

THE REACTIONS OF PERFLUOROALKYL RADICALS WITH METALS*

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A new, potentially general method for the synthesis of trifluoromethylated derivatives of metals has been used to prepare bistrifluoromethylditelluride. The procedure is derived from the classical one used by Paneth¹ to prepare metal alkyls by the action of alkyl radicals on metal mirrors. It has now been found that trifluoromethyl radicals react similarly with some metals.

Trifluoromethyl radicals, generated by pyrolysis of hexafluoroacetone,² were passed over a tellurium mirror and yielded the red liquid bistrifluoromethylditelluride ($\text{CF}_3\text{TeTeCF}_3$). This is the first reported perfluoroalkyltellurium compound and, apart from dimethylditelluride, the only ditelluride not containing aryl groups. Rice and Glasebrook³ prepared dimethylditelluride by the similar reaction of methyl radicals on tellurium. The thermal stability of the perfluoroalkyltellurium compound is less than that of dimethylditelluride. The perfluoroalkyl groups are readily split off by alkaline hydrolysis to yield fluoroform quantitatively. This reaction is similar to those found with the perfluoroalkyl derivatives of Group VB elements but differs from those with perfluoroalkyl derivatives of other Group VI elements which yield fluoride ions when treated with alkali.⁴

The infrared spectrum of bistrifluoromethylditelluride has the following bands: 1367w, 1321m, 1219s, 1150s, 1088s, 1043s, 917m, 722s.

Both lead and bismuth mirrors are removed, but very slowly by trifluoromethyl radicals under conditions similar to those used for the reaction with tellurium. The quantities of the lead and bismuth compounds formed so far have been too small to permit full chemical analyses to be performed. However, the infrared spectra of these compounds suggest the presence of trifluoromethyl groups, the compounds decompose on heating to give metal mirrors and yield fluoroform on treatment with alkali. In view of the known instability of dilead⁵ and dibismuth¹ alkyl compounds and the fact that the temperature of the reaction zone is greater than 100°C, it is considered that the reaction products are tetrakis(trifluoromethyl)-lead and tris(trifluoromethyl)bismuth.

Further work, designed to improve the yields of these products, is in progress.

* Manuscript received February 26, 1963.

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¹ Paneth, F., and Loleit, H. (1935).—*J. Chem. Soc.* **1935**: 366.

² Ayscough, P. B., and Steacie, E. W. (1956).—*Proc. Roy. Soc. A* **234**: 476.

³ Rice, F. O., and Glasebrook, A. L. (1934).—*J. Amer. Chem. Soc.* **56**: 2472.

⁴ Banks, R. E., and Haszeldine, R. N. (1961).—“Advances in Inorganic Chemistry and Radiochemistry.” Vol. 3. (Academic Press: New York.)

⁵ Coates, G. E. (1956).—“Organometallic Compounds.” pp. 141, 162. (Methuen: London.)

Experimental

(a) *Hexafluoroacetone*.—This compound was prepared by a method adapted from that used by Morse, Ayscough, and Leitch.⁶ "Teflon" was depolymerized by controlled heating to 450°C, and the tetrafluoroethylene produced was passed through a cylindrical furnace at 730°C at such a rate that a pressure of 70 cm of mercury was maintained. Vacuum fractionation was used to separate the perfluoroisobutene formed, from the other reaction products. This was oxidized by acid KMnO_4 , and the hexafluoroacetone hydrate produced extracted by ether, using a continuous extractor. Hexafluoroacetone was finally produced by dropping the hydrate onto P_2O_5 , the gaseous product being collected in a trap cooled in liquid air. The compound was used directly without further purification (Found: mol. wt., 166. Calc. for $\text{C}_3\text{F}_6\text{O}$: mol. wt., 166).

Free trifluoromethyl radicals were generated by passing the hexafluoroacetone at 2 mm pressure through a silica tube heated to 900°C.

