hydride reduction of trimethylacetic acid.[8] Benzaldehyde was freed of benzoic acid and redistilled immediately prior to use.

Preparation.—Six and one-half grams (0.074 mole) of neopentyl alcohol, 3.9 g. (0.037 mole) of benzaldehyde, 90 ml. of dry benzene and about 75 mg. of *p*-toluenesulfonic acid monohydrate were heated together until the calculated amount of water had been collected in a standard water separator. The acid was destroyed by the addition of a few ml. of sodium ethoxide in ethanol. The mixture was washed with water then dried over potassium carbonate. The product was collected by fractionation through 15 cm. of glass helices; yield 6.6 g. (68%); b.p. 102° at 0.8 mm.; $n^{22}\mathrm{D}$ 1.4682; $d^{22}{}_4$ 0.913; *MR* (calcd.) 80.4 (found) 80.5.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.2; H, 10.7. Found: C, 77.1; H, 10.6.

Hydrolysis.—Thirty milliliters of 1% sulfuric acid and 6.2 g. of dineopentyl acetal of benzaldehyde were placed in a 50-ml. round bottom flask connected to a simple head leading to a long-stemmed adapter and an 8-in. test-tube resting in an ice-water bath. Distillation was continued until the head temperature reached 100°. The organic layer was separated and to it was added ether extracts of the water layer. The mixture was dried over potassium carbonate. The material was distilled through 15 cm. of glass helices to yield 3.4 g. (80%) of neopentyl alcohol, b.p. 111–112°. The 3,5-dinitrobenzoate derivative showed no depression of the melting point when mixed with an authentic sample.

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(8) R. F. Nystrom and W. G. Brown, This Journal, **69**, 2548 (1947).

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Synthesis of Silylmethyl Thiocyanates and Isothiocyanates

By John E. Noll

Received November 24, 1954

In the course of a study of the reactions of chloromethyl- and aminomethylsilanes, a few silylmethyl thiocyanates and isothiocyanates were prepared. The isothiocyanates were prepared[1] by a series of reactions from the corresponding silylmethylamine.[2]

$$\begin{gathered}
\equiv\mathrm{SiCH_2NH_2 + CS_2 + OH^-} \rightleftarrows \\
\equiv\mathrm{SiCH_2NHC({=}S)S^- + H_2O} \\
\equiv\mathrm{SiCH_2NHC({=}S)S^- + C_2H_5OC({=}O)Cl} \rightleftarrows \\
\equiv\mathrm{SiCH_2NHC({=}S)SC({=}O)COC_2H_5 + Cl^-} \\
\downarrow \\
\equiv\mathrm{SiCH_2NCS + C_2H_5OH + COS}\uparrow
\end{gathered}$$

The thiocyanates were prepared from the corresponding chloromethylsilane and potassium thiocyanate in acetone.

$$\equiv\mathrm{SiCH_2Cl + KCNS} \rightleftarrows \equiv\mathrm{SiCH_2SCN + KCl}$$

The isothiocyanates were found to react with amines in the usual manner to produce substituted thioureas.

Experimental

Trimethylsilylmethyl Isothiocyanate.—Trimethylsilylmethylamine–water azeotrope[2] (30 g., 0.25 mole) dissolved in 200 cc. of alcoholic sodium hydroxide (10 g., 0.25 mole) was treated with carbon disulfide (15 g., 0.2 mole) at 0°. On standing, sodium N-trimethylsilylmethyl dithiocarbamate (37 g., 90% yield) precipitated. *Anal.* Calcd. for $C_5H_{12}NS_2SiNa$: Na, 11.40; S, 31.84. Found: Na, 11.37; S, 31.60, 31.57.

