b.p. 110–145°, was redistilled through a micro-distilling apparatus giving 25 g. of material, b.p. 128.5–130°.

Reaction of Trichlorosilane with Hexafluoropropene.—A 1.4-liter stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath and charged with 271 g. (2 moles) of trichlorosilane, 145 g. (1 mole) of hexafluoropropene,[17] and mechanically rocked 18 hours at 180°. Distillation of the reaction mixture through a 27″ fractionating column gave only starting materials.

Reaction of Methyldichlorosilane with Hexafluoropropene.—A 1.4-liter stainless steel reaction vessel was cooled in a Dry Ice–acetone-bath and charged with 300 g. (2.6 moles) of methyldichlorosilane, 240 g. (1.6 moles) of hexafluoropropene and 0.5 g. of platinum-on-charcoal catalyst. At 100° a violent explosion took place causing considerable damage to the autoclave.

Hydrolysis of (3,3,3-Trifluoropropyl)-methyldichlorosilane.—Hydrolysis of this compound was carried out using a procedure previously reported[18] for the hydrolysis of dimethyldichlorosilane except that the reaction temperature was held at approximately 2°. In this experiment 200 ml. of (3,3,3-trifluoropropyl)-methyldichlorosilane hydrolyzed in 400 ml. of water and 200 ml. of diethyl ether gave 58 g. (30%) of 2,4,6-trimethyl-2,4,6-tris-(3′,3′,3′-trifluoropropyl)-cyclotrisiloxane, b.p. 95° (3 mm.), and 16.7 g. (11%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(3′,3′,3′-trifluoropropyl)-cyclotetrasiloxane, b.p. 134° (3 mm.).

Hydrolysis of (2-Trifluoromethylpropyl)-methyldichlorosilane.—Using the procedure described above, 200 ml. of this compound were hydrolyzed in 400 ml. of water and 200 ml. of diethyl ether. Fractionation of the hydrolysis products gave 30.2 g. (15%) of 2,4,6-trimethyl-2,4,6-tris-(2′-trifluoromethylpropyl)-cyclotrisiloxane, b.p. 117.5° (3 mm.), and 15.3 g. (8%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(2′-trifluoromethylpropyl)-cyclotetrasiloxane, b.p. 152° (3 mm.).

Hydrolysis of (3,3,4,4,4-Pentafluorobutyl)-methyldichlorosilane.—Using the above procedure, 160 ml. of this compound was hydrolyzed in 320 ml. of water and 160 ml. of diethyl ether. Fractionation of the hydrolysis products gave 25.5 g. (15%) of 2,4,6-trimethyl-2,4,6-tris-(3′,3′,4′,4′-pentafluorobutyl)-cyclotrisiloxane, b.p. 107° (3 mm.), and 19 g. (11%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(3′,3′,4′,4′-pentafluorobutyl)-cyclotetrasiloxane, b.p. 147° (3 mm.).

Hydrolysis of (3,3,4,4,5,5,5-Heptafluoropentyl)-methyldichlorosilane.—Using the above procedure, 200 ml. of this compound was hydrolyzed in 400 ml. of water and 200 ml. of diethyl ether. Fractionation of the hydrolysis products gave 45 g. (20%) of 2,4,6-trimethyl-2,4,6-tris-(3′,3′,4′,4′,5′,5′,5′-heptafluoropentyl)-cyclotrisiloxane, b.p. 122° (3 mm.), and 41.5 g. (18%) of 2,4,6,8-tetramethyl-2,4,6,8-tetrakis-(3′,3′,4′,4′,5′,5′,5′-heptafluoropentyl)-cyclotetrasiloxane, b.p. 156° (3 mm.).

GAINESVILLE, FLORIDA

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

(18) W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA]

Substituted Phenylsilanes. II. The Bromination of the Tolyltrimethylsilanes[1,2]

BY ROLAND G. SEVERSON, ROBERT J. ROSSCUP, DUANE R. LINDBERG AND ROGER D. ENGBERG

RECEIVED AUGUST 7, 1957

The tolyltrimethylsilanes have been brominated with N-bromosuccinimide to give the trimethylsilylbenzyl bromides and the trimethylsilylbenzal bromides. The trimethylsilylbenzal bromides were hydrolyzed to the three isomeric trimethylsilylbenzaldehydes. *p*-Trimethylsilylbenzaldehyde also has been prepared from *p*-trimethylsilylbenzyl bromide by means of the Hass–Bender reaction. The trimethylsilylbenzyl bromides have been converted to the corresponding acetates and these acetates to the trimethylsilylbenzyl alcohols.