(b) *Bistrifluoromethyl ditelluride*.—Tellurium metal (0.1–0.2 g) was placed in a clear silica tube ($36 \times 1/8$ in. I.D.) and heated until a thick mirror 1–1½ in. long was formed on the walls of the tube. A movable tube furnace was used to pyrolyse the ketone vapour at a position in the proximity of the mirror such that the free radicals produced could react with the metal before recombining, and such that the mirror was at a temperature favourable for the formation of a metal-organic product. By intermittently strongly heating the outlet side of the reaction tube, and observing the new mirror formed by the thermal decomposition of the organometallic compound, it was possible to determine whether compound formation was proceeding at a satisfactory rate. A deep red liquid slowly collected in a trap cooled to -46°C . This compared with the red dimethyl ditelluride obtained by passing methyl radicals over tellurium.⁸ The new material was vacuum distilled to remove traces of other reaction products and unpyrolysed ketone until reproducible infrared spectra showing no absorption band corresponding to carbonyl C–O stretching were obtained. Bistrifluoromethyl ditelluride melts at *c.* -73°C but due to the thermal instability of the compound, its boiling point could not be determined. In the light it is less stable at room temperature than dimethyl ditelluride, although it can be kept in the dark for considerable periods of time and indefinitely at -78°C . It is soluble in most common organic solvents, stable to air, insoluble in and unchanged by water.

(i) *Hydrolysis*. Bistrifluoromethyl ditelluride (0.032 g; 0.082 mm), when heated with 5 ml 5*N* NaOH at 95°C for 2 hr, gave fluoroform (0.011 g, 0.159 mm) which was purified by distillation in the vacuum system. The quantitative recovery of CF_3 as fluoroform precluded the formation of any fluoride. Metallic tellurium was deposited in the solution as reaction proceeded.

(ii) *Analysis*. The compound was analysed for CF_3 by alkaline hydrolysis, tellurium being estimated as the metal in the solution after hydrolysis (Found: CF_3 , 34.1; Te, 66.2%. Calc. for $\text{C}_2\text{F}_6\text{Te}_2$: CF_3 , 35.1; Te, 65.1%).

(iii) *Infrared Analysis*. Measurements were made using a Perkin-Elmer model 21 double-beam spectrophotometer fitted with NaCl optics. Spectra were measured on samples of vapour in a 10 cm cell.

(c) *Reaction with Lead*.—A lead mirror was most satisfactorily prepared by pyrolysis of tetraethyl-lead vapour in the reaction tube. After passing trifluoromethyl radicals over this mirror for 6 hr only 10 mg of product had condensed into a trap cooled at -78°C . The material was a colourless, rather involatile liquid whose infrared spectrum suggested the presence of CF_3 groups. Treatment of this liquid with hot 5*N* NaOH yielded fluoroform, while metallic lead deposited when the compound was strongly heated. However there was insufficient of the material to enable full quantitative chemical analysis to be performed. Nevertheless the evidence suggests the existence of tetrakis(trifluoromethyl)-lead, as the formation of the trifluoromethyllead compound is unlikely because of the instability of the corresponding alkyl compound.

(d) *Reaction with Bismuth*.—Bismuth metal (0.1–0.2 g) was heated and, over the mirror formed, was passed a stream of trifluoromethyl radicals for 6 hr. A very involatile, colourless liquid (*c.* 5 mg) collected in a trap cooled to -46°C and infrared analysis and NaOH hydrolysis

⁶ Morse, A. T., Ayscough, P. B., and Leitch, L. C. (1955).—*Canad. J. Chem.* **33**: 453.

showed that it contained CF_3 groups. Bismuth metal deposited when this liquid was strongly heated. Again, due to the very small quantities of product formed, complete quantitative analysis was not possible, but it is suggested that the compound formed was tris(trifluoromethyl)bismuth.

We are grateful to the C.S.I.R.O. for the award of a Post-graduate Studentship to B.J.P.