Addition of ethyl chloroformate (27.5 g., 0.25 mole) to an aqueous solution of sodium N-trimethylsilylmethyl dithiocarbamate (50.4 g., 0.25 mole) produced an oil and evolved a gas. The oil was extracted and distilled in a still of about ten plates to yield trimethylsilylmethyl isothiocyanate (33 g., 91%), b.p. 199° (741 mm.), 90° (25 mm.), $n^{25}\mathrm{D}$ 1.4984, $d^{25}{}_4$ 0.938. *Anal.* Calcd. for $C_5H_{11}NSSi$: S, 22.07; sp. ref.,[3] 0.3083. Found: S, 22.08; sp. ref., 0.3128. Trimethylsilylmethyl isothiocyanate reacted with aniline to produce N-phenyl-N′-(trimethylsilylmethyl)-thiourea which was found to be identical to the thiourea prepared from phenyl isothiocyanate and trimethylsilylmethylamine by a mixed melting point (121–122°); N-phenyl-N′-(trimethylsilylmethyl)-thiourea, m.p. 122–123°. *Anal.* Calcd. for $C_{11}H_{18}N_2SSi$: Si, 11.77. Found: Si, 11.72.

Triethoxysilylmethyl Isothiocyanate.—Trimethylammonium triethoxysilylmethyl dithiocarbamate prepared from a benzene solution of trimethylamine (18 g.), triethoxysilylmethylamine[2] (48.5 g., 0.25 mole) and carbon disulfide (20 g.) on treatment with ethyl chloroformate (32.5 g., 0.3 mole) gave a precipitate of trimethylamine hydrochloride (m.p. 270–276° dec.). The filtrate was distilled to yield triethoxysilylmethyl isothiocyanate (29 g., 50% yield), b.p. 120° (3 mm.), $n^{25}\mathrm{D}$ 1.4558, $d^{25}{}_4$ 1.034. *Anal.* Calcd. for $C_8H_{17}O_3NSSi$: Si, 11.93; S, 13.62; sp. ref.,[3] 0.2586. Found: Si, 12.12, 12.27; S, 13.13, 13.51; sp. ref., 0.2628.

Tetramethyldisiloxane-1,3-bis-(methyl Thiocyanate).—Bis-chloromethyltetramethyldisiloxane (115 g., 0.5 mole) was refluxed in an acetone (2 l.) solution of potassium thiocyanate (116 g., 1.2 moles) for 24 hours. The acetone solution was diluted with water and the insoluble oil separated and dried over $CaCl_2$ to give pure tetramethyldisiloxane-1,3-bis-(methyl thiocyanate) (52 g., 40% yield), $n^{25}\mathrm{D}$ 1.4843, $d^{25}{}_4$ 1.083. *Anal.* Calcd. for $C_8H_{16}ON_2S_2Si_2$: Si, 20.32; sp. ref.,[3] 0.2656. Found: Si, 20.21, 20.29; sp. ref., 0.2642.

Trimethylsilylmethylthiocyanate.[4]—Trimethylsilylmethyl thiocyanate was prepared in 90% yield by refluxing chloromethyltrimethylsilane (61 g., 0.5 mole) with potassium thiocyanate (75 g., 0.77 mole) in 600 cc. of acetone. Distillation yielded trimethylsilylmethyl thiocyanate, b.p. 199° (741 mm.), $n^{25}\mathrm{D}$ 1.4650, $d^{25}{}_4$ 0.943. *Anal.* Calcd. for $C_5H_{11}NSSi$: Si, 22.07; sp. ref.,[3] 0.2931. Found: Si, 21.54, 21.5; sp. ref., 0.2936.

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(1) *Org. Syntheses*, **21**, 84 (1941).

(2) J. E. Noll, B. F. Daubert and J. L. Speier, This Journal, **73**, 3867 (1951).

(3) Calcd. from bond refraction values of E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(4) G. D. Cooper, *ibid.*, **76**, 2499 (1954), b.p. 196–197°; $n^{20}\mathrm{D}$ 1.4676; $d^{20}{}_4$ 0.9426.

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Highly Halogenated Alkanes Derived from Fluorine-containing Alcohols

By E. T. McBee, D. H. Campbell and C. W. Roberts

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The reaction of the *p*-toluenesulfonates of 2,2,2-trifluoroethanol, 2,2,3,3,3-pentafluoropropanol and 2,2,3,3,4,4,4-heptafluorobutanol[1] with alkali halides was utilized for the preparation of highly halogenated alkanes. The tosyl esters were prepared following standard procedures,[3,4] and the displacement of the tosyl group was effected by reaction with the suitable potassium halide in refluxing di-

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(1) 2,2,2-Trifluoroethanol and 2,2,3,3,4,4,4-heptafluorobutanol were obtained from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota. 2,2,3,3,3-Pentafluoropropanol was prepared by lithium aluminum hydride reduction[2] of pentafluoropropionic acid, obtained from the same company.

