66. *Ammonolysis and Aminolysis of Trifluoromethyl Arsenicals.*

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Chlorobistrifluoromethylarsine reacted with ammonia and amines. The new arsenicals, $(CF_3)_2As{\cdot}NH_2$, $[(CF_3)_2As]_2NH$, $(CF_3)_2As{\cdot}NHR$ ($R = Me$ or Et), and $(CF_3)_2As{\cdot}NMe_2$, were characterised. Tristrifluoromethylarsine also reacted with ammonia and amines, as did tristrifluoromethylstibine.

ARSENIC TRIHALIDES react with ammonia in the liquid or the gas phase and form initially the triamide, which loses ammonia above 0° to give ill-defined solid imides.[1, 2] The ammonolysis and aminolysis of organo-arsenic compounds has been incompletely investigated, though chlorodiphenylarsine and ammonia are known to form aminodiphenylarsine.[3, 4] It has been shown [5] that chlorobistrifluoromethylphosphine and ammonia give the stable compound aminobistrifluoromethylphosphine and, in this paper, a number of analogous reactions of trifluoromethyl arsenicals are described.

Chlorobistrifluoromethylarsine reacted readily with liquid ammonia at low temperatures to give perfluorocacodylamine, $[(CF_3)_2As]_2NH$, but with liquid ammonia at room temperature all the trifluoromethyl groups were liberated slowly as fluoroform. In the gas phase, however, both perfluorocacodylamine and aminobistrifluoromethylarsine resulted. Chlorodimethylarsine and ammonia were shown in preliminary experiments to give only solid products. Dichlorophenylarsine and dichloromethylarsine both form solids of the type $(RAs{=}NH)_x$, where $R = Me$ or Ph.[3] The reaction of dichlorotrifluoromethylarsine with ammonia likewise gave solid products, but fluoroform was also liberated. Its formation was almost quantitative with liquid ammonia at room temperature and this is a major point of difference between the alkyl and the trifluoromethyl arsenicals.

The reaction of chlorobistrifluoromethylarsine with primary and secondary amines in the gas phase gives the aminoarsines in good yield:

$$(CF_3)_2AsCl + 2HNRR' = (CF_3)_2As{\cdot}NRR' + RR'NH,HCl$$

The methylamino-, ethylamino-, and dimethylamino-compounds were made in this way, the results being analogous to those of Harris.[5] Only in the case of chlorobistrifluoromethylarsine and aniline was the reaction more complex. This is being further studied.

Fully alkylated or arylated compounds of the elements of Groups III—VI are stable to ammonia [1] and, in order to cleave the M–C bond it is necessary to add a catalyst such as sodium [6] or potassamide.[7] Ammonia and amines, however, solvolyse most organometallic derivatives of Groups I and II: for example, ammonia and diethylzinc give ethane and zinc amide,[8] while aniline and diphenylmagnesium form dianilinomagnesium and benzene.[9] There was no reaction between tristrifluoromethylarsine and ammonia in the gas phase but, with liquid ammonia at 20°, solvolysis was complete. Tristrifluoromethylstibine also reacted with liquid ammonia and the end-product was probably antimony nitride, as it is when antimony trihalides are subject to ammonolysis.[1] With the trifluoromethylarsine, reaction is slower than with arsenic trihalides, and the intermediates aminobistrifluoromethylarsine and diperfluorocacodylamine can be isolated if excess of ammonia is avoided or the reaction is carried out below room temperature. The rate of ammonolysis of the compounds $(CF_3)_3M$ ($M = P$, As, or Sb) appears to increase in the order $P < As <$

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[1] Fernelius and Bowman, *Chem. Rev.*, 1940, **26**, 3.

[2] Besson, *Compt. rend.*, 1890, **110**, 1258; Hugot, *ibid.*, 1904, **139**, 54.

[3] Ipatiew, Rasuwajew, and Stromski, *Ber.*, 1929, **62**, 598.

[4] Banks, Morgan, Clark, Hatlelid, Kahler, Paxton, Cragoe, Andres, Elpern, Coles, Lawhead, and Hamilton, *J. Amer. Chem. Soc.*, 1947, **69**, 927; Doak, *J. Amer. Pharm. Assoc.*, 1935, **24**, 453.

[5] Harris, *J.*, 1958, 512.

[6] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361.

[7] Hauser and Hance, *ibid.*, 1951, **73**, 5846.

[8] Fitzgerald, *ibid.*, 1907, **29**, 656.

[9] Schlenk, *Ber.*, 1931, **64**, 736.

Sb and this order is also found for alkaline hydrolysis.[10] Alkaline hydrolysis of tetrakistrifluoromethyldiarsine yielded[11] fluoroform (84%) and fluoride (16%), but ammonolysis of the diarsine gave at least 88% of the trifluoromethyl as fluoroform and no fluoride.

