fraction of 29.7 g., b.p. 70–100° (chiefly 95–100°) (90 mm.), was collected. The product yield was determined by gas chromatographic analysis of this sample; pure (95–99%) *p*-tolyl trifluoromethyl sulfide was obtained by careful fractionation through a 45-cm. spinning-band column or a glass helices-packed column.

B. Addition of Thiophenols to Tetrafluoroethylene.—The procedure described previously[3] was employed with the following modifications.[19] The thiophenol (0.25–0.50 mole) was dissolved in 150 ml. of dimethoxyethane (glyme), and 10–20 molar % of 53% sodium hydride dispersion in mineral oil was added. When the reaction was complete, the solution was diluted with 150 ml. of dimethylformamide and transferred to the reactor. The tetrafluoroethylene reaction was carried out as previously described,[3] and the product worked up in the normal manner.

C. Oxidation to Benzoic Acids.—A solution of 9.60 g. (0.05 mole) of *p*-tolyl trifluoromethyl sulfide and 16.0 g. (0.10 mole) of bromine in 100 ml. of carbon tetrachloride was radiated under reflux overnight with a General Electric sun lamp. At the end of this time, the bromine color had disappeared, and considerable HBr had evolved. The carbon tetrachloride was evaporated at room temperature under a nitrogen stream, and 50 ml. of concentrated nitric acid was added. The mixture was stirred vigorously overnight; bromine gradually evolved, and finally the product separated from the aqueous phase as a solid. The mixture was poured into several hundred milliliters of ice–water, and the solid product was separated by suction filtration and washed thoroughly with water. The yield of crude *p*-(trifluoromethylthio)benzoic acid, m.p. 157–158.5°, was 10.3 g. The product was purified to constant m.p. 161.0–162.4° by recrystallizations from approximately 125 ml. of 60% hexane–40% benzene, followed by sublimation at approximately 100° (5 mm.).

D. Nitration.—A solution of 5.0 g. (0.028 mole) of phenyl trifluoromethyl sulfide and 15 g. of concentrated sulfuric acid was cooled to 0°, and 3.2 g. (0.035 mole) of nitric acid (70%) was added dropwise while keeping the reaction temperature at 0°. After addition was completed, the reaction mixture was stirred for 40 min. at 0° and then poured into 200 ml. of ice–water. The oil was extracted in methylene chloride and after drying, the extracts were distilled through a 30-cm. spinning-band column. A total of 4.13 g. of pale yellow liquid, b.p. 90–91° (5.0 mm.), $n^{26}D$ 1.5125–1.5165, was identified by infrared and F^{19} n.m.r. analysis as chiefly *p*-nitrophenyl trifluoromethyl sulfide containing 20–30% of a second component with spectral properties characteristic for an *ortho* isomer. No *meta* isomer was detected. Gas chromatographic analysis on a column of 20% Dow Corning high vacuum grease on 60–80-mesh Celite also indicated 20% of a second component, but complete separation was not accomplished on a selection of columns usually suitable for fluorocarbons or aromatic isomer mixtures. A control reference mixture of *meta* and *para* isomers could not be separated under any of the conditions employed. A higher boiling fraction [93–105° (1.5 mm.), $n^{26}D$ 1.5515] was shown by spectral analysis (comparison with an authentic sample) to contain some nitrophenyl trifluoromethyl sulfone.

E. Reduction.—Chemical reduction of nitrophenyl trifluoromethyl sulfide with stannic chloride has been reported in the literature.[2] In this work, catalytic hydrogenation, as described by the following procedure, was found to be more convenient. A solution of 19.7 g. (0.077 mole) of *m*-nitrophenyl tetrafluoroethyl ether in 150 ml. of absolute ethanol containing 0.08 mole of hydrogen chloride was hydrogenated at approximately 3 atm. of pressure in a Parr apparatus using 0.30 g. of platinum oxide as catalyst. The theoretical amount of hydrogen was absorbed in a few minutes. The catalyst was removed by filtration, and the alcohol solution evaporated under nitrogen. The residual solid was triturated with 100 ml. of ether and filtered. The *m*-(tetrafluoroethylthio)aniline hydrochloride was obtained as white platelets in an approximately quantitative yield of 21 g. The free aniline was obtained by adding the hydrochloride to an excess of a stirred 10% solution of sodium carbonate layered with ether. The aniline obtained from the dried ether extract distilled at 80° (1.0 mm.).

