enebis-(2-cyanoethyldimethylphosphonium bromide) was added all at once to the resulting ethoxide solution. The mixture was heated to reflux briefly and then kept at room temperature overnight. The excess alcohol was removed and the residue was treated with 100 ml. of water and extracted with benzene. Upon distillation, the benzene extract yielded 5 g. (0.032 mole) of 2-cyanoethyldimethylphosphine (b.p. 70–72° at 1.5 mm., $n^{25}D$ 1.4762). Concentration of the original aqueous reaction mixture gave only brown tars.

d. Preparation of Trimethylenebis-(dimethylphosphine Oxide).—The phosphonium salt, trimethylenebis-(2-cyanoethyldimethylphosphonium bromide), was prepared by the procedure described for ethylenebis-(2-cyanoethylphosphonium bromide) from 30.6 g. (0.266 mole) of 2-cyanoethyldimethylphosphine and 20.2 g. (0.1 mole) of 1,3-dibromopropane. The desired phosphonium salt was obtained in 98% yield, m.p. 175–176°.

Anal. Calcd. for $C_{14}H_{26}N_2P_2 \cdot 2Br$: Br, 36.98. Found: Br, 34.48.[20]

This diphosphonium salt (36.6 g., 0.085 mole) was treated with 9.2 g. (0.170 g.-atom) of sodium in 200 ml. of methanol and refluxed for three hours under nitrogen. Upon working up the reaction mixture 71.5% of trimethylenebis-(2-cyanoethyldimethylphosphonium bromide) was recovered.

This reaction was repeated using 26.2 g. (0.062 mole) of the diphosphonium salt with sodium (2.82 g., 0.124 g.-atom) in 100 ml. of butanol and refluxing for approximately 72 hours. After distilling the excess solvent, the reaction residue was treated with 100 ml. of water and extracted with 100 ml. of benzene. The benzene extract after accidental exposure to air during work-up yielded a small amount of a very hygroscopic solid which was identified by infrared and mass spectroscopy as trimethylenebis-(dimethylphosphine oxide).

This material was distilled under reduced pressure, b.p. 115° at 0.20 mm.

Anal. Calcd. for $C_7H_{18}O_2P_2$: P, 31.58; mol. wt., 196. Found: P, 32.09, 32.12; mol., wt., 196 (determined by mass spectroscopy).

Acknowledgments.—Microanalyses were carried out under the supervision of Dr. J. A. Kuck and Mrs. E. C. Grim. Interpretation of infrared spectra was provided by Norman Colthup and mass spectrometer data by Rosemarie Herberich and A. H. Struck. McGill Valentine prepared bis-(2-cyanoethyl)-methoxypropylphosphine.

STAMFORD, CONN.

[CONTRIBUTION FROM THE RESEARCH DIVISION, BRISTOL LABORATORIES, INC.]

Synthesis of Trifluoromethylated Compounds Possessing Diuretic Activity[1]

BY CHARLES T. HOLDREGE, RICHARD B. BABEL AND LEE C. CHENEY

RECEIVED APRIL 3, 1959

4-Amino-6-trifluoromethyl-*m*-benzenedisulfonamide (VI) was synthesized from 4-chloro-3-nitrobenzotrifluoride. Compound VI reacted with formic acid to give 7-sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-dioxide (VII). Cyclization of VI with formaldehyde produced 3,4-dihydro-7-sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-dioxide (VIII). Reaction of VI with a variety of aldehydes and ketals gave 3-substituted dihydrobenzothiadiazine dioxides. Compounds VII and VIII were found to be potent orally active diuretic agents.

The synthesis of a series of compounds containing the trifluoromethyl group was carried out as part of a program aimed at developing useful oral diuretic and hypotensive agents. The compounds were prepared by the route illustrated in Chart I.

4-Chloro-3-nitrobenzotrifluoride was converted to I by a modification of the literature procedure.[2] Conversion of I to II was accomplished by chlorination of a suspension of I in aqueous acetic acid.[3] Compound II could not be prepared by chlorination of I in a mixture of concentrated hydrochloric and nitric acids at 80°.[4] It was interesting to note that Caldwell and Sayin[5] could not satisfactorily prepare the isomeric 4-nitro-2-trifluoromethylbenzenesulfonyl chloride by either procedure.