In a previous paper, the preparation of the trimethylsilylacetophenones by the autoxidation of the trimethylsilylethylbenzenes was described.[3] This work on substituted phenylsilanes has been extended and we are now reporting convenient syntheses for the trimethylsilylbenzaldehydes and some related compounds.

The easily accessible tolyltrimethylsilanes have been brominated, in good yield, with N-bromosuccinimide to form the trimethylsilylbenzyl bromides and the trimethylsilylbenzal bromides. These compounds serve as useful intermediates for the introduction of other functional groups into phenylsilanes. Thus, by refluxing the benzyl bromides with sodium acetate in glacial acetic acid, the trimethylsilylbenzyl acetates are formed easily. These acetates were saponified with methanolic sodium hydroxide to produce the trimethylsilylbenzyl alcohols.

The direct hydrolysis of the trimethylsilylbenzal bromides by refluxing with water in the presence of calcium carbonate under a nitrogen atmosphere gave the trimethylsilylbenzaldehydes. The pure aldehydes were obtained as colorless liquids in good yield from the reaction mixture by steam distillation followed by vacuum distillation. *p*-Trimethylsilylbenzaldehyde was also prepared in very good yield from *p*-trimethylsilylbenzyl bromide using the Hass–Bender[4] reaction. It is interesting to note that during the preparation of these compounds there has been no indication of cleavage of the phenyl–silicon bond.

p-Trimethylsilylbenzaldehyde was reported previously by Frisch and Shroff[5] to be a solid, m.p. 109–110°. We have not found this aldehyde to be a solid; however, on standing in air all three aldehydes are quite rapidly converted to solids melting in the vicinity of 100° which yield, on purification, pure samples of the corresponding benzoic acids. In order to get maximum yields of the aldehydes by our procedure, particularly with the *meta* and the *para* compounds, we found it necessary to carry out the reactions in an inert atmosphere; otherwise, considerable quantities of the acids were formed by the autoxidation of the aldehydes.

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(2) Presented in part in the Symposium on Carbon-Functional Silanes at the 125th Meeting of the American Chemical Society in Kansas City, Missouri, March, 1954.

(3) R. G. Severson and R. J. Rosscup, THIS JOURNAL, **76**, 4552 (1954).

(4) H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767 (1949).

(5) K. C. Frisch and P. D. Shroff, *ibid.*, **75**, 1249 (1953).

Experimental[6]

p-Trimethylsilylbenzyl Bromide.—A mixture of 16.4 g. (0.1 mole) of *p*-tolyltrimethylsilane, 16.9 g. (0.095 mole) of N-bromosuccinimide and 60 ml. of dry carbon tetrachloride was stirred under gentle reflux with 0.1 g. of benzoyl peroxide. After a short period of time a vigorous reaction took place which quickly subsided. The reaction mixture was refluxed gently for two additional hours, cooled in an ice-bath and then filtered. This removed most of the succinimide. The cold filtrate was washed with cold 5% aqueous sodium hydroxide to remove the succinimide dissolved in the carbon tetrachloride solution. The carbon tetrachloride solution was then washed with water and dried over Drierite. The carbon tetrachloride was removed from this dry solution by distillation and the product was then distilled through a short Vigreux column. In this way 15.3 g. (66%) of *p*-trimethylsilylbenzyl bromide, b.p. 128–129° (12 mm.), was obtained. An analytical sample obtained by distillation through a Wheeler concentric tube column had the following properties: b.p. 125° (10.2 mm.), $n^{20}D$ 1.5400, d^{20}_4 1.2067; *MR* (calcd.)[7] 62.41, *MR* (found) 63.23.