Tristrifluoromethylarsine reacted with aliphatic amines, but not with aniline, with evolution of fluoroform, but only in the case of dimethylamine was the expected amino-arsine, dimethylaminobistrifluoromethylarsine, formed. It is likely, however, that ethyltrifluoromethylamine, $CF_3 \cdot NHEt$, was formed in the reaction of the arsine with ethylamine. Tristrifluoromethylstibine was extensively aminolysed by dimethylamine.

The aminotrifluoromethylarsines were colourless liquids. Dimethylaminobistrifluoromethylarsine reacted readily with water, yielding fluoroform, dimethylamine, and arsenious acid. Cyanobistrifluoromethylarsine reacts similarly with water.[11] The dimethylamino-compound was stable to oxygen but, with hydrogen chloride, gave chlorobistrifluoromethylarsine and dimethylammonium chloride. It was stable at 160° above its boiling point, whereas the monomethylamino-compound decomposed at less than 40° above its boiling point: in both cases fluoroform was the main volatile product. It would be expected that hydrogen atoms attached to nitrogen atoms in these compounds would be acidic because of the strong inductive effect of the trifluoromethyl groups. Methylaminobistrifluoromethylarsine did not, however, react with sodium at 50°, and the only evidence of acid character was a gradual increase in conductivity of a solution of tristrifluoromethylarsine in ammonia at −64°. This may be due to partial ammonolysis, followed by ionisation to $[(CF_3)_2AsNH]^-$ and NH_4^+.[12]

EXPERIMENTAL

Trifluoroiodomethane and the trifluoromethyl arsenicals were prepared by recorded methods.[11, 13] All were tensimetrically pure and the techniques used were similar to those previously described.

Reaction of Chlorobistrifluoromethylarsine with Ammonia.—Chlorobistrifluoromethylarsine (1·705 g.) and dry ammonia (0·53 g.) were allowed to react at −64° (45 min.), and the products were separated by repeated fractional condensation in traps cooled to 0°, −23°, and −46°. The main product, condensed at −23°, was *diperfluorocacodylamine*, $[(CF_3)_2As]_2NH$ (Found: C, 10·8; H, 0·26; N, 3·4%; *M*, 439. $C_4HNF_{12}As_2$ requires C, 10·9; H, 0·23; N, 3·4%; *M*, 441). Vapour pressures (84—125°) were given by $\log_{10} p(\text{mm.}) = 7{\cdot}974 - 2030/T$. The b. p. was 126·5° ± 0·5°, the latent heat of vaporisation 9300 cal./mole, and Trouton's constant 23·3.

Chlorobistrifluoromethylarsine (0·913 g.) and ammonia (0·127 g.) were allowed to react in the gas phase by introducing the two gases into 500 ml. bulbs connected by a wide-bore tap. The products separated were impure diperfluorocacodylamine (0·425 g.; *M*, 380), which showed the same infrared spectrum as the material above, and a fraction, condensed at −78° (0·140 g.), which had the infrared spectrum of aminobistrifluoromethylarsine (Found: *M*, 275. $C_2H_2NF_6As$ requires *M*, 229). The latter arsine was best prepared by the ammonolysis of tristrifluoromethylarsine (see below). With excess of ammonia (1 g.) at 20° (5 days) chlorobistrifluoromethylarsine (0·312 g.) was completely ammonolysed to fluoroform (0·175 g. Found: *M*, 79·0).

Reaction of Chlorobistrifluoromethylarsine with Methylamine.—Chlorobistrifluoromethylarsine (0·571 g.) and methylamine (0·162 g.) reacted immediately in the gas phase at 20°, forming a mixture which on fractionation gave *methylaminobistrifluoromethylarsine* (0·510 g., 92%) (Found: C, 15·0; H, 1·8; N, 5·9%; *M*, 244. $C_3H_4NF_6As$ requires C, 14·8; H, 1·6; N, 5·8%; *M*, 243). The vapour pressure (20—82°) was given by $\log_{10} p(\text{mm.}) = 7{\cdot}986 - 1825/T$. The b. p. was 84° ± 0·5°, the latent heat of vaporisation 8360 cal./mole, and Trouton's constant 23·4. Methylaminobistrifluoromethylarsine (0·260 g.) did not react with sodium at 50°. A sample (0·588 g.) heated at 120° for 15 hr. gave fluoroform (0·180 g.), tristrifluoromethylarsine

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[10] Haszeldine and West, *J.*, 1957, 3880.

[11] Emeléus, Haszeldine, and Walaschewski, *J.*, 1953, 1552.

[12] Cullen, Ph.D. Thesis, Cambridge, 1958.