(19) We wish to thank Dr. D. C. England of this laboratory for suggesting these modifications.

Aryl Fluoroalkyl Sulfides. II. Preparation by Condensation of Trifluoromethanesulfenyl Chloride with Aromatic Systems

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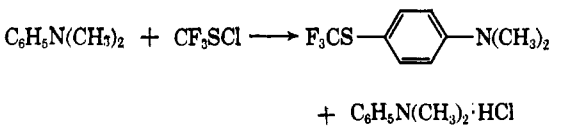
Received October 18, 1963

The condensation of trifluoromethanesulfenyl chloride with aromatic compounds provides a convenient new synthesis of aryl trifluoromethyl sulfides. Activated aromatic derivatives, such as phenols or dimethylaniline, react at room temperature without a catalyst to give high yields of the corresponding *p*-substituted aryl trifluoromethyl sulfide. Benzene, toluene, and halobenzenes require higher temperatures and Lewis acid catalysts, such as hydrogen fluoride or boron trifluoride.

In the previous paper,[1] the literature on aryl fluoroalkyl sulfides was reviewed, and the reaction of Grignard reagents with CF_3SCl was described as a new synthetic route to aryl trifluoromethyl sulfides. The condensation of alkyl- or arylsulfenyl chlorides with aromatic compounds has been reported as a method for preparation of aryl sulfides.[2] As an extension of this reaction, we wish to report the convenient preparation of aryl trifluoromethyl sulfides by substitution of aromatic derivatives with CF_3SCl. The method is particularly advantageous for aromatic systems with electron-donating substituents.

Introduction of gaseous CF_3SCl into dimethylaniline in ether or phenol in chloroform–pyridine at room temperature gave the corresponding aryl trifluoromethyl sulfide in yields of 58 to 75%. As normally observed in electrophilic, aromatic-type substitutions in aromatic rings highly activated by groups such as $N(CH_3)_2$ or OH, substitution was almost exclusively in the *para* position.



Benzene did not react with CF_3SCl at room temperature even in the presence of a Lewis acid. By carrying out the reaction in a stainless steel autoclave at 100° in the presence of boron trifluoride, phenyl trifluoromethyl sulfide was obtained in a yield of 57%. Similar conditions were needed for reaction with toluene. The over-

(1) W. A. Sheppard, *J. Org. Chem.*, **29**, 895 (1964).

(2) (a) C. M. Buess and N. Kharasch, *J. Am. Chem. Soc.*, **72**, 3530 (1950); (b) H. Brintzinger and M. Langheck, *Ber.*, **86**, 557 (1953); H. Brintzinger and H. Ellwanger, *ibid.*, **87**, 300 (1953).

all yield of tolyl trifluoromethyl sulfides was higher, and the product was a mixture of *ortho* and *para* isomers with a trace of *meta*. Chloro- and bromobenzene required a catalyst (anhydrous hydrogen fluoride) and a temperature of 200°; total yield of the resulting *ortho*, *meta*, and *para* isomer mixture of haloaryl trifluoromethyl sulfides was approximately 25%. The yield of *meta* isomer was low, as expected, and the products were contaminated with dihalobenzenes from disproportionation or chlorination as a result of the drastic conditions required. Disubstitution of benzene with CF_3SCl did not occur to any detectable extent even under forcing conditions. It previously has been shown that the deactivating effect of an SCF_3 group in withdrawing electrons is significantly greater than that of a halogen.[3]

Thiophenol gave only phenyl trifluoromethyl disulfide ($C_6H_5SSCF_3$). In the reaction of phenols with CF_3SCl, substitution occurs in the ring, but it is possible that the sulfenate ester ($ArOSCF_3$)[4] may form initially and rearrange rapidly into the ring.