Crude II was converted to III[6] either by reaction with concentrated ammonium hydroxide or by treatment of a toluene solution with an excess of anhydrous ammonia at 0–4°. In addition to III there was obtained a complex mixture of by-products which made the purification of III tedious.

Reduction of the nitro group of III to give IV was best carried out with either iron and acetic acid or, preferably, with iron and ammonium chloride. Catalytic hydrogenation of III at low pressure with Raney nickel catalyst gave yields of IV in the range of 76–80% provided that III was carefully purified.

The preparation of V[7] by the chlorosulfonation of IV was carried out by an adaptation of the procedure of Lustig and Katscher.[8] The heating period of several hours at 150°, used by these authors, was found to be excessive in the present case. With 20–90-g. quantities of IV the best results were obtained with a heating period of 15–20 minutes at a bath temperature of 150°. Substantially longer heating periods increased the amount of tarry by-products and drastically reduced the yield of V. If sodium chloride was omitted the desired product was not obtained. A major side reaction in the chlorosulfonation was judged to be an attack on the trifluoromethyl group, a supposition supported by the work of LeFave[9] and Scheurer.[10]

(1) Presented in part at the 135th Meeting of the American Chemical Society, Division of Medicinal Chemistry, April 5–10, 1959, at Boston, Mass.

(2) A. I. Kiprianov and L. M. Yagupol'skiĭ, *Zhur. Obshcheĭ, Khim.*, **22**, 2209 (1952); *C. A.*, **47**, 4769 (1953).

(3) H. J. Barber, *J. Chem. Soc.*, 101 (1943).

(4) E. Wertheim, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 471.

(5) W. T. Caldwell and A. N. Sayin, THIS JOURNAL, **73**, 5125 (1951).

(6) Some sensitive individuals developed a dermatitis while working with this reaction mixture.

(7) Compound V has been alternatively prepared by the chlorosulfonation of *m*-aminobenzotrifluoride. This reaction will be the subject of a future publication from our laboratories.

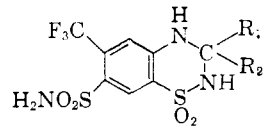
(8) O. Lustig and E. Katscher, *Monatsh.*, **48**, 87 (1927).

(9) G. M. LeFave, THIS JOURNAL, **71**, 4148 (1949).

(10) P. G. Scheurer and G. M. LeFave, *ibid.*, **72**, 3308 (1950).

