Organosilicon Chemistry. Part IX.¹ Reaction of Bis(trimethylsilyl)mercury with Some Polyfluoro-olefins²

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Bis(trimethylsilyl)mercury reacts readily under u.v. irradiation with chlorotrifluoroethylene to give initially the 1:1adduct trimethylsilyl-(1-chloro-1,2,2-trifluoro-2-trimethylsilylethyl)mercury, which loses mercury and fluorotrimethylsilane to give a mixture of cis- and trans-2-chloro-1.2-difluorovinyltrimethylsilane. Trimethyltrifluorovinylsilane and chlorotrimethylsilane are also formed, but by another route. The 1:1-adduct has been identified spectroscopically and by its reactions with sodium stannite and with bromine. Bis(trimethylsilyl)mercury reacts more slowly under similar conditions with trifluoroethylene, and the reaction may be non-regiospecific.

BIS(TRIMETHYLSILYL)MERCURY reacts readily under u.v. illumination of $\lambda > 315$ nm with perfluoro-olefins 2,3 such as tetrafluoroethylene, perfluoropropene, and perfluorocyclobutene, apparently via addition of the elements of Me₃Si-Hg·SiMe₃ across the double bond to give a saturated intermediate. This loses mercury and fluorotrimethylsilane by β -elimination to give an olefin in which vinylic fluorine has been replaced by a trimethylsilvl group. Intermediate mercurials were detected in the reaction with tetrafluoroethylene and perfluoropropene, but although the intermediate from perfluoropropene was assigned the structure (Ia) rather than (Ib) on the basis of its n.m.r. spectrum, its decomposition products, and the reaction sequence established,³ its ready decomposition prevented a chemical proof of structure. We now report the reactions of some fluorin-

$$\begin{array}{c} \mathrm{CF}_3 \cdot \mathrm{CF}(\mathrm{Hg} \cdot \mathrm{SiMe}_3) \cdot \mathrm{CF}_2 \cdot \mathrm{SiMe}_3 & \mathrm{CF}_3 \cdot \mathrm{CF}(\mathrm{SiMe}_3) \cdot \mathrm{CF}_2 \cdot \mathrm{Hg} \cdot \mathrm{SiMe}_3 \\ & (\mathrm{Ia}) & (\mathrm{Ib}) \end{array}$$

ated olefins containing other substituents, and the unequivocal establishment by chemical methods of the direction of addition to the double-bond of chlorotrifluoroethylene.

Chlorotrifluoroethylene.—When a mixture of chlorotrifluoroethylene and bis(trimethylsilyl)mercury was irradiated in vacuo, fluorotrimethylsilane, chlorotrimethylsilane, and some unchanged olefin were readily identified. Trimethyltrifluorovinylsilane was identified by comparison of its i.r. and n.m.r. spectra with those of

a sample obtained from tetrafluoroethylene,³ and a highboiling liquid, which deposited mercury on standing, remained. Prolonged distillation in vacuo at low temperature, followed by g.l.c., allowed the separation from this mixture of *cis*- and *trans*-2-chloro-1,2-diffuorovinyltrimethylsilane, identified by their i.r. (C=C $6.08 \mu m$), n.m.r. (see Experimental section) and mass spectra $(M^+, 170 \text{ and } 172)$, and readily distinguished by the values for I(FF-cis) and I(FF-trans), which fall in the usual ranges,⁴ and which accord well with the values calculated from the group contributions reported 5 for Cl and derived for Me₃Si from the spectrum of trimethyltrifluorovinylsilane.³

The high-boiling residue from the distillation had a ¹⁹F n.m.r. spectrum which showed an ABX pattern with J_{AB} 327 Hz, J_{AX} 13.5 Hz, and J_{BX} 9 Hz, which is consistent only with either of the structures (II) or (III).

Me₃Si•Hg•CF₂•CFCl•SiMe₃	Me₃Si·CF₂·CFCl·Hg·SiMe₃
AB X	AB X
(II)	(III)

 J_{AB} Is slightly lower than the value obtained ⁶ for 2-chloro-1,1,2-trifluoroethyltrimethylsilane (J_{AB} 340 Hz), but since no model compounds containing mercury adjacent to a non-equivalent geminal pair of fluorine atoms are available, a choice cannot be made on this basis. The chemical shifts of the CF_2 and CFCl groups also fail to distinguish between the structures.