No study was made of the mechanism of this reaction, but it is considered to be an ionic reaction that proceeds as a typical electrophilic aromatic substitution. The attacking species is probably CF_3S^+, formed by coordination of CF_3SCl with a Lewis acid.

Experimental

Materials.—The trifluoromethanesulfenyl chloride, b.p. −2–0°, was prepared from trichloromethanesulfenyl chloride and sodium fluoride in tetramethylene sulfone by the method of Tullock.[5] All other reagents were obtained from chemical supply houses.

A. Trifluoromethyl *p*-(N,N-Dimethylamino)phenyl Sulfide.—To a solution of 63 g. of trifluoromethanesulfenyl chloride dissolved in 700 ml. of anhydrous ether was added 110 g. of dimethylaniline over a period of 30 min. The mixture was filtered and the precipitate rinsed with ether on the filter. The washings and filtrate were combined and evaporated *in vacuo*. Upon distillation of the residue through a 45-cm. spinning-band still, there was obtained 59.2 g. (58%) of *p*-(N,N-dimethylamino)phenyl trifluoromethyl sulfide, b.p. 43–74° (0.9 mm.), $n^{25}D$ 1.5297–1.5301. This material was shaken once with aqueous sodium bicarbonate, once with water, dried over anhydrous magnesium sulfate, and redistilled. The product was obtained as a colorless liquid distilling at 54° (0.15 mm.), $n^{24}D$ 1.5309.

Anal. Calcd. for $C_9H_{10}F_3NS$: C, 48.9; H, 4.6; S, 14.5. Found: C, 49.0; H, 4.5; S, 14.5.

The proton n.m.r. spectrum (neat) showed a single sharp resonance at τ 7.63 assigned to the methyl groups and a typical AB pattern centered at 3.43 (J_{AB} = 9 c.p.s.), as usually observed with *p*-substituted aromatic compounds.

B. Trifluoromethyl Hydroxyaryl Sulfides.—A mixture of 18.8 g. (0.2 mole) of phenol, 16.0 g. (0.20 mole) of pyridine, and 100 ml. of chloroform was cooled to 0° while 32.0 g. (0.23 mole) of trifluoromethanesulfenyl chloride was added. After addition was complete, approximately 75 ml. of chloroform was removed by distillation, and 150 ml. of ether was added to the viscous mixture. Pyridine hydrochloride precipitate was removed by pressure filtration. The filtrate was distilled to give 30.0 g. (72.5%) of *p*-(trifluoromethylthio)phenol as a colorless liquid, b.p. 71–75° (3 mm.).[6] This phenol slowly crystallized on standing.

Anal. Calcd. for $C_7H_5F_3SO$: C, 43.3; H, 2.6; F, 29.4. Found: C, 43.4; H, 2.6; F, 29.6.

The proton n.m.r. spectrum in chloroform-*d* displayed an AB pattern for the aromatic hydrogens centered at τ 2.9 (J_{AB} = 9 c.p.s.) and a single phenolic OH resonance at 3.7 which disappeared when methanol-O-*d* was added. The relative integrated intensity ratio was 4:1, respectively. The infrared spectrum of the product was also consistent with the *para* isomer assignment. In addition to the strong O–H absorption at 3400 cm.$^{-1}$, bands in the 2000–1660-cm.$^{-1}$ region and a strong band at 840 cm.$^{-1}$ were consistent with a *p*-disubstituted benzene.

From the reaction of CF_3SCl with *o*-cresol under the conditions described above, 2-methyl-4-(trifluoromethylthio)phenol, b.p. 70–76° (0.4–0.5 mm.), was obtained in 75% yield.