TABLE I

3-SUBSTITUTED-3,4-DIHYDRO-1,2,4-BENZOTHIADIAZINE 1,1-DIOXIDES

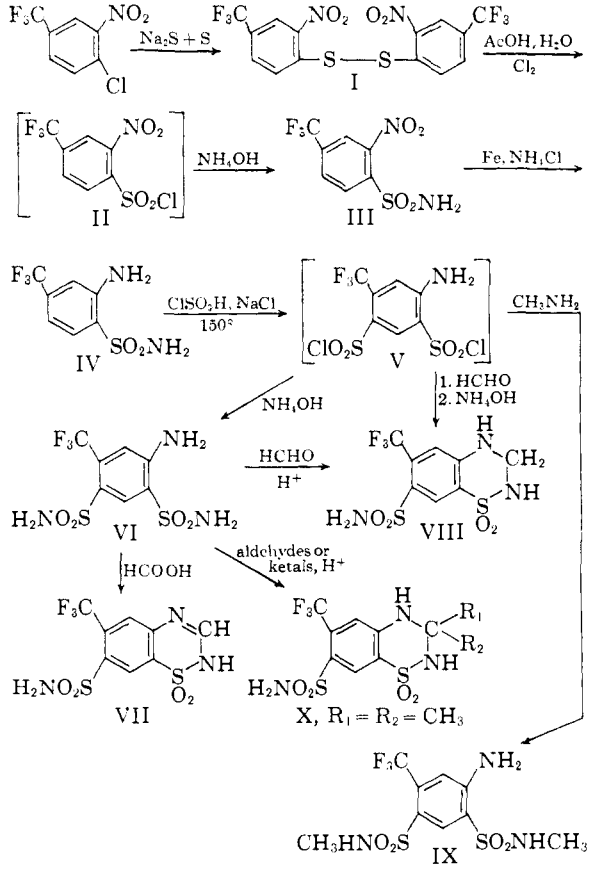


R_1	R_2	M.p., °C.	Method	Reactant	Yield, %	Reflux, hr.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
CH_2CH_3	H	262–263 d.	A	Propionaldehyde	59	4	$C_{12}H_{12}F_3N_3O_4S_2$	33.4	33.7	3.37	3.44	11.7	11.9
CH_3	H	247–250 d.	A	Acetaldehyde	70	0.25	$C_9H_{10}F_3N_3O_4S_2$	31.3	31.3	2.92	3.00	12.17	12.18
$CH_2C_6H_5$	H	221–223	B	Phenylacetaldehyde	35	16	$C_{15}H_{14}F_3N_3O_4S_2$	42.7	43.7	3.35	3.58	9.97	10.31
Pyridyl	H	310–311	A[a]	2-Pyridinealdehyde	19	0.5	$C_{13}H_{11}F_3N_4O_4S_2$	38.2	38.9	2.72	2.58	13.7	13.4
CCl_3	H	283–285 d.	A	Chloral hydrate	22	21	$C_9H_7Cl_3F_3N_3O_4S_2$	24.1	24.4	1.57	1.83	9.37	9.33
C_6H_5	H	220–224	B[b]	Benzaldehyde	17	24	$C_{14}H_{12}F_3N_3O_4S_2$	41.3	41.6	2.97	3.27	10.32	10.25
$-(CH_2)_5-$		260–262	C	Ethylene ketal of cyclohexanone	23	1.5	$C_{13}H_{16}F_3N_3O_4S_2$	39.1	39.3	4.04	4.29	10.52	10.79
$-(CH_2)_4-$		225–226 d.	C	Ethylene ketal of cyclopentanone	19	2	$C_{12}H_{14}F_3N_3O_4S_2$	37.4	37.0	3.66	3.61	...	

[a] The sulfuric acid catalyst was omitted. [b] Addition of a few drops of 6 *N* hydrochloric acid to the recrystallization solvent gave a better product.

Aqueous methylamine reacted with V to give 4-amino-6-trifluoromethyl-N,N'-dimethyl-*m*-benzenedisulfonamide (IX). This established that V was the *m*-benzenedisulfonyl chloride rather than 4-amino-2-trifluoromethyl-5-sulfamylbenzenesulfonyl chloride.

CHART I



Crude V was converted to 4-amino-6-trifluoromethyl-*m*-benzenedisulfonamide (VI) by reaction with an excess of concentrated ammonium hydroxide. Heating VI with formic acid gave 7-sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-dioxide (VII).

Refluxing VI with an equivalent amount of formaldehyde, preferably in aqueous solution, in the presence of a catalytic amount of mineral acid gave 3,4-dihydro-7-sulfamyl-6-trifluoromethyl-2H 1,2,4-benzothiadiazine 1,1-dioxide (VIII). Cyclization also occurred under either neutral or alkaline conditions, however, with inferior yields. The amount of formaldehyde was critical. If more than a slight excess was used a gummy resinous mass was obtained from which none of the desired product was isolated. This was not unexpected in view of the known reactions of sulfonamides with excess formaldehyde to give resinous products.[11] Compound VIII was alternatively prepared from V but in lower yield.

Reaction of VI with alkyl, aromatic and heterocyclic aldehydes[12] was found to be a general method for the preparation of 3-substituted derivatives of VIII (Table I). Acid reaction conditions were generally preferred to alkaline conditions. In contrast to aldehydes, ketones failed to react with VI. Acetone and cyclopentanone did not react by the techniques which were successful for aldehydes. It was discovered that ketals would react with VI to give, by an indirect route, the 3,3-disubstituted derivatives of VIII which could not be obtained directly from ketones (Table I).

Pharmacology.[13]—Compounds VII and VIII were found to be potent orally active diuretic agents of low toxicity. Compound VIII was tested in experimental animals and found to be about 10 times as active orally as VII.