Evidence for the structure of the 1:1-adduct was provided by the reaction with bromine at -24° , which gave a product which was identified spectroscopically as

⁶ J. Lee and J. Dyer, Trans. Faraday Soc., 1966, 62, 257.

[†] Reaction with bromine at room temperature was exothermic and resulted only in decomposition.

¹ Part VIII, J. M. Birchall, R. N. Haszeldine, M. J. Newlands, P. Rolfe, D. L. Scott, A. E. Tipping, and D. Ward, *J. Chem. Soc.* (A), 1971, 3760.
² Preliminary communication, R. Fields, R. N. Haszeldine,

and A. F. Hubbard, Chem. Comm., 1970, 647. Presented in part at the 6th International Fluorine Symposium, Durham, 1971.

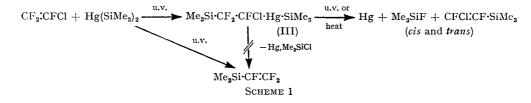
³ R. Fields, R. N. Haszeldine, and A. F. Hubbard, J. Chem. Soc. (C), 1971, 3838.
⁴ J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolu-

tion N.M.R. Spectroscopy,' Pergamon, Oxford, 1966, vol. 2, p. 909. ⁵ M. G. Barlow, Chem. Comm., 1966, 703.

2-bromo-2-chloro-1,1,2-trifluoroethyltrimethylsilane, implying that the 1:1-adduct has structure (III). Attempts to synthesise the bromo-compound unambiguously by u.v. irradiation of 2-chloro-1,1,2-trifluoroethyltrimethylsilane and bromine failed.

A sample of the l: l adduct was treated in a nitrogen atmosphere with alkaline sodium stannite solution, known⁷ to replace mercury in fluoroalkyl-mercury compounds by hydrogen and thus to provide a label for the site of attachment of the mercury. The product was identified as 2-chloro-1,1,2-trifluoroethyltrimethylsilane by comparison of its n.m.r. spectra with those of a sample prepared, albeit in low yield, by the photochemical addition ⁸ of trimethylsilane to chlorotrifluoroethylene, and with the parameters reported.⁶ The l: l-adduct is thus identified as (III) (Scheme 1).

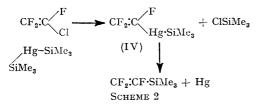
rather than of fluorine might be the cause. Rapid loss of β -chlorine from the product formed by double insertion of dichlorocarbene into one Hg-Si bond of bis(trimethylsilyl)mercury has recently ⁹ been suggested as the route by which trimethyltrichlorovinylsilane is formed. However, in view of indications from the reaction of bis(trimethylsilyl)mercury with 1,1-dichloro-2,2-difluoroethylene,¹⁰ and of recent experiments¹¹ in which trifluorovinyl(trimethylsilyl)mercury has been isolated from among the reaction products of bis(trimethylsilyl)mercury with bromotrifluoroethylene, it seems likely that reaction is taking place at the C-Cl bond to give a trimethylsilyl(vinyl)mercury intermediate which loses mercury under the reaction conditions to give the observed trimethyltrifluorovinylsilane (Scheme 2).



Decomposition of (III), either under u.v. irradiation or in the dark at 60°, gave fluorotrimethylsilane, mercury, and a mixture of the *cis*- and *trans*-2-chloro-1,2-difluorovinyltrimethylsilanes in varying proportions, but no chlorotrimethylsilane or trimethyltrifluorovinylsilane was formed. Thus although (III) is clearly established as an intermediate in the formation of the 2-chloro-1,2-difluorovinyltrimethylsilanes from chlorotrifluoroethylene and bis(trimethylsilyl)mercury, the trimethyltrifluorovinylsilane and chlorotrimethylsilane must be formed by some other route. This might involve β -elimination from the other possible 1:1adduct (II), or a different type of reaction at the C-Cl bond as in Scheme 2.

$$\begin{array}{c} \operatorname{Me}_{3}\mathrm{Si}\cdot\mathrm{Hg}\cdot\mathrm{CF}_{2}\cdot\mathrm{CFCl}\cdot\mathrm{Si}\mathrm{Me}_{3} \xrightarrow{-\mathrm{Hg}} \mathrm{Me}_{3}\mathrm{Si}\mathrm{Cl} + \mathrm{CF}_{2}\cdot\mathrm{CF}\cdot\mathrm{Si}\mathrm{Me}_{3} \\ (\mathrm{II}) \end{array}$$

Neither (II) nor any intermediate of the type (IV) could be detected in the reaction mixture. It is difficult to see why (II) might be so much less stable than (III),



although the possibility of β -elimination of chlorine

⁷ H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 1949, 2953.

