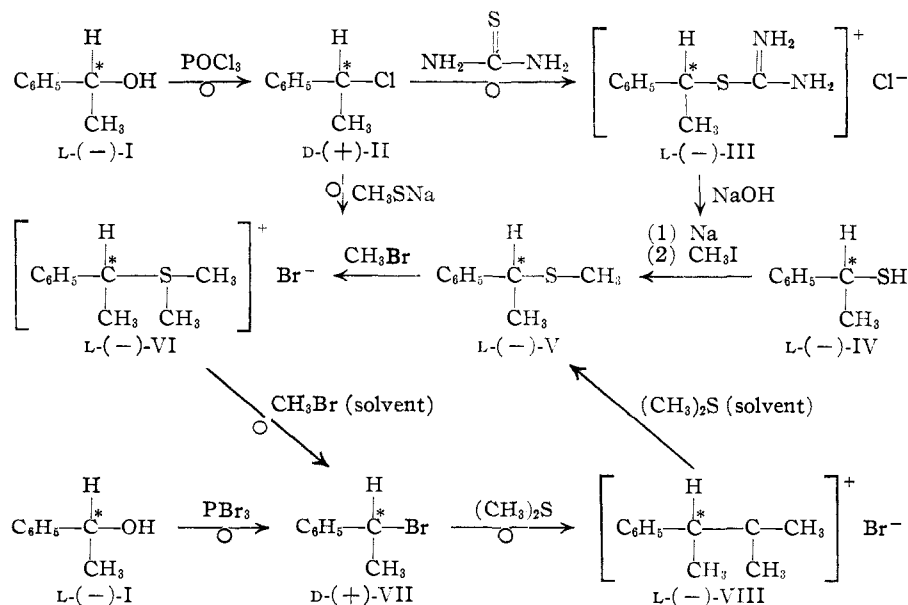
Fig. 1.—Reaction of methyl sulfide with α -phenethyl bromide at $23 \pm 0.10^\circ$; no solvent; mole ratio of unity; ●, reaction tubes containing glass wool. Each aliquot contained initially 0.200 g. of methyl sulfide; $AgNO_3$ (0.0502 N).

The Effect of Surface on the Rate of Formation of Dimethyl α -Phenethylsulfonium Bromide.—The rate of formation of dimethyl α -phenethylsulfonium bromide from methyl sulfide and α -phenethyl bromide was studied to determine whether the reaction took place in solution or on the surface of the container or crystals which formed. Two series of experiments were performed with the same ratio of reactants (ratio of unity) but differing in that one set of tubes contained glass wool. The reaction mixtures were analyzed for bromide ion and the results are shown in Fig. 1. It is clear that the rate is independent of the area of the glass surface and of the surface area of the salt which is being formed. The reaction is therefore homogeneous.

Discussion of Results

The data of Tables I and II indicate that it is possible to isolate dimethyl- α -phenethylsulfonium bromide substantially free from other contaminants from either the reaction of methyl bromide and methyl α -phenethyl sulfide or the reaction of α -phenethyl bromide with dimethyl sulfide. The principal contaminant, trimethylsulfonium bromide, appears in appreciable amounts only after 10–20% of the original materials have been converted to salt. If the mixtures are allowed to stand for very long periods, then the composition of the salt no longer corresponds to a mixture of the above two salts, and a third component, possibly methyl di- α -phenethylsulfonium bromide, is suspected; however, it was not isolated.

The reactions which establish the relative configurations of the compounds studied are represented schematically below. For each compound the sign of rotation is given, as deduced from that of its immediate precursor.¹⁷ In addition, the



asymmetric carbon atom is in each case marked by an asterisk and, in anticipation of the argument which follows, those reactions which proceed with an inversion of configuration about the asymmetric carbon atom are indicated with a looped arrow.

The assignment of relative configurations to the optically active compounds depends largely upon

(17) For example, if a levorotatory compound gave a levorotatory product in an experiment, this fact may be represented as such, or in the equivalent representation of the dextrorotatory compound affording the dextrorotatory product.

analogy.¹⁸ Thus the configuration of dextrorotatory α -phenethyl chloride (II) and α -phenethyl bromide (VII) are taken to be the same. The conversion of either compound to levorotatory methyl α -phenethyl sulfide (V) *via* the more direct paths indicated, undoubtedly involves a single inversion. The displacement of a halide ion from carbon by a negative ion (in this instance CH_3S^-) in a medium of high polarity (ethanol) invariably leads to an inversion of configuration. Apparently thiourea, a powerful nucleophilic agent, must react with inversion as well. Levorotatory dimethyl- α -phenethylsulfonium bromide (VI) obtained by methylating V must have the same configuration as the sulfide because the asymmetric carbon atom is not affected in this change. If these relative configurations are accepted, then it follows that the formation and decomposition of dimethyl- α -phenethylsulfonium bromide according to equation 1 must take place predominantly with the inversion of the configuration of the asymmetric carbon atom. The rate data clearly show that the reaction is homogeneous in that it takes place in solution rather than at a polar surface. Thus even in a medium provided by relatively non-polar reactants in which electrostatic effects might be expected to be most pronounced, there is no support for the suggestion that this effect can influence the steric course of the displacement reaction.

The decrease in optical activity of the salt with time may be explained in a number of ways. The low concentration of bromide ion present may cause racemization of the active α -phenethyl bromide through consecutive displacement reactions.¹⁹ Secondly, the formation or decomposition of the salt may proceed through a solvated ionic intermediate of the type suggested by Doering.²⁰ And finally, the formation or decomposition of the salt may proceed along parallel paths, a portion of the reaction proceeding through a transition complex which yields a product of the same configuration as the reactants, while the major path yields inversion. Whatever the explanation for the racemization observed, it is clear that inversion is the predominant mode of reaction.