Experimental[14]

Bis-(2-nitro-4-trifluoromethylphenyl) Disulfide (I).[2]—Sodium sulfide (0.887 mole, 113.5 g. of Hooker hydrated flakes assaying 61% sodium sulfide), sulfur (28.4 g., 0.886 mole), and 500 ml. of water were warmed on the steam-bath until solution occurred. This solution was added dropwise to a stirred refluxing solution of 400 g. (1.77 moles) of 4-chloro-3-nitrobenzotrifluoride (Antara) in 1.5 l. of methanol. The reaction mixture was refluxed for one hour, cooled in an ice-bath, and the yellow product filtered and washed with

(11) L. McMaster, THIS JOURNAL, **56**, 204 (1934).

(12) J. H. Freeman and E. C. Wagner, *J. Org. Chem.*, **16**, 815 (1951).

(13) The pharmacology of VII and VIII was presented by D. E. Tisch, J. B. Hoekstra and M. H. Pindell at the Meeting of the Federation of American Societies for Experimental Biology, April 13–17, 1959, at Altantic City, N. J.

(14) Melting points are uncorrected except as otherwise noted. Microanalyses were performed by Mr. Richard M. Downing.

methanol; yield 359 g. (91.3%), m.p. 146–150°. This material was used for the preparation of II without further purification. Two recrystallizations from acetic acid afforded pure I, m.p. 158–161°.

Anal. Calcd. for $C_{14}H_6F_6N_2O_4S_2$: C, 37.8; H, 1.36; N, 6.31. Found: C, 38.1; H, 1.33; N, 6.40.

2-Nitro-4-trifluoromethylbenzenesulfonyl Chloride (II).—Chlorine was bubbled into a suspension of 1000 g. (2.25 moles) of I in 2.3 l. of glacial acetic acid and 250 ml. of water at such a rate that it was nearly completely absorbed. The temperature was maintained in the range of 5–14°. After four hours the chlorine addition was stopped and the flask allowed to stand overnight. During this time the ice-bath melted and the flask came to room temperature. The reaction mixture was cautiously heated on the steam-bath for two hours to a maximum temperature of 70°. The flask was cooled to 10° and chlorinated for seven additional hours. After standing overnight the flask was again heated on the steam-bath for one-half hour and then poured into 6 l. of ice and water. The crude II, which was a dense oil, was separated. The aqueous phase was extracted with 1 l. of toluene in two portions. The toluene was removed at reduced pressure from the extracts and the residual oil combined with the main portion of product. The crude II was used in the next reaction without further purification.

2-Nitro-4-trifluoromethylbenzenesulfonamide (III).[6]—The crude II obtained from 1000 g. of I was added over a 3-hour period to 2 l. of cold concentrated ammonium hydroxide (maximum temperature of 15°). After standing overnight the solids were collected by filtration and slurried with 4 l. of 10% sodium hydroxide at 15°. The alkaline mixture was filtered to remove a quantity of insoluble material and the filtrates acidified (maximum temperature of 25°) to precipitate crude III. After chilling in an ice-bath the crude III was collected by filtration and recrystallized from 2 l. of 2-propanol; yield 490 g. (40%), m.p. 161–165°. The 2-propanol filtrates were distilled to one-half of their initial volume to give a second crop of 66 g. (5.4%).

The reaction was repeated with the same quantities of materials, but the chlorination time for the preparation of II was doubled. A 54% yield of III resulted. An analytical sample was recrystallized from toluene and dried *in vacuo* over phosphorus pentoxide at 111°, m.p. 165–167°.

Anal. Calcd. for $C_7H_5F_3N_2O_4S$: C, 31.1; H, 1.86; N, 10.37. Found: C, 31.4; H, 2.05; N, 10.00.