Trifluoroethylene.—The reaction of bis(trimethylsilyl)mercury with trifluoroethylene took place much more slowly than that with perfluoro- or with fluorochloroolefins, and bis(trimethylsilyl)mercury (29%) and trifluoroethylene (60%) were recovered after irradiation for 23 h. Trimethylsilane (3%), hexamethyldisilane (22%), and mercury (72%) were also recovered, together with fluorotrimethylsilane (71% based on olefin consumed) and a liquid which was tentatively identified from its i.r. and n.m.r. spectra as an approximately equimolar mixture of 2,2- and cis-1,2-difluorovinyltrimethylsilanes suggesting that bis(trimethylsilyl)mercury may add

$$\begin{array}{c} CF_2:CHF \xrightarrow{u.v.} \\ + \\ (Me_3Si)_2Hg \end{array} \left[\begin{array}{c} Me_3Si \cdot Hg \cdot CF_2 \cdot CHF \cdot SiMe_3 \\ + \\ Me_3Si \cdot CF_2 \cdot CHF \cdot Hg \cdot SiMe_3 \end{array} \right] \longrightarrow CF_2:CH \cdot SiMe_3 \\ \longrightarrow CHF:CF \\ | \\ SiMe_3 \end{array}$$

non-regiospecifically to this olefin. The relatively high yield of hexamethyldisilane shows that the decomposition of bis(trimethylsilyl)mercury is to a considerable extent independent of the presence of this olefin.

EXPERIMENTAL

Bis(trimethylsilyl)mercury was prepared as described previously.¹² All manipulations were carried out *in vacuo* or under dry nitrogen. Even so, small amounts of hexamethyldisiloxane, presumed to have arisen by reaction of mercury-containing intermediates or of halogeno-trimethyl-

¹⁰ R. Fields, R. N. Haszeldine, and A. F. Hubbard, unpublished results.

¹¹ R. Fields, R. N. Haszeldinc, and P. J. Palmer, *Tetrahedron* Letters, 1971, 1879.

¹² R. Fields, R. N. Haszeldine, and R. E. Hutton, *J. Chem. Soc.* (*C*), 1967, 2559.

⁸ Cf. W. I. Bevan and R. N. Haszeldine, unpublished results cited in ref. 6.

⁹ D. Seyferth, R. J. Cross, and B. Prokai, J. Organometallic Chem., 1967, 7, P20; D. Seyferth, E. M. Hanson, B. Prokai, and R. J. Cross, J. Organometallic Chem., 1970, 24, 33.

silanes with water, were observed in some experiments. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer, mass spectra on an A.E.I. MS902 spectrometer, and n.m.r. spectra on a Perkin-Elmer R10 spectrometer at $60 \cdot 0$ (¹H) or $56 \cdot 46$ (¹⁹F) MHz at 35° . Chemical shifts are in p.p.m. to high field of external benzene and external trifluoroacetic acid respectively. All irradiations were carried out with reactants sealed *in vacuo* in thickwalled Pyrex tubes placed *ca*. 20 cm from a Hanovia UVS 500 medium-pressure mercury lamp. Yields of mercury, hexamethyldisilane, and hexamethyldisiloxane are based on the amount of initial bis(trimethylsilyl)mercury, and those of other products are based on olefin consumed during the reaction.

