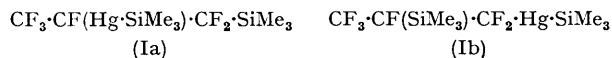


Organosilicon Chemistry. Part IX.¹ Reaction of Bis(trimethylsilyl)-mercury with Some Polyfluoro-olefins²

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Bis(trimethylsilyl)mercury reacts readily under u.v. irradiation with chlorotrifluoroethylene to give initially the 1:1-adduct 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 $\text{Me}_3\text{Si-Hg-SiMe}_3$ 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 This loses mercury and fluorotrimethylsilane by β -elimination to give an olefin in which vinylic fluorine has been replaced by a trimethylsilyl group.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-

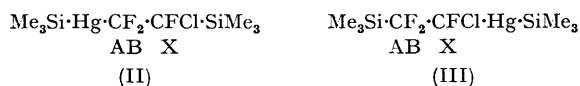


ated olefins containing other substituents, and the unequivocal establishment by chemical methods of the direction of addition to the double-bond of chlorotrifluoroethylene.

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 high-boiling 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-difluorovinyltrimethylsilane, identified by their i.r. ($\text{C}=\text{C}$ 6.08 μm), n.m.r. (see Experimental section) and mass spectra (M^+ , 170 and 172), and readily distinguished by the values for $J(\text{FF-}i\text{cis})$ and $J(\text{FF-}i\text{trans})$, which fall in the usual ranges,⁴ and which accord well with the values calculated from the group contributions reported⁵ for Cl and derived for Me_3Si 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).



J_{AB} is slightly lower than the value obtained⁶ 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

† 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 Resolution N.M.R. Spectroscopy,' Pergamon, Oxford, 1966, vol. 2, p. 909.

⁵ M. G. Barlow, *Chem. Comm.*, 1966, 703.

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

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 60.0 (^1H) or 56.46 (^{19}F) 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 thick-walled 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%) [^{19}F n.m.r., +39 p.p.m., +80.5, $J(\text{FF-}trans)$ 132 Hz, ^1H , +6.4] and 2-chloro-*cis*-1,2-difluorovinyltrimethylsilane (0.17 g, 10%) (Found: M^+ , 170. Calc. for $\text{C}_6\text{H}_9\text{ClF}_2\text{Si}$: M , 170) [^{19}F n.m.r. +85, +68, $J(\text{FF-}cis)$ 4.5 Hz, ^1H , +6.4] separated by g.l.c., and trimethylsilyl(1-chloro-1,2,2-trifluoro-2-trimethylsilylethyl)mercury (2.09 g, 47%) [^{19}F n.m.r. +23.6 (F_A), +34.6 (F_B), +49.5 (F_X), ^1H , +6.2 (apparently overlapping Me_3Si 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 μm (C:C) and ^{19}F 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 ^{19}F 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*-1,2-difluorovinyltrimethylsilane (0.038 g, 0.2 mmol), identified by ^{19}F n.m.r., and by g.l.c., and mercury (0.07 g, 0.35 mg-atom). 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 ^{19}F 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. spectrum⁶ and by independent synthesis from chlorotrifluoroethylene and trimethylsilane⁸ 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 ^{19}F n.m.r. spectrum showed major bands at +15.8 (J_{AB} 327, J_{AX} 6.5 Hz), +32.2 (J_{AB} 327, J_{BX} 8.5), and +32.2 p.p.m. with intensities 1:1:1, together with SiF_4 and a number of by-products, with no trace of bands due to the adduct.

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