(2) D. R. Husted and A. H. Ahlbrecht, This Journal, **74**, 5422 (1952).

(3) C. S. Marvel and V. C. Sekera, *Org. Syntheses*, **20**, 50 (1940).

(4) A. T. Roos, H. Gilman and N. J. Beaber, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.

TABLE I

NEW COMPOUNDS

Compound	B.p., °C.	n^{20}_{D}	d^{25}_{4}	Analyses[d] Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
$CF_3CH_2OSO_2C_6H_5$	91[a]	1.4582	1.403[c]	40.00	39.90	2.91	3.71
$C_2F_5CH_2OSO_2C_7H_7$	52.5–53[b]			39.45	39.60	2.97	2.69
$C_3F_7CH_2OSO_2C_6H_5$	108[a]	1.4240	1.508[c]	35.30	35.34	2.06	2.30
CF_3CCl_2Br	69.2	1.3977	1.950	10.34	10.43	0.0	0.1
$C_2F_5CH_2Cl$	27.2	1.292	1.395	21.35	21.19	1.20	1.59
$C_2F_5CH_2Br$	46.5	1.3204	1.756	16.92	17.10	0.95	1.17
$C_2F_5CH_2I$	70.5	1.3728	2.038	13.86	13.91	.78	0.90
$C_2F_5CHCl_2$	45.5	1.3196	1.543	17.75	17.64	.49	.56
$C_2F_5CCl_3$	70.5	1.3527	1.637	15.15	14.85	.0	.16
$C_3F_7CHCl_2$	76.5	1.3212	1.612	18.98	18.86	.79	.82
$C_3F_7CFCl_2$	62.8	1.3067	1.633	17.72	17.39	.00	.30
$C_2F_5CFClCH_2Cl$	72.0	1.3386	1.471	20.45	20.49	.85	1.24

At 1 mm.. [b] Melting point. [c] At 26.5°. [d] Analyses were done by Mrs. C. S. T. Yeh, Purdue University.

ethylene glycol, a modification of the previously described method.[5]

The vapor phase chlorination of 2-bromo-1,1,1-trifluoroethane, 3-chloro-1,1,1,2,2-pentafluoropropane and 4-chloro-1,1,1,2,2,3,3-heptafluorobutane gave 1-bromo-1,1-dichlorotrifluoroethane, 3,3-dichloro-1,1,1,2,2-pentafluoropropane, 1,1,1-trichloroperfluoropropane, 4,4-dichloro-1,1,1,2,2,3,3-heptafluorobutane and 1,1,1-trichloroperfluorobutane, respectively.[6]

1,1-Dichlorooctafluorobutane was prepared from 1,1,1-trichloroheptafluorobutane by reaction with an antimony trifluoride–antimony pentachloride mixture at 200°.

Both 4-bromo-1,1,1,2,2,3,3-heptafluorobutane and 4-iodo-1,1,1,2,2,3,3-heptafluorobutane underwent reaction with zinc dust to yield the same olefin, 2,3,3,4,4,4-hexafluoro-1-butene.[7] The addition of chlorine to the double bond of this olefin resulted in the formation of 3,4-dichloro-1,1,1,2,2,-3-hexafluorobutane.

The new compounds prepared and their physical properties are reported in Table I.

The authors gratefully acknowledge the support of this work by the Mallinckrodt Chemical Works.

Experimental[8]

2-Bromo-1,1,1-trifluoroethane, 3-Chloro-, 3-Bromo-, and 3-Iodo-1,1,1,2,2-pentafluoropropane, 4-Chloro-, 4-Bromo-, 4-Iodo-1,1,1,2,2,3,3-heptafluorobutane.—The procedure utilized was essentially that described previously[5] except that the potassium halides were used rather than the lithium. The *p*-toluenesulfonate or benzenesulfonate, a 50% excess of the potassium halide, and sufficient diethylene glycol to form a slurry were placed in a 1-necked flask of appropriate size having a thermometer well and fitted with short glass-helices-packed column connected to a condenser and receiver, and the mixture was heated to vigorous reflux for 4 hr. During this time the reaction temperature rose to 240° and the product distilled. The crude material was washed twice with cold water, dried over Drierite and rectified using a Todd column: CF_3CH_2Br,[6] 97.2%; $C_2F_5CH_2Cl$, 75%; $C_2F_5CH_2Br$, 81%; $C_2F_5CH_2I$, 81%; $C_3F_7CH_2Cl$,[5] 95.5%; $C_3F_7CH_2Br$,[5] 91.2%; $C_3F_7CH_2I$,[5] 82.7%. The pertinent data are listed in Table I.