The failure to observe retention of configuration in this displacement reaction under what appears

(18) E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

(19) E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley and J. Weiss *ibid.*, 1525 (1935).

(20) W. von E. Doering and A. Streitwieser, Jr., Division of Organic Chemistry of the A.C.S., Abstracts of Papers presented at Boston, Mass., April 4, 1951, p. 45M.

to be favorable circumstances may reflect the requirement that the transition state in the formation of the salt be solvated to reduce its energy to an accessible value. The solvation weakens the electrostatic interactions which provide chemical inertia to the formation of the salt. And though the reverse reaction, the decomposition of the salt, derives a driving-force from the electrostatic interactions under discussion, this is diminished because the ions must be solvated to remain in solution, a

condition which applies to the transition state though to a lesser extent. In this way the electrostatic effect is so weakened as to leave the non-electrostatic factors dominant.

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CHICAGO, ILLINOIS

[CONTRIBUTION NO. 64 FROM THE CENTRAL RESEARCH DEPARTMENT OF MINNESOTA MINING AND MANUFACTURING COMPANY]

Pyrolyses of the Salts of the Perfluoro Carboxylic Acids¹

BY J. D. LAZERTE, L. J. HALS, T. S. REID AND G. H. SMITH

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The thermal decomposition of a number of salts of the straight chain perfluoro acids has been investigated. From the sodium salts, terminally unsaturated perfluoro olefins were prepared in yields ranging from 65 to 100%. The reaction is represented by the equation $C_nF_{2n+1}CF_2CO_2Na \rightarrow C_nF_{2n+1}CF=CF_2 + CO_2 + NaF$. Salts of other metals occurring in groups I, II and III of the periodic table, gave varying yields of olefins. Silver perfluorobutyrate and silver perfluorocaprylate decomposed to give C_4F_{14} and $C_{11}F_{30}$, respectively. Tetrafluoroethylene was formed when a mixture of CF_3CO_2Na and NaOH was heated. A series of fluorocarbon hydrides, $C_nF_{2n+1}H$ was prepared by heating salts of the perfluoro acids in ethylene glycol.

While the literature contains references to the decomposition of salts of trifluoroacetic acid, no data had been reported on the pyrolyses of salts of the longer chain perfluoro acids until recently.² Experimentation with other salts and other reaction conditions warrant further discussion of these pyrolytic reactions at this time.

The formation of an olefin by the decomposition of a salt was first reported by Pagenstecher³ who found that when an aqueous solution of sodium α -methyl- β -iodobutyrate was warmed, butene-2 was formed. Wislicenus⁴ observed that a hot aqueous solution of sodium 2,3-dichlorobutyrate decomposed to give 1-chloropropene. Later Boeseken⁵ found that sodium perchloropropionate underwent a similar type of reaction at 25° to give tetrachloroethylene.

While the salts of the straight chain perfluoro acids do not decompose under such mild conditions to give perfluoro olefins, it has been observed in this Laboratory that when certain of the dry salts containing three or more carbon atoms were heated, the following reaction takes place



By means of this reaction, excellent yields of perfluoro olefins were obtained. Since many of the perfluoro acids are now available from the electrochemical fluorination⁶ of the parent hydrocarbon acids, a simple synthesis of these olefinic compounds is now available.

(1) Presented before the Section on Industrial and Engineering Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, 1952.

(2) L. J. Hals, T. S. Reid and G. H. Smith, *THIS JOURNAL*, **73**, 4054 (1951).

(3) A. Pagenstecher, *Ann.*, **195**, 115 (1879).

(4) J. Wislicenus, *Ann.*, **248**, 297 (1888).

(5) E. Boeseken, *Rec. trav. chim.*, **46**, 841 (1927).

(6) E. A. Kauck and A. R. Diesslin, *Ind. Eng. Chem.*, **43**, 2332 (1951).

The yields of perfluoro olefin resulting from the pyrolytic reaction varied widely with the cation present in the salt. The sodium salts consistently gave the highest yields of terminally unsaturated olefins. The thermal decomposition of the sodium salts of the straight chain acids began at about 230° with the rate of decomposition increasing rapidly as the temperature was raised. At 250–260° a rapid, yet controllable, evolution of perfluoro olefin and CO₂ was obtained. The products from many of the reactions were pure enough after treatment with aqueous base to make fractionation unnecessary. The yields, some of the physical properties, and the analytical data obtained for the terminally unsaturated perfluoro olefins prepared from the sodium salts are shown in Table I. Identification of these unsaturates was based on molecular data, oxidation to perfluoro acids,⁷ elemental analyses and infrared absorption spectra of the compounds. Each member of the series having three or more carbon atoms had an infrared absorption peak at 1795 cm.⁻¹, which is characteristic of the double bond in $C_nF_{2n+1}CF=CF_2$.^{7,8}

The products resulting from the decomposition of other salts of perfluoro acids are shown in Table II.

Pyrolyses of potassium salts gave good yields of perfluoro olefins. Potassium perfluorobutyrate decomposed to give a 98% yield of perfluoropropene. Potassium perfluorovalerate, not shown in the table, gave both perfluorobutene-1 and perfluorobutene-2 in a ratio of about 1:4. To form the internally unsaturated olefin, a shift of fluorine in the molecule had to occur. With the perfluorobutyric acid salts of the alkaline earth metals it was

(7) T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearson, *THIS JOURNAL*, **75**, 2698 (1953).

(8) Infrared curves on the olefins and hydrides have been filed with Dr. E. C. Crellin of the National Bureau of Standards.