Anal. Calcd. for $C_{10}H_{15}BrSi$: Si, 11.54. Found: Si, 11.53, 11.65.

m-Trimethylsilylbenzyl bromide was prepared by the same procedure as the *p*-isomer. From 24.6 g. (0.15 mole) of *m*-tolyltrimethylsilane, 26.7 g. (0.15 mole) of N-bromosuccinimide and 0.2 g. of benzoyl peroxide in 100 ml. of dry carbon tetrachloride was obtained 21.5 g. (59%) of colorless liquid, b.p. 128–129° (13 mm.), $n^{20}D$ 1.5379, d^{20}_4 1.2087; *MR* (calcd.)[7] 62.41, *MR* (found) 62.92.

Anal. Calcd. for $C_{10}H_{15}BrSi$: Si, 11.54. Found: Si, 11.62.

o-Trimethylsilylbenzyl Bromide.—The reaction of 24.6 g. (0.15 mole) of *o*-tolyltrimethylsilane with 26.7 g. (0.15 mole) of N-bromosuccinimide in 100 ml. of dry carbon tetrachloride using 0.2 g. of benzoyl peroxide as catalyst following the procedure given for the *p*-isomer gave 23.1 g. (65%) of colorless liquid, b.p. 130° (15 mm.). An analytical sample had the following properties: b.p. 121.5° (10.2 mm.), $n^{20}D$ 1.5483, d^{20}_4 1.2329; *MR* (calcd.)[7] 62.41, *MR* (found) 62.68.

Anal. Calcd. for $C_{10}H_{15}BrSi$: Si, 11.54. Found: Si, 11.44, 1.51.

p-Trimethylsilylbenzal Bromide.—A mixture of 49.2 g. (0.3 mole) of *p*-tolyltrimethylsilane, 110.4 g. (0.6 mole) of N-bromosuccinimide and 0.2 g. of benzoyl peroxide in 200 ml. of dry carbon tetrachloride was stirred under gentle reflux. The reaction mixture was heated for a total of 36 hr. with an additional 0.2 g. of benzoyl peroxide added after 12 hr. and again after 24 hr. The reaction mixure was then cooled in an ice-bath and filtered. The cold filtrate was washed with cold 5% sodium hydroxide to remove the remaining succinimide. After the carbon tetrachloride solution was washed with water, it was dried over anhydrous sodium sulfate and the carbon tetrachloride was removed by distillation. Distillation of the residue through a short Vigreux column gave 68 g. (70.5% of *p*-trimethylsilylbenzal bromide, b.p. 123–124° (1.9 mm.). This material solidified on standing, giving a white solid, m.p. 47.5–48°.

Anal. Calcd. for $C_{10}H_{14}Br_2Si$: Si, 8.71. Found: Si, 8.51.

m-Trimethylsilylbenzal Bromide.—The reaction of 26.8 g. (0.16 mole) of *m*-tolyltrimethylsilane with 58.2 g. (0.33 mole) of N-bromosuccinimide in the presence of 0.1 g. of benzoyl peroxide following the procedure given for the *p*-isomer gave 27.4 g. (52.1%) of *m*-trimethylsilylbenzal bromide, b.p. 105° (2.4 mm.), $n^{20}D$ 1.5665, d^{20}_4 1.5106; *MR* (calcd.)[7] 70.09, *MR* (found) 69.60.

Anal. Calcd. for $C_{10}H_{14}Br_2Si$: Si, 8.72. Found: Si, 8.69.

o-Trimethylsilylbenzal bromide was prepared by the same procedure as the *p*-isomer. From 49.2 g. (0.3 mole) of *o*-tolyltrimethylsilane, 106.8 g. (0.6 mole) of N-bromosuccinimide and 0.2 g. of benzoyl peroxide in 165 ml. of carbon tetrachloride was obtained 44.6 g. (46.4%) of *o*-trimethylsilylbenzal bromide, b.p. 111° (2.4 mm.), $n^{20}D$ 1.5730, d^{20}_4 1.5054; MR (calcd.)[7] 70.09, MR (found) 70.50.

