

1115. *The Reaction of Bisfluoroalkylmercurials with Aluminium.*

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An investigation of the interactions of a variety of bisfluoroalkylmercurials with aluminium indicates that reaction occurs only in the presence of water, the products being the corresponding fluorocarbon, mercury, aluminium hydroxide, and hydrogen. No direct evidence was found for the existence of intermediate fluoroalkylaluminium compounds.

ALTHOUGH bisperfluoroalkylmercurials¹ and partially fluorinated mercurials² are well-characterized compounds, there is a notable lack of information concerning the use of these compounds as intermediates in the preparation of other perfluoroalkylmetal derivatives. Several incidental reports^{2a,3} indicate that secondary and tertiary perfluoroalkylmercurials react with aluminium, and it has been suggested that perfluoroalkylaluminium compounds are formed in the reaction of aluminium metal with $[(CF_3)_2CF]_2Hg$.^{3a} We have been unable to isolate, or detect the presence of, any fluoroalkylaluminium compounds from the reactions of a variety of fluoroalkylmercurials with aluminium metal, but have observed a reaction in the presence of water vapour.

EXPERIMENTAL

Bis(trifluoromethyl)mercury was prepared by the method of Emelús and Haszeldine,¹ and other mercurials were prepared by the interaction of mercuric fluoride and the appropriate olefin in anhydrous hydrogen fluoride.² Volatile substances were manipulated in a conventional vacuum system and identified by their molecular weights and infrared spectra. Reactions between the mercurials and aluminium at 180° were conducted in sealed evacuated tubes; after 12 hr. under these conditions the aluminium was unattacked and the mercurials were recovered quantitatively. However, a reaction occurred if water was present in the reaction mixture.

In a typical experiment, bis-(1,2,2,2-tetrafluoroethyl)mercury, $(CF_3-CHF)_2Hg$, (0.66 g.) was placed in an aluminium-foil cup (2.0 g.) contained in a glass reaction vessel which was then connected to the vacuum system, the reaction vessel evacuated, water (approximately 1.0 g.) condensed on to the mercurial, and the refrigerant bath (−196°) removed. As the water in the reaction mixture melted, the aluminium acquired a dull grey cast; the system was allowed to remain at 25° for 12 hr. after which time the aluminium was coated with fibrous aluminium hydroxide. The gaseous reaction products were taken into the vacuum system through a drying tube filled with anhydrous alumina into a trap surrounded by liquid nitrogen. The non-condensable gas was shown to be hydrogen (mass spectrum). The condensable fraction (0.28 g., 85%) was identified by its infrared spectrum⁴ and molecular weight as 1,1,1,2-tetrafluoroethane (Found: *M*, 100. Calc. for $C_2H_2F_4$: *M*, 102).

The other mercurials reacted with aluminium in the presence of water under the same conditions to give the corresponding fluorocarbons in yields of 85—90%. In all instances, the non-volatile

¹ H. J. Emelús and R. N. Haszeldine, *J.*, 1949, 2953.

² (a) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *J. Org. Chem.*, 1963, **28**, 184; (b) C. G. Krespan, *ibid.*, 1960, **25**, 105.

³ (a) W. T. Miller and M. B. Freedman, *J. Amer. Chem. Soc.*, 1963, **85**, 180; (b) H. B. Powell, private communication, 1962.

⁴ C. B. R. Ward, Ph.D. Dissertation, Purdue University, 1956.

products were aluminium hydroxide and metallic mercury; fluoride ion was found only among the products of the reaction of bis-(2,2,2-trifluoroethyl)mercury. No volatile aluminium-containing fraction was obtained in any reaction, and the infrared spectra of the non-volatile residues contained no C-F bands.

DISCUSSION

Bisperfluoromethyl-, bisperfluoroethyl-, bisperfluoroisopropyl-, and bis-(1*H*-tetrafluoroethyl)-mercury react vigorously with aluminium at 25° in the presence of either water vapour or liquid water to yield the fluorocarbons trifluoromethane, pentafluoroethane, 2*H*-heptafluoropropane, and 1,1,1,2-tetrafluoroethane, respectively; the other products are mercury, aluminium hydroxide, and hydrogen. It would be tempting to suggest that the corresponding fluoroalkylaluminium compounds were formed as intermediates which were then hydrolyzed to give the observed products. However, none of the mercurials investigated reacted with aluminium or aluminium amalgam at 25°, nor was any reaction with aluminium evident at 180°. The hydrogen formed in the presence of water presumably arises from the action of the latter on either aluminium or aluminium amalgam formed during the course of decomposition of the mercurial. The fact that the mercurials are stable to freshly prepared aqueous suspensions of aluminium hydroxide indicates that the reaction observed does not proceed by the hydrolysis of the mercurial.

It might be expected that fluoroalkylaluminium compounds would be relatively strong Lewis acids, forming strong complexes with water, which could readily decompose to give the fluorocarbon and aluminium hydroxide. Accordingly, an attempt was made to trap the suggested fluoroalkylaluminium compound with pyridine, a stronger electron-pair donor than water, possessing no easily displaceable hydrogen atoms. The mercurials investigated do not react with aluminium in anhydrous pyridine under the conditions described, but reaction occurs upon the addition of water to give the products mentioned above. Thus, the data available at present are not sufficient to elucidate the course of these reactions.

The reaction of bis-(2,2,2-trifluoroethyl)mercury with aluminium at 25° is anomalous since the main gaseous product formed in the presence of water is 1,1-difluoroethylene; fluoride ion occurs among the solid reaction products. This mercurial does not react with aluminium at 25°, although it yields the same olefin and fluoride ion at 180°.

Since partially fluorinated mercurials can be prepared in good yield by the addition of mercuric fluoride to partially substituted fluoro-olefins,² the observations presented here suggest an attractive method for the synthesis of certain fluorocarbons, *e.g.*,



Other published methods^{5,6} for the preparation of 1,1,1,2-tetrafluoroethane are not as specific or as direct as the one outlined here.

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⁵ R. N. Haszeldine and B. R. Steele, *J.*, 1957, 2800.

⁶ W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.*, 1955, **77**, 4899; L. A. Bigelow and F. E. Deutero, Abstracts 130th Meeting Amer. Chem. Soc., 1956, 16M, Atlantic City, New Jersey; D. A. Rausch, R. A. Davis, and D. W. Osborne, *J. Org. Chem.*, 1963, **28**, 494.