[13] Haszeldine, *J.*, 1951, 584; Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552; Walaschewski, *Ber.*, 1953, **86**, 272.

(0·07 g.) (Found: *M*, 257. Calc. for C_3F_9As: *M*, 282), identified by the infrared spectrum, and a black solid which after treatment with water contained 3% of carbon and showed the *X*-ray powder photograph of elementary arsenic.

Reaction of Chlorobistrifluoromethylarsine with Ethylamine.—Chlorobistrifluoromethylarsine (0·297 g.) and ethylamine (0·110 g.) in the gas phase gave *ethylaminobistrifluoromethylarsine* (0·240 g., 78%) (Found: C, 18·9; H, 2·2; N, 5·6%; *M*, 258. $C_4H_6NF_6As$ requires C, 18·7; H, 2·3; N, 5·5%; *M*, 257). Vapour pressures (19—95°) were given by $\log_{10} p(\text{mm.}) = 7{\cdot}609 - 1711/T$. The b. p. was 98·5° ± 0·5°, the latent heat of vaporisation 8520 cal./mole, and Trouton's constant 23·0.

Reaction of Chlorobistrifluoromethylarsine with Dimethylamine.—Chlorobistrifluoromethylarsine (0·855 g.) and dimethylamine (0·318 g.) in the gas phase gave *dimethylaminobistrifluoromethylarsine* (0·728 g., 80%) (Found: C, 18·8; H, 2·6; N, 5·6%; *M*, 259. $C_4H_6NF_6As$ requires C, 18·7; H, 2·3; N, 5·4%; *M*, 257). Vapour pressures (23—85°) were given by $\log_{10} p(\text{mm.}) = 7{\cdot}868 - 1858/T$. The b. p. was 89° ± 0·5°, the latent heat of vaporisation 7840 cal./mole, and Trouton's constant 21·7. Dimethylaminobistrifluoromethylarsine did not react with oxygen at 20° (7 days; 96% recovery of arsenical). The arsenical (0·264 g.) and hydrogen chloride (0·062 g.) reacted immediately at room temperature, forming a white solid and chlorobistrifluoromethylarsine (0·160 g.), identified by its infrared spectrum. The solid was dimethylammonium chloride (m. p. 166°; lit.,[14] 171°). Dimethylaminobistrifluoromethylarsine (0·311 g.) when heated in a Carius tube was stable to 250° but decomposed at 250—280°, giving fluoroform (0·065 g.) and a black solid. The solid was attacked by water to give a water-insoluble residue which contained elemental arsenic. The arsenical was hydrolysed by water to fluoroform, dimethylamine, and arsenious acid.

Reaction of Tristrifluoromethylarsine with Ammonia.—The vapours of tristrifluoromethylarsine and ammonia did not react at 20° (2 hr.). Reaction of the arsenical (0·566 g.) and ammonia (0·150 g.) at −64° gave *aminobistrifluoromethylarsine* (0·2 g.) (Found: C, 10·6; H, 0·5; N, 6·3%; *M*, 229. $C_2H_2NF_6As$ requires C, 10·5; H, 0·9; N, 6·1%; *M*, 229). Vapour pressures (40—85°) were given by $\log_{10} p(\text{mm.}) = 7{\cdot}470 - 1662/T$. The b. p. was 89° ± 1°, the latent heat of vaporisation 7610 cal./mole, and Trouton's constant 21·0. Fluoroform (0·063 g.) was also formed (Found: *M*, 69·5. Calc. for CHF_3: *M*, 70). Tristrifluoromethylarsine (1·584 g.) and ammonia (*ca.* 1 g.) in a Carius tube (1 week) gave fluoroform (1·084 g.), equivalent to 92% of the trifluoromethyl present. In an experiment with 2 g. of ammonia the yield was 97%. Reaction of the arsenical (3·029 g.) and ammonia (0·293 g.) at 20° for 2 days gave fluoroform (0·33 g.), diperfluorocacodylamine (0·34 g.) (Found: *M*, 410. Calc. for $C_4HNF_{12}As_2$: *M*, 441), and aminobistrifluoromethylarsine (0·228 g.) (Found: *M*, 227. Calc. for $C_2H_2NF_6As$: *M*, 229). The arsine (6·130 g.) and ammonia (0·170 g.) did not react at −78° in 4 days. At 20° in 7 days fluoroform (0·047 g.) was produced and ammonia (0·161 g.) was recovered.