Anal. Calcd. for $C_{10}H_{14}Br_2Si$: Si, 8.72. Found: Si, 8.79.

p-Trimethylsilylbenzaldehyde. A. From p-Trimethylsilylbenzal Bromide.—A mixture of 44.7 g. (0.14 mole) of *p*-trimethylsilylbenzal bromide, 40 g. of calcium carbonate and 400 ml. of water was refluxed with vigorous stirring for 16 hr. under an atmosphere of nitrogen. The reaction mixture was then steam distilled while the receiving flask was kept under a nitrogen atmosphere. The distillate was extracted with ether and the ethereal solution was dried over Drierite. The ether was then removed by distillation and the residue was fractionally distilled through a small Vigreux column giving 17.2 g. (69%) of *p*-trimethylsilylbenzaldehyde, b.p. 118° (15 mm.), $n^{20}D$ 1.5245, d^{20}_4 0.9862; *MR* (calcd.)[7] 54.73, *MR* (found) 55.36.

Anal. Calcd. for $C_{10}H_{14}OSi$: Si, 15.75. Found: Si, 16.13.

The *p*-nitrophenylhydrazone of *p*-trimethylsilylbenzaldehyde was prepared[8] and after recrystallization from 95% ethanol melted at 190–191.5°.

Anal. Calcd. for $C_{16}H_{19}N_3O_2Si$: Si, 8.96. Found: Si, 9.24.

A sample of this aldehyde, on exposure to air was quite rapidly converted to a white crystalline solid. This solid was dissolved in 10% aqueous sodium bicarbonate and the resulting solution was filtered. Acidification of the filtrate with 10% sulfuric acid gave a white solid which was collected, washed and dried. This material, m.p. 116–118°, was recrystallized from Skellysolve B giving white crystals, m.p. 117–118°, which did not depress the melting point of an authentic sample of *p*-trimethylsilylbenzoic acid.

B. From p-Trimethylsilylbenzyl Bromide.—Under a nitrogen atmosphere, 2.3 g. (0.1 g. atom) of sodium was dissolved in 100 ml. of absolute ethanol. After the sodium had dissolved, 11.6 g. (0.13 mole) of 2-nitropropane was added, followed by 24.3 g. (0.1 mole) of *p*-trimethylsilylbenzyl bromide. After thorough mixing the reaction mixture was allowed to stand at room temperature under a nitrogen atmosphere for 15 hr. The precipitated sodium bromide was removed by filtration and the filtrate was concentrated at atmospheric pressure to remove the ethanol. During this process additional sodium bromide precipitated. The residue was dissolved in ether and water. The ethereal solution was washed with 10% sodium hydroxide and with water and was then dried over Drierite. The ether was removed by distillation and the residue was fractionally distilled through a small Vigreux column giving 13.87 g. (87%) of *p*-trimethylsilylbenzaldehyde, b.p. 118–119° (16 mm.).

m-Trimethylsilylbenzaldehyde was prepared from 27.4 g. (0.085 mole) of *m*-trimethylsilylbenzal bromide, 20 g. of calcium carbonate and 200 ml. of water following procedure A given for the *p*-isomer. There was obtained 8.96 g. (59.3%) of *m*-trimethylsilylbenzaldehyde, b.p. 114° (14 mm.), $n^{20}D$ 1.5218, d^{20}_4 1.0017; *MR* (calcd.)[7] 54.73, *MR* (found) 54.27.

Anal. Calcd. for $C_{10}H_{14}OSi$: Si, 15.75. Found: Si, 15.54.

The *p*-nitrophenylhydrazone of *m*-trimethylsilylbenzaldehyde was prepared[8] and after recrystallization from 95% ethanol melted at 147–148°.

Anal. Calcd. for $C_{16}H_{19}N_3O_2Si$: Si, 8.96. Found: Si, 8.83.

A sample of this aldehyde gave, after exposure to air and working up in a manner similar to the *p*-isomer, *m*-trimethylsilylbenzoic acid, m.p. 110–111°.

o-Trimethylsilylbenzaldehyde was prepared from 39.6 g. (0.123 mole) of *o*-trimethylsilylbenzal bromide, 40 g. of calcium carbonate and 400 ml. of water following procedure A given for the *p*-isomer. There was obtained 14.97 g. (68.5%) of *o*-trimethylsilylbenzaldehyde, b.p. 110° (15 mm.), $n^{20}D$ 1.5290, d^{20}_4 1.0052; *MR* (calcd.)[7] 54.73, *MR* (found) 54.69.