2-Amino-4-trifluoromethylbenzenesulfonamide (IV). **A. Iron–Acetic Acid Method.**—Compound III (5 g., 0.0185 mole) and 5 ml. (5.2 g., 0.874 mole) of glacial acetic acid in 150 ml. of water were heated on the steam-bath while iron filings, 6 g. (0.1075 mole), were added in two approximately equal portions five minutes apart. The reaction mixture was stirred on the steam-bath for three hours, 100 ml. of 95% ethanol was added and the mixture heated to boiling, filtered, and the hot filtrate neutralized with saturated sodium carbonate solution. The hot mixture was again filtered, the filtrates chilled in an ice-bath, and the crystalline product collected by filtration; yield 3 g. (67%), m.p. 140–144°. An analytical sample was recrystallized from ethanol–water and dried *in vacuo* over phosphorus pentoxide at 111°, m.p. 143–146°.

Anal. Calcd. for $C_7H_7F_3N_2O_2S$: C, 35.0; H, 2.94; N, 11.66. Found: C, 35.2; H, 3.04; N, 11.88.

B. Iron–Ammonium Chloride Method.—Iron filings (242 g., 4.33 moles) were added in portions over a period of 1.5 hours to a gently refluxing, stirred mixture of 190 g. (0.704 mole) of III, 242 g. (4.56 moles) of ammonium chloride, 2 l. of methanol and 1 l. of water. The reaction mixture was refluxed for 1.5 hours and filtered while hot. The flask and filter cake were washed with 400 ml. of methanol in four portions. The combined methanolic filtrates were diluted with 4.5 l. of water, heated to boiling, and filtered. The filtrates were chilled to 0° and the crystalline product filtered. Recrystallization from a mixture of 400 ml. of water and 250 ml. of methanol, containing 2 ml. of 6 *N* hydrochloric acid to give a slightly acid solution, gave 126 g. (74.6%) of IV, m.p. 141–145°.

4-Amino-6-trifluoromethyl-*m*-benzenedisulfonyl Chloride (V).[7]—Compound IV (35 g., 0.146 mole) was added over a period of one-half hour to 96 ml. (170 g., 1.46 moles) of chlorosulfonic acid with stirring and cooling. The ice-bath was removed, and 87.6 g. (1.5 moles) of sodium chloride was added over a period of one hour. A wax-bath, which had been pre-heated to 85°, was placed around the flask. The temperature of the bath was increased as rapidly as possible to 150°, held there for 15 minutes, and then removed at once. Near the end of the heating period the mixture solidified and gas evolution subsided. The reaction mixture was quenched with 600 g. of ice and water. The crude V separated as a gum which was used in subsequent reactions without purification.

4-Amino-6-trifluoromethyl-*m*-benzenedisulfonamide (VI).—The crude V obtained from the chlorosulfonation of 35 g. (0.146 mole) of IV was added to 200 ml. of concentrated ammonium hydroxide. After standing overnight the excess ammonia was removed by heating on the steam-bath.[14a] After chilling in an ice-bath the crystalline product was collected by filtration; 15.7 g. (33.8% from IV[15]), m.p. 220–225°. Product melting at 232° or higher, obtained by recrystallization from either water or 1-butanol, was of adequate purity for the reactions described for VI. An analytical sample was recrystallized several times from water and dried *in vacuo* at 111° over phosphorus pentoxide, m.p. 239.5–241.5°.

Anal. Calcd. for $C_7H_8F_3N_3O_4S_2$: C, 26.3; H, 2.53; N, 13.16. Found: C, 26.5; H, 2.62; N, 13.30.

7-Sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-Dioxide (VII).—Compound VI (1 g.) and 4 ml. of 98% formic acid[16] were refluxed for four hours. The reaction mixture was chilled in an ice-bath and the crystalline product collected by filtration; m.p. 296–298°. The product was recrystallized from 1:1 water–95% ethanol and dried *in vacuo* over phosphorus pentoxide; m.p. 300–302° (corrected m.p. 305–307°).

Anal. Calcd. for $C_8H_6F_3N_3O_4S_2$: C, 29.2; H, 1.84; N, 12.76. Found: C, 29.3; H, 1.81; N, 12.52.

3,4-Dihydro-7-sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-Dioxide (VIII). **A. Preparation from V.**—One-half of the crude V obtained by the chlorosulfonation of 45 g. (0.1875 mole) of IV was extracted with 125 ml. of dioxane. To the dioxane solution was added 15 ml. of 40% aqueous formaldehyde solution and the flask stored at 10° overnight. After the addition of 125 ml. of concentrated ammonium hydroxide the flask was stored for 90 minutes at room temperature, then heated on the steam-bath for one hour and at reflux for 2.5 hours. After cooling in ice the small amount of crystalline solid was collected by filtration. Two recrystallizations from water–95% ethanol gave 0.6 g. of VIII, m.p. 260–264°, corrected m.p. 269–273°.