Vapor Phase Chlorination of 2-Bromo-1,1,1-trifluoroethane, 3-Chloro-1,1,1,2,2-pentafluoropropane and 4-Chloro-1,1,2,2,3,3-heptafluorobutane.—The chlorination apparatus consisted of a Pyrex tube (2 × 80 cm.) wound with Chromel wire and encased in a Pyrex jacket and mounted at a slight angle from the horizontal. The upper end of the tube was fitted with an adapter which extended 10 cm. into the tube. A 500-ml. addition funnel with pressure release tube was mounted on the adapter and connected, through suitable traps, to a cylinder of chlorine. The other end of the chlorination tube was attached to an ice-water trap and two Dry Ice traps in series, the last trap being vented to the hood. In operation, the apparatus was heated to the desired temperature, a slow stream of chlorine added and the rate of addition of the starting material so adjusted that the latter vaporized in the chlorine adapter tube. Recovered starting material was recycled through the apparatus.

At 250°, 177 g. (0.81 mole) of $C_3F_7CH_2Cl$ on distillation gave 16 g. (9%) of $C_3F_7CH_2Cl$, 51 g. (24.9%) of $C_3F_7CHCl_2$, b.p. 76.5°, and 127 g. (54.7%) of $C_3F_7CCl_3$, b.p. 96.5°.

The chlorination of 405 g. (2.48 moles) of CF_3CH_2Br, at 220–240°, gave 124 g. (30.6%) of CF_3CH_2Br and 75 g. (18.8% yield) of CF_3CCl_2Br, b.p. 69.0°. A large fraction was obtained, b.p. 42–51°, which could not be separated into its constituents even by rectification on a 50-plate column.

The chlorination of 54 g. (0.35 mole) of $C_2F_5CH_2Cl$ at 250° gave 20 g. (28.5%) of $C_2F_5CHCl_2$, b.p. 45.5°, and 35 g. (43%) of $C_2F_5CH_2Cl$, b.p. 70.5°.

3,4-Dichloro-1,1,1,2,2,3-hexafluorobutane.—A 1-liter, 3-necked flask was fitted with a stirrer, an addition funnel and a reflux condenser connected to two vapor traps cooled in Dry Ice. A mixture of 80 g. (1.27 g. atom) of zinc dust and 500 ml. of glacial acetic acid was placed in the flask and heated to moderate reflux. During 2.5 hours, 256 g. (0.83 mole) of $C_3F_7CH_2I$ was added to the reaction mixture which was heated and stirred an additional 2 hr. The material that had collected in the traps was distilled to give 126 g. (93.2%) of crude $C_2F_5CF{=}CH_2$, b.p. 3–7°. Subsequent addition of chlorine was carried out with 126 g. (0.76 mole) of $C_2F_5CF{=}CH_2$ sealed in four Carius tubes with 32 g. (0.45 mole) of chlorine. The mixture was allowed to stand at room temperature for 5 days; although the tubes were kept in the dark some substitution occurred as was evidenced by the formation of hydrogen chloride. The yield of $C_2F_5CFClCH_2Cl$, b.p. 72°, was 55 g. (73.3%) based on recovery of 78 g. of the starting olefin.

1,1-Dichloroperfluorobutane.—A mixture of 249 g. (0.87 mole) of $C_3F_7CCl_3$, 155 g. (0.87 mole) of SbF_3 and 130 g. (0.49 mole) of antimony trichloride was placed in a stainless steel autoclave of 500-ml. capacity. The mixture was heated to 210° for 12 hr. after which the autoclave was cooled and the products removed and washed with concentrated hydrochloric acid to remove the antimony salts.

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(5) G. V. D. Tiers, H. A. Brown and T. S. Reid, THIS JOURNAL, **75**, 5978 (1953).

