Preparation of Bis-[trifluoromethyl] Disulfide

R. E. A. Dear* and E. E. Gilbert**

Allied Chemical Corporation, Morristown, N.J., U.S.A.

Bis-[trifluoromethyl] disulfide has been known for several years. Our interest in this material was as a fumigant for the control of pest organisms[1] and as a telogen for the preparation of stable polyfluorinated fluids[2]. Prior methods of preparation[3] have suffered from several disadvantages in that they require either expensive starting materials or very high reaction temperatures, necessitating special equipment. Invariably, the yield of disulfide is lowered by contaminants such as carbon disulfide, trifluoromethanesulfenyl chloride, and polysulfides.

We have found that bis-[trifluoromethyl] disulfide may be made by two procedures, both originating from the inexpensive trichloromethanesulfenyl chloride. The reactions are:

$$(1a)\quad Cl_3C{-}SCl + HBr\,(aq) \longrightarrow Cl_3C{-}SBr + HCl\,(aq)$$

$$(1b)\quad 2\,Cl_3C{-}SBr + 6\,KF \xrightarrow{\text{solvent}} F_3C{-}S{-}S{-}CF_3 + 6\,KCl + Br_2$$

$$(2a)\quad 2\,Cl_3C{-}SCl + c\text{-}C_6H_{12} \xrightarrow{h\nu} Cl_3C{-}S{-}S{-}CCl_3 + c\text{-}C_6H_{11}{-}Cl + HCl$$

$$(2b)\quad Cl_3C{-}S{-}S{-}CCl_3 + 6\,KF \longrightarrow F_3C{-}S{-}S{-}CF_3 + 6\,KCl$$

Reaction *(1a)* has been described in Ref.[4], but we find that the large excess of hydrobromic acid and the washing and drying procedures are unnecessary (see experimental part). Reaction *(1b)* is new and gives a 68% yield of disulfide. The comparable reaction with trichloromethanesulfenyl chloride gives a mixture of bis-[trifluoromethyl] disulfide and trifluoromethanesulfenyl chloride in which the sulfenyl chloride predominates[5]. Reaction *(2a)* is a convenient preparation of bis-[trichloromethyl] disulfide[6]. Reaction *(2b)* is novel and unexpected in that Brandt, Emeleus, and Haszeldine predicted that the instability of bis-[trichloromethyl] disulfide is such that a halogen exchange reaction would have little chance of success[7]. Our results show this prediction to be unfounded, since we obtained bis-[trifluoromethyl] disulfide in 58% yield. G.L.C. examination of the material produced by both reactions (*1b* and *2b*) showed the only impurity to be carbon disulfide (1–3%), which was easily removed by distillation. The reactions were carried out in tetramethylene sulfone (Sulfolan) and best yields were obtained at temperatures of 150–160°. Sodium fluoride was substituted successfully for potassium fluoride in Reaction *(2b)*, but was not tried in Reaction *(1b)*.

Caution! *Bis-[trifluoromethyl] disulfide is very toxic and must be handled with great care. Owing to the volatility of the material, all operations involving its use should be carried out in an efficient hood.*

Trichloromethanesulfenyl Bromide:

In a 1000-ml Erlenmeyer flask, trichloromethanesulfenyl chloride (372 g, 2.0 mol) was cooled to 5–10° and 48% hydrobromic acid (454 g, containing 218 g of hydrogen bromide, 2.7 mol) was added over a 15 min period. Rapid stirring was maintained throughout the experiment by means of a large magnetic stirring bar. The internal temperature rose to 12–15° during the addition. The two-phase system was stirred vigorously overnight at ambient temperatures (~16 hr at 23–25°). The dark red oil was separated and distilled. A small forerun was followed by 350 g (76%) of trichloromethanesulfenyl bromide; b.p. 35–40°/0.8–1.4 mm. A small amount of bromodichloromethanesulfenyl bromide was also collected; b.p. 46°/1 mm.

The large excess of hydrobromic acid and the washing and drying steps reported previously[4] do not appear to be necessary.

Bis-[trifluoromethyl] Disulfide:

From Trichloromethanesulfenyl Bromide: A 2-l three-necked Morton flask was fitted with a nitrogen gas inlet, dropping funnel, high-speed blade stirrer, a thermometer dipping below the liquid surface, a take-off head, condenser, and cooled (−10°) receiver. The dry flask was charged with tetramethylene sulfone (700 ml) and potassium fluoride (127 g, 2.19 mol). The resulting slurry was stirred and heated to 160° and trichloromethanesulenyl bromide (125 g, 0.532 mol) was added. An exothermic reaction took place and the internal temperature spontaneously rose to 175°. The rate of addition of sulfenyl bromide was controlled so that this latter temperature was not exceeded. A slow nitrogen sweep was maintained throughout the experiment and vigorous and rapid stirring was employed at all times. A pale yellow distillate began to collect, with the take-off head temperature registering 30–40°. After all the sulfenyl bromide had been added and no more distillate was collected the temperature of the reaction flask was raised to 200°, but no further product was formed. The crude product was distilled; yield: 36.5 g (68%); b.p. 32–36°/atmospheric pressure.

From Bis-[trichloromethyl] Disulfide: Tetramethylene sulfone (700 ml) was charged to the 2-l Morton flask and potassium fluoride (198 g, 3.4 mol) was added. The slurry was stirred and heated under a slow nitrogen sweep to 150–160°. Bis-[trichloromethyl] disulfide[6] (100 g, 0.333 mol) was added over the course of 1 hr. The internal temperature of the reaction mixture spontaneously rose to 185° under the influence of the exothermic reaction. A colorless distillate collected, which upon redistillation gave pure bis-[trifluoromethyl] disulfide; yield: 39 g (58%); b.p. 34–35°.

In a separate experiment, sodium fluoride was found to be equally effective as the fluorinating agent.

Received: January 26, 1972

---

* Present address: CIBA-Geigy Corporation, Ardsley, New York 10502, U.S.A.

** Present address: Picatinny Arsenal, Dover, New Jersey 07801, U.S.A.

[1] R. E. A. Dear, E. E. Gilbert, U.S. Patent 3505459 (1970), Allied Chemical Corp.; C.A. **73**, 24314 (1970).

[2] R. E. A. Dear, E. E. Gilbert, U.S. Patent 3646221 (1972) Allied Chemical Corp.

[3] R. E. Banks, *Fluorocarbons and their Derivatives*, Oldbourne Press, London, 1964, p. 114.

[4] J. N. Ospenson, U.S. Patent 2824136 (1958), California Spray-Chemical Corp.; C.A. **52**, 11890 (1958).

[5] C. W. Tullock, D. D. Coffman, J. Org. Chem. **25**, 2016 (1960). C. W. Tullock, U.S. Patent 2884453 (1959), Dupont; C.A. **53**, 16963 (1959).

[6] V. Prey, E. Gutschik, H. Berbalk, Monatsh. Chem. **91**, 556 (1960).

[7] G. A. R. Brandt, H. J. Emeleus, R. N. Haszeldine, J. Chem. Soc. **1952**, 2198.