Anal. Calcd. for $C_{10}H_{14}OSi$: Si, 15.75. Found: Si, 16.16.

The *p*-nitrophenylhydrazone of *o*-trimethylsilylbenzaldehyde was prepared[8] and after recrystallization from 95% ethanol melted at 192–193.5°.

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[6] All melting points were determined on a Kofler Micro Hot-Stage, Arthur H. Thomas Co., Philadelphia, Pa.

[7] E. L. Warrick, THIS JOURNAL, **68**, 2457 (1946).

[8] The Staff of the Hopkin and Williams Research Laboratory, "Organic Reagents for Organic Analysis," Chemical Publishing Co., Inc., Brooklyn, N. Y., 1950, p. 96.

Anal. Calcd. for $C_{16}H_{19}N_3O_2Si$: Si, 8.96. Found: Si, 9.18.

A sample of this aldehyde gave, after exposure to air and working up in a manner similar to the *p*-isomer, *o*-trimethylsilylbenzoic acid, m.p. 98–99.5°.

p-**Trimethylsilylbenzyl Acetate.**—To a mixture of 34.76 g. (0.143 mole) of *p*-trimethylsilylbenzyl bromide and 22.49 g. (0.274 mole) of anhydrous sodium acetate was added 37.55 g. (0.625 mole) of glacial acetic acid. The reaction mixture became quite viscous and heat was evolved during the addition. The reaction mixture was then refluxed gently with stirring for 13 hr. Approximately 30 ml. of acetic acid was then distilled from the reaction mixture, the residue was cooled and 95 ml. of water was added. The resulting mixture was extracted with ether and the ether solution was dried over Drierite. The ether was then removed by distillation and the residue was distilled through a short Vigreux column. This gave 27.9 g. (87.8%) of *p*-trimethylsilylbenzyl acetate, b.p. 145° (15.5 mm.), $n^{20}{}_D$ 1.4960, $d^{20}{}_4$ 0.9837; *MR* (calcd.)[7] 65.76, *MR* (found) 66.02.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: Si, 12.62. Found: Si, 12.61.

m-**Trimethylsilylbenzyl acetate** was prepared from 32.3 g. (0.133 mole) of *m*-trimethylsilylbenzyl bromide, 22.5 g. (0.274 mole) of sodium acetate and 37.55 g. (0.625 mole) of glacial acetic acid following the directions given for the *p*-isomer. There was obtained 22.1 g. (74.6%) of *m*-trimethylsilylbenzyl acetate, b.p. 139° (15.5 mm.), $n^{20}{}_D$ 1.4955, $d^{20}{}_4$ 0.9832; *MR* (calcd.)[7] 65.76, *MR* (found) 66.00.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: Si, 12.62. Found: Si, 12.99.

o-**Trimethylsilylbenzyl Acetate.**—From 32.4 g. (0.133 mole) of *o*-trimethylsilylbenzyl bromide, 22.5 g. (0.274 mole) of sodium acetate and 37.55 g. (0.625 mole) of glacial acetic acid, following the directions given for the *p*-isomer, there was obtained 24.18 g. (81.8%) of *o*-trimethylsilylbenzyl acetate, b.p. 139.5° (15.5 mm.), $n^{20}{}_D$ 1.5045, $d^{20}{}_4$ 1.0025; *MR* (calcd.)[7] 65.76, *MR* (found) 65.72.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: Si, 12.62. Found: Si, 12.98.

p-**Trimethylsilylbenzyl Alcohol.**—A solution of 13.3 g. (0.06 mole) of *p*-trimethylsilylbenzyl acetate in 40 ml. of hot methanol was thoroughly mixed with 28 g. of 15% aqueous sodium hydroxide. The reaction mixture was heated with stirring for 10 min. and then poured onto approximately 350 ml. of an ice–water mixture. This aqueous mixture was extracted with ether. The ether solution was dried over Drierite and the ether was removed by distillation. The residue was distilled through a small Vigreux column giving 8.44 g. (78%) of *p*-trimethylsilylbenzyl alcohol, b.p. 139° (16 mm.), $n^{20}{}_D$ 1.5140, $d^{20}{}_4$ 0.9605; *MR* (calcd.)[7] 56.28, *MR* (found) 56.51.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si. 15.56. Found: Si. 15.78.