Anal. Calcd. for $C_8F_7OF_3S$: F, 27.4; S, 15.4. Found: F, 26.8; S, 14.8.

The isomer assignment in this case was based on infrared data. The 2000–1650-cm.$^{-1}$ region was indicative of only 1,2,4 substitution, and additional bands at 1210, 1040, 995, and 885 cm.$^{-1}$ were consistent with this assignment. By gas chromatographic analysis, this product was noted to contain small amounts of impurities, one of which was probably the 1,2,3 isomer.

C. Phenyl Trifluoromethyl Disulfide.—When the above reaction was repeated with thiophenol, the product was a liquid, b.p. 35.5–37.5° (0.48 mm.), which was characterized as phenyl trifluoromethyl disulfide (yield 67%).

Anal. Calcd. for $C_7H_5F_3S_2$: C, 40.0; H, 2.4; F, 27.1; S, 30.5. Found: C, 40.4; H, 2.6; F, 27.1; S, 30.0.

The characterization was confirmed by infrared data (monosubstituted benzene, no SH absorption), and by comparison of infrared and ultraviolet spectral properties to those of the known compound, phenyl trichloromethyl disulfide. The ultraviolet spectrum in 95% ethyl alcohol showed a λ_{max} at 271 mμ (ϵ 1318) and a shoulder at 230 mμ (ϵ 7980). No product resulting from electrophilic substitution on the ring was found.

D. Phenyl Trifluoromethyl Sulfide.—An evacuated 240-ml. "Hastelloy"-lined bomb was charged with 50 g. of benzene, 27 g. (0.20 mole) of CF_3SCl, and 5 g. of boron trifluoride. The mixture was heated at 50° for 2 hr. and 100° for 4 hr. The resulting solution was distilled through a spinning-band column. After stripping the excess benzene, 20.0 g. (57%) of phenyl trifluoromethyl sulfide,[1] b.p. 141–142°, was obtained. Slightly higher yields were obtained in larger scale reactions in a 1-l. autoclave. No disubstituted product was obtained when an excess of CF_3SCl was employed. Also, no reaction occurred between CF_3SCl and benzene with boron trifluoride etherate as catalyst at atmospheric pressure and temperatures up to 80°.

E. Tolyl Trifluoromethyl Sulfides.—The conditions described above for the benzene reaction were employed. Tolyl trifluoromethyl sulfide, b.p. 98–100° (100 mm.) [lit.[1] b.p. 95° (23 mm.) and 79° (8.5 mm.) of *m*- and *p*-tolyl trifluoromethyl sulfide, respectively], was obtained in a yield of 75%. Gas chromatographic and spectral analyses were employed to determine the isomer ratio of a fractionated sample of a portion of the product, b.p. 103–105° (112 mm.) and $n^{25}D$ 1.4741–1.4720.

Gas chromatographic analyses were carried out on a 2-m. column packed with 20% diglyceride on 60–80-mesh firebrick at 123° using helium as carrier gas. The retention time of authentic sample mixtures of the tolyl trifluoromethyl sulfide was *meta*, 10.3 min., and *para*, 11.6 min. (an authentic sample of *ortho* isomer was not available). The main product fractions eluted at 10.2–10.6 min. and 11.5–11.8 min. From infrared analysis of fractions collected from elution, the 10.2–10.6-min. peak was identified as chiefly *ortho* and the 11.5–11.8-min. peak as *para*. The small amount of *meta* product was apparently eluted with the large *ortho* fraction.