Anal. Calcd. for $C_8H_8F_3N_3O_4S_2$: C, 29.0; H, 2.43; N, 12.68. Found: C, 29.2; H, 2.51; N, 12.62.

B. Preparation from VI.—Compound VI (63.8 g., 0.2 mole), 16.5 g. (0.22 mole of formaldehyde) of 40% aqueous formaldehyde solution, 300 ml. of water and 0.1 ml. of concentrated sulfuric acid were stirred at reflux for 3.5 hours. The product VIII was collected by filtration of the cooled reaction mixture and recrystallized from methanol (400 ml.)–water (200 ml.) (treated with 1.5 g. of decolorizing carbon); yield 43.3 g. (65.4%), m.p. 262–265°, corrected m.p. 271–274°. This material was concluded to be identical with VIII prepared from V by mixed melting point and infrared spectra.

4-Amino-6-trifluoromethyl-N,N′-dimethyl-*m*-benzenedisulfonamide (IX).—The crude V obtained from the chlorosulfonation of 22 g. (0.0917 mole) of IV was added to 250 ml. of 40% aqueous methylamine. After standing overnight at room temperature the reaction mixture was filtered and the excess methylamine removed from the filtrates at reduced pressure. The crude IX separated in crystalline form and was filtered from the chilled mixture. The product was recrystallized by dissolving in a minimum amount of methanol at room temperature and diluting with an equal volume of water; yield 11 g. (34%), m.p. 167–169°. Recrystallization from water (carbon treated) gave 9.6 g. (30%), m.p. 168–170°.

Anal. Calcd. for $C_9H_{12}F_3N_3O_4S_2$: C, 31.1; H, 3.48. Found: C, 31.3; H, 3.52.

(14a) Compound VI was very soluble in concentrated ammonium hydroxide and was precipitated in crystalline form on evaporation of the excess ammonia.

(15) After some experience with the chlorosulfonation reaction yields in the range of 40–55% based on IV could be reliably produced.

(16) Equivalent results were obtained with 88% formic acid.

3,4-Dihydro-3,3-dimethyl-7-sulfamyl-6-trifluoromethyl-2H-1,2,4-benzothiadiazine 1,1-Dioxide (X).—Compound VI (5 g., 0.0157 mole) and 45 ml. of 2,2-dimethoxypropane (Dow) were refluxed for 24 hours. The excess 2,2-dimethoxypropane was removed at reduced pressure and the residue recrystallized from methanol–water; yield 1.6 g. (28%), m.p. 216–221°.

Anal. Calcd. for $C_{10}H_{12}F_3N_3O_4S_2$: C, 33.4; H, 3.34. Found: C, 33.1; H, 3.49.

Compounds of Table I. General Method A.—Compound VI (5 g., 0.0157 mole), 0.0173 mole of the appropriate aldehyde, one drop of concentrated sulfuric acid and 30 ml. of water were heated at reflux. The product was collected by filtration from the cooled reaction mixture and recrystallized from either methanol–water or acetone–water.

General Method B.—Compound VI (5 g., 0.0157 mole), 0.0173 mole of the appropriate aldehyde and 30 ml. of glacial acetic acid were heated at reflux. The solvent was removed at reduced pressure and the product recrystallized from methanol–water.

General Method C.—Compound VI (5 g., 0.0157 mole), 0.0173 mole of the ethylene ketal of cyclohexanone[17] (or cyclopentanone[18]), two drops of concentrated sulfuric acid, and 50 ml. of 1-butanol were heated at reflux. The solvent was removed at reduced pressure and the residue recrystallized from methanol–water.

(17) M. Salzbacher, E. Bergmann and E. R. Pariser, THIS JOURNAL, **70**, 2827 (1948).

(18) E. J. Salmi, *Ber.*, **71**, 1806 (1938).

SYRACUSE 1, N. Y.

