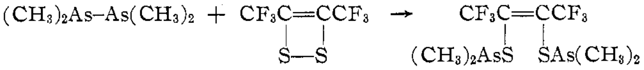
ultraviolet irradiation to give trifluoromethylthiodifluoramine. We wish to report some analogous reactions of compounds containing As–As and S–S bonds.

Tetramethyldiarsine and bis(trifluoromethyl) disulfide react at 20° to give dimethyl(trifluoromethylthio)arsine, b.p. 115°, in good yield.

$$(CH_3)_2As\text{–}As(CH_3)_2 + CF_3S\text{–}SCF_3 \rightarrow 2(CH_3)_2AsSCF_3$$

The identity of the new compound is confirmed by its synthesis from chlorodimethylarsine and bis(trifluoromethylthio)mercury. The S–S bond of bis(trifluoromethyl)-1,2-dithietene is also readily cleaved by tetramethyldiarsine yielding 1,4-bis(dimethylarsino)2,3-bis(trifluoromethyl)1,4-dithiobut-2-ene, an air-sensitive, pale red liquid, b.p. 92–95° (10^{-3} mm.). The infrared spectrum of the product shows a strong C=C band at 1535 cm.$^{-1}$, indicating the expected *cis* configuration. Krespan and McKusick[3] report a similar frequency, 1540 cm.$^{-1}$, for the *cis* isomer of $CF_3(CH_3S)C{=}C(SCH_3)CF_3$.



$$(CH_3)_2As\text{–}As(CH_3)_2 + \underset{S\text{—}S}{CF_3C{=}CCF_3} \rightarrow \underset{(CH_3)_2AsS\quad SAs(CH_3)_2}{CF_3C{=}CCF_3}$$

It has also been found that tetramethyldiarsine reacts with bis(trifluoromethyl) peroxide and with tetrafluorohydrazine, although in neither case was the expected product isolated at 20°.

Experimental[4]

Reaction of Tetramethyldiarsine with Bis(trifluoromethyl) Disulfide.—The diarsine (3.2 g.) and the disulfide (6.3 g.) were left for 7 days at 20°. No diarsine was left and distillation of the reaction mixture gave 5.0 g. of dimethyl(trifluoromethylthio)-arsine, b.p. 115°. *Anal.* Calcd. for $C_3H_6AsF_3S$: As, 36.4; F, 27.7; S, 15.6. Found: As, 36.2; F, 27.9; S, 15.5. The n.m.r. spectrum showed a single proton signal at τ 8.40. Infrared spectrum (liquid film, main bands): 3000 (m), 2910 (m), 1415 (m), 1262 (m), 1223 (m), 1110 (broad, vs), 900 (m), 752 (m) cm.$^{-1}$.

Reaction of Tetramethyldiarsine with Bis(trifluoromethyl)1,2-dithietene.—The diarsine (6.4 g.) and the dithietene (7.2 g.) were left at 20° (2 days). Distillation at 10^{-3} mm. resulted in considerable decomposition; however, 3.0 g. of a pale red product was isolated which distilled in the range 92–95°. This was identified as 1,4-bis(dimethylarsino)2,3-bis(trifluoromethyl)1,4-dithiobut-2-ene. *Anal.* Calcd. for $C_8H_6As_2F_6S_2$: C, 22.1; H, 2.5; As, 34.4; F, 26.1; S, 14.7. Found: C, 22.2; H, 2.9; As, 34.2; F, 26.1; S, 14.6. The n.m.r. spectrum showed a single proton peak at τ 8.22. Infrared spectrum (liquid film, main bands): 1535 (m), 1416 (m), 1235 (br, vs), 1150 (br, vs), 890 (m), 836 (m), 716 (m), 677 (m), 655 (m) cm.$^{-1}$.

Reaction of Chlorodimethylarsine with Bis(trifluoromethylthio)-mercury.—Chlorodimethylarsine and excess mercurial react at 20° (2 days) to give a nearly quantitative yield of dimethyl(trifluoromethylthio)arsine, identified by means of its boiling point of 115° and its infrared spectrum.

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[3] C. G. Krespan and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 3438 (1961).

[4] Reactions were done in sealed tubes. N.m.r. spectra were run on a Varian A60 instrument; neat liquid samples were used and peaks are reported relative to an external tetramethylsilane standard. Microanalyses were done by Dr. Alfred Bernhardt, Mulheim, Germany.

Correspondence

Concerning Recently Reported Values of the Association Constants of Silver Chloro Complexes in Fused Lithium Nitrate–Potassium Nitrate Eutectic

Sir:

As a result of some recently acquired information,[1] it has become apparent that an error in calculation was committed in our recent paper.[2] We should like to take this opportunity to correct the error and comment on the general method.

It is now experimentally apparent[1,3] that quasi-lattice type calculations are applicable to systems in which the sizes of the ions differ appreciably. When applied to the Ag^+–Cl^- ion pair in $LiNO_3$–KNO_3 eutectic at 225°, the association constant reported in our paper seems much too high. Re-evaluating our work, it became apparent that an error was made in calculating the equilibrium concentration of chloride ion using eq. 12.[2] The total final concentration of KCl was used instead of the total incremental concentration for each particular point in the titration. Using the data given in the paper,[2] but in the proper fashion, the values of the association constants β_1 and β_2 are 96 ± 11 kg./mole and 16 ± 12 kg.^{2}/mole^2, respectively.

It will be noted that the error limits for each of the constants are quite large, especially that for β_2. These are larger than the limits reported earlier for the incorrect constants. It appears now, from an experimental point of view, that the graphical method of Leden, when calculated properly, does lead to rather large errors, as has been suggested earlier.[4]

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RECEIVED APRIL 6, 1964

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[1] J. Braunstein, University of Maine, private communication.

[2] H. T. Tien and G. W. Harrington, *Inorg. Chem.*, **3**, 215 (1964).

[3] J. Braunstein and A. S. Minano, *ibid.*, **3**, 218 (1964).

[4] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).