F^{19} n.m.r. analysis of fractions showed resonances at −24.15 (*para*), −24.63 (*meta*), and −24.93 p.p.m. (assigned to *ortho*), with the solvent carbon tetrachloride (internally referenced from $CFCl_2CFCl_2$). The *meta* and *para* were assigned by comparison to

TABLE I

Fraction	Weight, g.	Isomer, % ortho G.c.	ortho N.m.r.	para G.c.	para N.m.r.	meta, N.m.r.
2	1.57	67	72	32	28	Trace
3	3.65	64	64	36	34	3
4	3.59	51	45	49	53	2
5	2.68	34	33	66	66	2

(3) W. A. Sheppard, *J. Am. Chem. Soc.*, **85**, 1314 (1963).

(4) S. Andreades [U. S. Patent 3,081,350 (1963)] reports the preparation of sulfenate esters, $ROSCF_3$, by reaction of aliphatic alcohols with CF_3SCl in the presence of a base.

(5) C. W. Tullock, U. S. Patent 2,884,453 (1959); C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **28**, 2016 (1960).

(6) L. M. Yagupolsky and M. S. Marenets [*J. Gen. Chem. USSR*, **24**, 885 (1954)] have reported *p*-(trifluoromethylthio)phenol, b.p. 77–78° (7 mm.) and m.p. 57–58°, prepared by hydrolysis of *p*-(trifluoromethylthio)benzenediazonium sulfate.

authentic samples, and the relative intensities were measured from integrated spectra.

Isomer assignments were confirmed by infrared comparison of the spectrum of each fraction with authentic spectra of *m*- and *p*-tolyl trifluoromethyl sulfides: *para*, 812 (s), 755 (w), and 705 cm.$^{-1}$; *meta*, 782 (s), 690 (m), and 685 cm.$^{-1}$. In particular, a comparison was made of the CH out-of-plane deformation bands. In the spectrum of each fraction, the strong band at 815 cm.$^{-1}$ was assigned to *para* and was noted to increase in relative intensity in going from fraction 2–5. In accord with the other analysis, a strong band at 760 cm.$^{-1}$ was assigned to the *ortho* isomer and decreased in relative intensity from fraction 2–5. Weak absorption at 685 and 785 cm.$^{-1}$ was assigned to the *meta* isomer. A weak absorption at 715 cm.$^{-1}$ may be associated with the *para* isomer but was not definitely assigned.

On the basis of the above analyses, the approximate isomer composition of the product was *ortho*, 52%; *para*, 47%; and *meta*, 1–2%.

F. Halobenzenes.—Twenty-seven grams of CF_3SCl was treated with 40 g. of chlorobenzene in the presence of 10 g. of anhydrous hydrogen fluoride in a 240-ml. "Hastelloy" bomb heated at 100° for 2 hr., 150° for 2 hr., 175° for 2 hr., and 200° for 2 hr. A total of 10.5 g. of product, b.p. 171–177°, $n^{23}D$ 1.509–1.497, was obtained. From gas phase chromatographic analyses, confirmed with infrared and proton n.m.r. studies as described for the tolyl derivative, the product was shown to contain relative isomer ratios of *ortho*, 24%; *meta*, 2–3%; and *para*, 74%. In this case, the *ortho* isomer concentrated in the higher boiling fraction and was eluted at longer times in gas chromatographic analysis on the same column as above. Identification of product was made on an eluted sample by mass spectrometric, infrared, and n.m.r. analyses. Dichlorobenzenes also are believed to be present as impurities in reaction mixtures.

The above reaction was repeated using 50 g. of bromobenzene instead of chlorobenzene. A total of 20.3 g. of product, b.p. 105–118° (50 mm.), was collected. This material partially crystallized; the crystals were removed by filtration and were found not to contain fluorine. The liquid fraction, 13.1 g., was analyzed by gas chromatography as described above. It was shown to contain the *ortho*, *meta*, and *para* isomers in approximately the same relative amounts as from chlorobenzene but with approximately 30% impurity of a mixture of dibromo- and bromochlorobenzenes, tentatively characterized by mass spectrometric analysis of fractions eluted by gas chromatography. The crystallized fraction also was characterized tentatively by spectral analysis as a mixture of dihalobenzenes.