(6) E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 409, 420 (1947), reported this procedure for the chlorination of 1,1,1-trifluoroethane.

(7) Previous reports of the formation of olefinic compounds from $C_nF_{2n-1}CH_2I$ and $C_nF_{2n+1}I$ may be noted utilizing metallic zinc, W. T. Weller, Jr., A. H. Fainberg and E. Bergman, Abstracts, 122nd A.C.S. Meeting, Atlantic City, 1952, p. 14K, and R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 3607 (1953). Grignard reagents of fluorine-containing alkyl halides are also known to dehalogenate to give the corresponding olefins: R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952), and H. Gilman and R. G. Jones, THIS JOURNAL, **65**, 2037 (1943).

(8) Boiling and melting points are uncorrected.

After washing with water and drying over Drierite, the crude product was distilled to yield 168 g. (77%) of C_3F_7-$CFCl_2$, b.p. 62.8°.

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The Structure of Kornatzki's Nitrotoluenedisulfonic Acid

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RECEIVED DECEMBER 18, 1954

In 1883, Kornatzki[1] reported the sulfonation of *p*-bromotoluene to yield a disulfonic acid which, on treatment with concentrated nitric acid, was converted into a nitrotoluenedisulfonic acid. The 4-nitro-2,6-disulfo structure (I) has been assigned, without proof, to the latter compound.[2] It appeared desirable to investigate the structure of Kornatzki's nitro compound. Even on the assumption that the bromotoluenedisulfonic acid intermediate was the 4-bromo-2,6-disulfo compound,[3] the possibility of rearrangement during the reaction with nitric acid cannot be excluded.[4] We have carried out reactions with Kornatzki's nitro compound which confirm the structure I. The nitrotoluenedisulfonic acid, which was isolated as the potassium salt, first was converted into the disulfonyl chloride. A highly purified sample of the chloride was hydrolyzed, and the acidic product reconverted to the potassium salt, whose infrared absorption spectrum proved to be identical with that of the original potassium salt, establishing the isomeric purity of the product. Reduction of the disulfonyl chloride to the disulfinate, and conversion of this into the bischloromercuri compound and finally into the known[5] 4-nitro-2,6-dibromotoluene, completed the confirmation of structure.

Through a similar sequence of reactions, the disulfonyl chloride was used to prepare the hitherto unreported 4-nitro-2,6-diiodotoluene.

Acknowledgments.—The authors are grateful to Dr. Alexander Ritchie of Thomas Hedley & Co., Ltd., Newcastle-on-Tyne, England, for experimental details concerning the preparation and purification of the Kornatzki product. They are indebted also to a number of members of this Laboratory for experimental assistance.

Experimental[6]

Potassium 4-Nitrotoluene-2,6-disulfonate.[1]—A mixture of 156 g. (82 ml.) of 20% oleum and 468 g. (246 ml.) of sulfur trioxide (totaling 499 g., or 6.2 moles, of sulfur trioxide) was added with stirring over a period of one to 1.5 hours to 260 g. (1.52 moles) of *p*-bromotoluene and the temperature of the mixture rose to about 130°. The sulfonation mixture (which usually solidified on cooling) was quenched in ice-water and neutralized with lime. The calcium sulfate was filtered off, and the cake was thrice washed with boiling water. The combined filtrate and washings were evaporated to 2.5 l., diluted with 1.5 l. of methanol, and 50% sulfuric acid was added to the resulting mixture until precipitation ceased. Precipitated calcium sulfate was filtered off and washed as before, and the combined filtrate and washings were concentrated to a volume of two liters and made neutral to litmus by the addition of barium carbonate. After filtration and copious washing, the resulting solution of barium bromotoluenedisulfonate was concentrated to 2.5 l., cooled to 10°, and the precipitated barium salt was collected, washed with ethanol and dried. For conversion into the free acid, the barium salt was slurried in water and treated with dilute sulfuric acid until no further precipitation occurred. The precipitate was filtered off and washed, and filtrate and washings were evaporated to dryness on the steam-bath to yield 190–220 g. (38–44%) of free acid, as a tenacious mat of almost-white material melting diffusely over the range 140–150°.