Reactions of Bis(trimethylsilyl)mercury with Polyfluoroolefins.---(a) With chlorotrifluoroethylene. After 20 h chlorotrifluoroethylene (2.80 g, 24.1 mmol) and the mercurial (3.64 g, 10.5 mmol) gave recovered olefin (1.68 g, 60%), fluorotrimethylsilane (0.36 g, 40%), chlorotrimethylsilane (0.04 g, 4%), hexamethyldisiloxane (0.18 g, 10%), mercury (1.14 g, 54%), trimethyltrifluorovinylsilane (0.28 g, 18%), a mixture of 2-chloro-trans-1,2-difluorovinyltrimethylsilane (0.18 g, 11%) [¹⁹F n.m.r., +39 p.p.m., +80.5, J(FF-trans) 132 Hz, ¹H, +6·4] and 2-chloro-cis-1,2-difluorovinyltrimethylsilane (0.17 g, 10%) (Found: M^+ , 170. Calc. for $C_5H_9ClF_2Si: M, 170$ [¹⁹F n.m.r. +85, +68, J(FF-cis) 4.5 Hz, ¹H, +6.4] separated by g.l.c., and trimethylsilyl(1chloro-1,2,2-trifluoro-2-trimethylsilylethyl)mercury (2.09 g, 47%) [¹⁹F n.m.r. +23.6 (F_A), +34.6 (F_B), +49.5 (F_X), ¹H, +6.2 (apparently overlapping Me₃Si groups)].

(b) With trifluoroethylene. After 23 h, the mercurial (4.68 g, 13.5 mmol) and trifluoroethylene (0.942 g, 11.5 mmol) gave unchanged olefin (0.557 g, 59%) and mercurial (1.36 g, 29%) together with trimethylsilane (0.024 g, 3%) fluorotrimethylsilane (0.317 g, 71%), hexamethyldisiloxane (0.10 g, 11%), hexamethyldisilane (0.435 g, 22%), mercury (1.956 g, 72%), and high-boiling material (0.87 g) showing i.r. bands at 5.9 and 6.05 μ m (C:C) and ¹⁹F n.m.r. equal intensity bands at -15.5 [d (24 Hz), d (10 Hz)], -5.5 [d (43 Hz), d (23 Hz)], +67.2 [d (74 Hz), d (23 Hz)], and +78.5

[t (23 Hz)] and ¹H n.m.r. +0.7 [d (75 Hz), d (22 Hz)], +2.92 [d (41 Hz), d (9 Hz)], also of equal intensity.

Reactions of Trimethylsilyl(1-chloro-1,2,2-trifluoro-2-trimethylsilylethyl)mercury.—(a) Thermal decomposition. A solution in ether, shown by ¹⁹F n.m.r. to contain no other fluorinated material, was kept in the dark at 60° (2 h) to give fluorotrimethylsilane (0.050 g, 0.5 mmol), hexamethyldisiloxane (0.022 g, 0.1 mmol), 2-chloro-trans-1,2-difluorovinyltrimethylsilane (0.040 g, 0.2 mmol), 2-chloro-*cis*-1,2difluorovinyltrimethylsilane (0.038 g, 0.2 mmol), identified by ¹⁹F n.m.r., and by g.l.c., and mercury (0.07 g, 0.35 mgatom). Trimethyltrifluorovinylsilane was absent.

(b) Photochemical decomposition. A sample of the adduct, containing 2-chloro-trans- (14%) and -cis- (8%) -1,2-difluorovinyltrimethylsilane as impurities did not deposit mercury at 20° (4 days) under laboratory lighting. After u.v. irradiation (76 h), mercury (0.178 g) had been deposited, the ¹⁹F n.m.r. spectrum showed the presence of the adduct (44%), 2-chloro-cis-1,2-difluorovinyltrimethylsilane (17%), and the trans-isomer (34%), and fluorotrimethylsilane, which was isolated (0.07 g, 0.8 mmol) as the only volatile product.

(c) With sodium stannite. An aqueous solution of alkaline sodium stannite was added to a sample of the adduct in ether until deposition of mercury ceased, all the operations being carried out under a nitrogen atmosphere. The organic layer was separated and distilled *in vacuo* to give a -45° fraction which was identified by its n.m.r. spectrum ⁶ and by independent synthesis from chloro-trifluoroethylene and trimethylsilane ⁸ as 2-chloro-1,1,2-trifluoroethyltrimethylsilane.

(d) With bromine. The adduct, dissolved in ether, was kept in vacuo at -196° in an n.m.r. tube, bromine was condensed in, and the tube was sealed in vacuo. After 2 h at -24° , the ¹⁹F n.m.r. spectrum showed major bands at $+15\cdot8$ (J_{AB} 327, J_{AX} 6.5 Hz), $+32\cdot2$ (J_{AB} 327, J_{BX} 8.5), and $+32\cdot2$ p.p.m. with intensities 1:1:1, together with SiF₄ and a number of by-products, with no trace of bands due to the adduct.

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