m-**Trimethylsilylbenzyl Alcohol.**—From 15.2 g. (0.068 mole) of *m*-trimethylsilylbenzyl acetate, following the procedure given for the *p*-isomer, there was obtained 8.72 g. (71%) of *m*-trimethylsilylbenzyl alcohol, b.p. 137° (16 mm.), $n^{20}{}_D$ 1.5150, $d^{20}{}_4$ 0.9648; *MR* (calcd.)[7] 56.28, *MR* (found) 56.35.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.56. Found: Si, 15.88.

o-**Trimethylsilylbenzyl Alcohol.**—From 15.1 g. (0.068 mole) of *o*-trimethylsilylbenzyl acetate, following the procedure given for the *p*-isomer, there was obtained 10.62 g. (88%) of *o*-trimethylsilylbenzyl alcohol, b.p. 134° (16 mm.), $n^{20}{}_D$ 1.5265, $d^{20}{}_4$ 0.9887; *MR* (calcd.)[7] 56.28, *MR* (found) 56.02.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.56. Found: Si, 15.87.

GRAND FORKS, NORTH DAKOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Solvolysis of *cis*- and *trans*-2-Chlorocycloalkyl Aryl Sulfides in 80% Aqueous Ethanol[1]

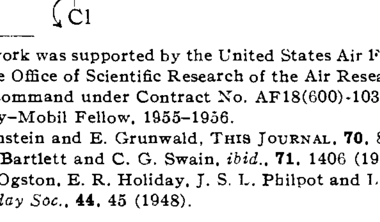
BY HARLAN L. GOERING AND KING L. HOWE[2]

RECEIVED AUGUST 19, 1957

The rates of solvolysis of *cis*-(Ia) and *trans*-2-chlorocyclohexyl phenyl sulfide (IIa) and *cis*-(IIIa) and *trans*-2-chlorocyclopentyl phenyl sulfide (IVa) and *p*-substituted derivatives of these β-chlorosulfides in 80% aqueous ethanol have been determined. In both the cyclohexyl and cyclopentyl systems the *trans* isomers, in which the neighboring sulfide group can participate in the ionization step, are more reactive than the corresponding *cis* isomers by factors of 10^5 to 10^6. Electron-withdrawing substituents retard the rate of solvolysis of the *trans*-2-chlorocycloalkyl phenyl sulfides (II and IV) but do not affect the reactivity of the *cis* isomers (I and III). At 118° the *cis*-2-chlorocyclohexyl aryl sulfides (I) are one-sixth as reactive as cyclohexyl chloride and the *cis*-2-chlorocyclopentyl aryl sulfides are one-fifteenth as reactive as cyclopentyl chloride. Similar values of ρ and k_{trans}/k_{cis} for the cyclohexyl and cyclopentyl chlorosulfides show that sulfur participates about equally well in the two systems.

Introduction

As has been pointed out previously[3,4] it is clear from the high solvolytic reactivities of β-chlorosulfides, *e.g.*, β,β′-bis-chloroethyl sulfide,[4,5] that the sulfide group participates in the rate-determining ionization step.



Such participation is also indicated by the effect of substituents on the rates of solvolysis of substituted phenyl β-chloroethyl sulfides in 50% aqueous acetone.[6] The sign and magnitude of ρ (-1.671[7]) for this reaction is consistent with a process involving participation by the neighboring sulfide group. In the absence of such participation the effect of substituents would be expected to be negligible.

In order to obtain quantitative information concerning the rate enhancement (anchimeric assistance[8]) resulting from participation by a neighboring sulfide group we have measured the rates of solvolysis of several *cis*- (I) and *trans*-2-chlorocyclohexyl aryl sulfides (II) and *cis*- (III) and

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[2] Socony–Mobil Fellow, 1955–1956.

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

[4] P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949).

[5] A. G. Ogston, E. R. Holiday, J. S. L. Philpot and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948).

[6] G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, 1676 (1927); G. Baddely and G. M. Bennett, *ibid.*, 261 (1933).

[7] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[8] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).