Catalytic Hydrogenation of Some Naphthyl Alkenes[1-3]

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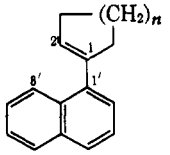
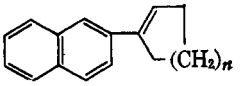
Received September 18, 1963

Rates of catalytic hydrogenation of twelve naphthyl alkenes and two cycloalkyl naphthalenes have been studied using acetic and propionic acids as solvents, Adams' platinum as catalyst, both constant volume and constant temperature (5–40°), and 1–2-atm. pressure. For most of the naphthyl alkenes, first-order rate plots (with respect to the pressure of hydrogen) showed two linear portions corresponding to (1) more rapid reduction of the alkenyl double bond (accompanied by some reduction of the naphthalene ring) and to (2) slower reduction of the resultant alkyl naphthalene, respectively. In general, rate constants for hydrogenation increased with increasing temperature, with change from acetic acid to propionic acid, and (for process 1) with decrease in number of substituents on the carbon atoms of the alkenyl double bond. There was no evidence of preliminary double bond migration.

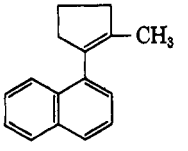
In an earlier publication Klemm and Hodes[4] found that 1-(1-naphthyl)cyclohexene (III) hydrogenated at a slower rate (for reduction of the alkenyl double bond) than that found for its analogs, 1-(1-naphthyl)cyclopentene (I), 1-(2-naphthyl)cyclopentene (II), and 1-(2-naphthyl)cyclohexene (IV), which hydrogenated at essentially identical rates. These results, obtained at 25° with Adams' platinum catalyst in glacial acetic acid, were interpreted in terms of steric hindrance to the attainment of coplanarity in III (but not in the others) during the complex-forming phase of the reaction owing to the fact that collision between hydrogen atoms on C-2 and -8′ would occur. The present investigation is an extension of the previous work. Compounds studied were I–X, 1-vinylnaphthalene (XI), 2-vinylnaphthalene (XII), 1-cyclopentylnaphthalene (XIII), and 1-cyclohexylnaphthalene (XIV).



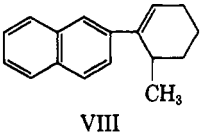
I, n = 1
III, n = 2
V, n = 3



II, n = 1
IV, n = 2
VI, n = 3



VII



VIII

Experimental

Compounds I–XIII were available or prepared in the purified forms previously described[4-9] and were stored as the narrow-melting polynitro aromatic molecular compounds indicated. Immediately before use each complex was dissociated by adding

(1) Abstracted (in part) from the Ph.D. thesis of R. Mann, University of Oregon, June, 1959. A detailed description of the construction and manipulation of the apparatus used in this research as well as plots of many kinetic runs may be found in this thesis.

(2) Part XIII, in the series on Chemical Reactivities of Arylcycloalkenes. For part XII, see L. H. Klemm, W. C. Solomon, and A. J. Kohlik, *J. Org. Chem.*, **27**, 2777 (1962).

(3) This research was supported (in part) through sponsorship by the Office of Ordnance Research, U. S. Army, Contract No. DA-04-200-ORD-176; by the U. S. Air Force under Contract No. AF 49(638)-473, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command; and (in part) by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to these donors.

(4) L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

(5) L. H. Klemm and H. Ziffer, *J. Org. Chem.*, **20**, 182 (1955).

(6) For the revised structure of VII, see footnote 7 in ref. 25 and the discussion in the present paper.

(7) L. H. Klemm, J. W. Sprague, and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

(8) L. H. Klemm, B. T. Ho, C. D. Lind, B. I. MacGowan, and E. Y. K. Mak, *ibid.*, **24**, 949 (1959).

(9) W. E. Bachmann and L. H. Klemm, *J. Am. Chem. Soc.*, **72**, 4911 (1950).