Aminolysis of Tristrifluoromethylarsine.—Tristrifluoromethylarsine (0·670 g.) and methylamine (0·240 g.) at 20° in 7 days gave fluoroform (0·20 g.; *M*, 70·5). Tristrifluoromethylarsine (1·038 g.) and a large excess of ethylamine in a Carius tube in 1 week gave fluoroform (0·31 g.), equivalent to 40% of the trifluoromethyl present. At least two solid phases were produced in addition to a volatile fraction which condensed in a trap at −64° and was possibly *ethyltrifluoromethylamine*, v. p. 65 mm. at 20° (Found: C, 32·1; H, 5·3; N, 12·8%; *M*, 113—115. $C_3H_6NF_3$ requires C, 31·9; H, 5·7; N, 12·5%; *M*, 113). The fraction was strongly adsorbed by tap grease and decomposed to a brown-red solid when left in a glass tube at 20°. It was not formed when the arsine (2·067 g.) and ethylamine (2 g.) were kept together at 20° for 28 days. There was no reaction between tristrifluoromethylarsine (0·680 g.) and aniline (2 g.) at 20° in 14 days.

Reaction of Dichlorotrifluoromethylarsine with Ammonia.—Dichlorotrifluoromethylarsine (0·521 g.) and ammonia (0·169 g.) in a Carius tube at 20° in 8 days gave fluoroform (0·113 g.; *M*, 71·0), equivalent to 66% of the trifluoromethyl present. With a large excess of ammonia, in a second experiment, 90% of the trifluoromethyl was liberated as fluoroform in 4 days at 20°.

Ammonolysis and Aminolysis of Tristrifluoromethylstibine.—The stibine (0·424 g.) and ammonia (1 g.) in a Carius tube in 24 hr. gave fluoroform (0·265 g.; *M*, 70·5) equivalent to 98% of the trifluoromethyl present. A yellow solid was also formed which was probably mainly antimony nitride (Found: N, 10·95. Calc. for SbN: N, 10·3%). Tristrifluoromethylstibine

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[14] Delépine, *Ann. Chim.* (*France*), 1896, **8**, 439.

(1·137 g.) and dimethylamine (4·0 g.) reacted at 20° in 28 days, to give fluoroform (0·663 g.; *M*, 70·3) equivalent to 91% of the trifluoromethyl present.

Reaction of Tristrifluoromethylphosphine with Ammonia.—The phosphine (0·229 g.) and ammonia (1 g.) at 20° in 48 hr. gave fluoroform (0·074 g.; *M*, 70·4) equivalent to 37% of the trifluoromethyl present. No solid phase was produced.

Reaction of Tetrakistrifluoromethyldiarsine with Ammonia.—The diarsine (0·244 g.) and ammonia (1·5 g.) reacted at low temperature in a Carius tube, to give a green solution and a white precipitate which slowly became red-brown. The colour gradually faded from the liquid layer and after 28 days at 20° 89% of the trifluoromethyl was liberated as fluoroform (0·143 g.; *M*, 70·5). No fluoride was produced.

Reaction of Chlorodimethylarsine with Ammonia and Dimethylamine.—The arsine (0·551 g.) and ammonia (0·5 g.) reacted in a cold finger in the liquid phase at −46°, giving solid products. Fractionation failed to isolate any unchanged arsine. No part of the solid was soluble in benzene or ether. Chlorodimethylarsine and dimethylamine gave a fraction which condensed at −64° and had an infrared spectrum consistent with that expected from dimethylaminodimethylarsine. The fraction was decomposed by tap grease.

Infrared Spectra.—The spectra were measured on a Perkin-Elmer Model 21 Spectrometer with rock-salt optics and were obtained from liquid films. The results were as follows (the letters have their usual meaning).

$(CF_3)_2As{\cdot}NH_2$: 3430w, 3350m, 2240w, 1840vw, 1630vw, 1567w, 1552w, 1450vw, 1264m, 1172vs, 1146vs, 945vw, 896w, 805s, 728s.

$[(CF_3)_2As]_2NH$: 3360m, 2920vw, 2240w, 1840vw, 1645vw, 1440vw, 1264m, 1175vs, 1124vs, 805s, 728s.

$(CF_3)_2As{\cdot}NHMe$: 3375w, 2920w, 2820w, 2210w, 1580vw, 1483w, 1463w, 1473w, 1370vw, 1260w, 1174vs, 1122vs, 1073vs, 757w, 725w.

$(CF_3)_2As{\cdot}NHEt$: 3375m, 2975s, 2885m, 2220w, 1648vw, 1563vw, 1475w, 1456m, 1391m, 1348w, 1322w, 1260m, 1172vs, 1120vs, 1067vs, 910w, 803w, 755w, 724m.

$(CF_3)_2As{\cdot}NMe_2$: 2910s, 2870m, 2820m, 2220w, 1640w, 1470m, 1457m, 1448m, 1262m, 1174vs, 1123vs, 1075vs, 955w, 775m, 724m.

One of the authors (W. R. C.) is grateful to the University of New Zealand for the award of a Postgraduate Scholarship.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August 27th,* 1958.]