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

A New Class of Sulfenyl Derivatives; Perhalogenated Aliphatic Sulfenyl Fluorides[1]

BY EHRENFRIED KOBER

RECEIVED MARCH 4, 1959

The first two representatives of the hitherto unknown class of sulfenyl fluorides, namely, trichloromethanesulfenyl fluoride and heptafluoro-*n*-propanesulfenyl fluoride, have been prepared. The synthesis of aromatic sulfenyl fluorides could not be achieved by the methods successfully applied for the perhalogenated aliphatic sulfenyl fluorides.

All recorded attempts to synthesize sulfenyl fluorides have failed,[2–6] while a number of more or less stable sulfenyl chlorides is known. On the assumption that the sulfenyl fluorides would have the same order of stability as the sulfenyl chlorides, we thought it would be most promising to employ the most stable sulfenyl chlorides for fluorination experiments in order to obtain the corresponding sulfenyl fluorides.

The most stable representative of this class appears to be the trichloromethanesulfenyl chloride (I).[7] Other rather stable compounds are the recently described perfluorinated aliphatic sulfenyl chlorides.[8,9] As a new representative of this class, heptafluoro-*n*-propanesulfenyl chloride (II) has been prepared in this Laboratory. All these compounds have one common characteristic: the SCl group is attached to a strongly electronegative group which might be responsible for the stability of the aforementioned perhalogenated aliphatic sulfenyl chlorides.

Therefore, compound I which is commercially available and compound II which was obtained in good yields by ultraviolet light-catalyzed chlorination of the corresponding perfluorinated polysulfides were selected as starting materials.

Trichloromethanesulfenyl chloride (I) was used in the first reported attempt to synthesize a sulfenyl fluoride.[2] The authors used zinc fluoride as a fluorinating agent, but isolated only carbon tetrachloride. In a similar experiment, using a mixture of antimony fluorides, the so-called Swarts reagent,[10] we obtained a mixture of perhalogenated fluorochloromethanes and ethanes, indicating complete cleavage of the original sulfenyl moiety under the rather severe reaction conditions.

Mercuric fluoride is reported to be a relatively mild fluorination agent.[11] Therefore, a solution of I in dichloromethane was refluxed over mercuric fluoride to give the desired trichloromethanesulfenyl fluoride (III) in good yield. The same reaction product was obtained when (I) was heated over silver fluoride. In both cases small amounts of by-products, such as trichloromethyl sulfur difluoro chloride (VII), bis-(trichloromethyl) disulfide (VIII), and bis-(trichloromethyl) trisulfide (IX) were isolated and identified.

Trichloromethane sulfenyl fluoride is a yellow liquid, having an odor similar to that of the corresponding sulfenyl chloride. This compound is relatively stable against hydrolysis; it does not react with water upon shaking at room temperature. That the fluorine atom of the product III is attached to the sulfur atom was proved by the reaction of III with potassium phthalimide. The reaction product was identical with the known N-trichloromethanesulfenphthalimide (IV)[12] obtained by the reaction of trichloromethanesulfenyl chloride (I) and potassium phthalimide.

Although heptafluoro-*n*-propanesulfenyl chloride (II) was recovered nearly quantitatively after refluxing over mercuric fluoride or silver fluoride, the desired heptafluoro-*n*-propanesulfenyl fluoride (V) could be obtained when II was heated with silver

(1) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.

(2) O. B. Helfrich and E. E. Reid, THIS JOURNAL, **43**, 591 (1921).

(3) H. J. Emeleus and H. G. Heal, *J. Chem Soc.*, 1126 (1946).

(4) D. L. Chamberlain and N. Kharasch, THIS JOURNAL, **77**, 1041 (1955).

(5) D. L. Chamberlain, D. Peters and N. Kharasch, *J. Org. Chem.*, **23**, 381 (1958).

(6) A product cited as $CF_3(CF_2)_7SF$ is claimed in U. S. Patent 2,519,983, but no details or structure proof are given.

(7) N. Kharasch, *Chem. Revs.*, **39**, 269 (1946).

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(10) A. Henne, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 49.

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(12) A. R. Kittleson, *Science*, **115**, 85 (1952).