This material was refluxed for 16 hours with 2.8 times its weight of 95% nitric acid, and the reaction mixture was evaporated on the steam-bath to remove excess nitric acid. The residue, which sometimes solidified on cooling, was dissolved in 1.5 l. of water and neutralized with barium carbonate. Solid material was filtered off and washed with much boiling water, and the combined filtrate and washings were evaporated to 1 l. and cooled to 10° to obtain a precipitate which was collected and washed with ethanol. The combined filtrate and washings were treated with potassium carbonate until precipitation had ceased, and the resulting barium carbonate was filtered off and washed with boiling water. Evaporation to dryness of the combined filtrate and washings left a brown residue which was extracted eight times with boiling 95% ethanol and then recrystallized from water to yield 6–17 g. (1.1–3.0%, based on *p*-bromotoluene) of potassium 4-nitrotoluene-2,6-disulfonate ranging from tan to white in color.

Anal. Calcd. for $C_7H_5K_2NO_8S_2$: C, 22.52; H, 1.35; K, 20.95; N, 3.75; S, 17.16. Found: C, 22.47, 22.71; H, 1.27, 1.35; K, 20.86, 20.90; N, 3.85, 3.72; S, 17.17, 17.24.

4-Nitrotoluene-2,6-disulfonyl Chloride.—The free disulfonic acid, obtained by exchanging a 1% solution of the potassium salt on a column of Amberlite-120 resin, was heated on the steam-bath overnight with 3.5 times its weight of phosphorus pentachloride. The resulting solution was poured over ice, and the solidified product was filtered off and air-dried. Recrystallization from isoöctane gave an average yield of 67% of product, m.p. 112.5–113.5°. Repeated recrystallizations led to a constant m.p. of 114.5–115.0°.

Anal. Calcd. for $C_7H_5Cl_2NO_6S_2$: C, 25.18; H, 1.51; Cl, 21.23; N, 4.18; S, 19.19. Found: C, 25.23; H, 1.44; Cl, 21.03; N, 4.21; S, 19.15.

A highly purified sample of the dichloride was hydrolyzed by heating with water in a sealed tube for 5.5 hours at 150°. Evaporation of the resulting homogeneous solution left a white residue which was neutralized with aqueous potassium hydroxide. Addition of ethanol precipitated the potassium salt, whose infrared absorption spectrum showed it to be identical with the potassium salt from which the sulfonyl chloride had been prepared.

Conversion of the Disulfonyl Chloride to 4-Nitro-2,6-dibromotoluene.—To 5.0 g. (0.015 mole) of the disulfonyl chloride in a nitrogen-swept vessel was added a solution of 4.0 g. (0.0318 mole) of sodium sulfite in 30 ml. of water, with stirring. As the highly exothermic reduction proceeded, sodium hydroxide was added as necessary to maintain alkalinity. The reaction continued for about 30 minutes, during the last 20 of which the mixture was heated in a water-bath. Then a little hydrochloric acid was added to make the disulfinate solution barely acidic, and the mixture was poured into a hot solution of 17.2 g. (0.0636 mole) of mercuric chloride in about 30 ml. of water. The resulting clear orange solution deposited a copious precipitate after about ten seconds, and the odor of sulfur dioxide was noticed. After heating for 30 minutes, the mixture was filtered hot, and the residue washed with hot water and dried to yield 5.8 g. (64%) of crude mercury compound. This product,

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[1] O. Kornatzki, *Ann.*, **221**, 191 (1883).

[2] Beilstein's "Handbuch," Vol. 11, p. 207.

[3] The likelihood of more than one orientation in reactions of this type is emphasized by the fact that oleum sulfonation of *p*-bromotoluene has been shown to yield a mixture of 2- and 3-sulfonic acids, and that potassium 4-chlorotoluene-2-sulfonate on oleum treatment yields a mixture of the 2,5- and the 2,6-disulfo compounds. See C. M. Suter in R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 168–169.

[4] The formation of a dibromonitrotoluenesulfonic acid as one of Kornatzki's by-products[1] illustrates the ability of groups to wander under the conditions of the reaction with nitric acid.

[5] R. H. C. Nevile and A. Winther, *Ber.*, **13**, 973 (1880); **14**, 419 (1881).

[6] All melting points are uncorrected. Analyses by Huffman Microanalytical Laboratories.