Addition of Bis(trimethylsilyl)mercury to Fluoro-olefins: Isolation of Intermediate 1:1-Adducts

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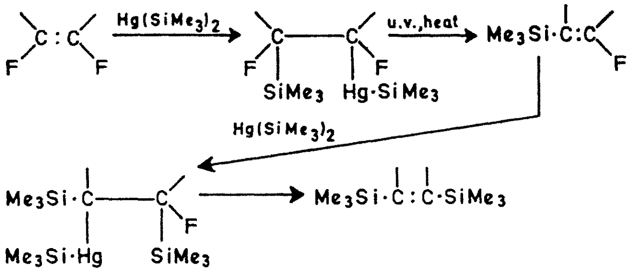
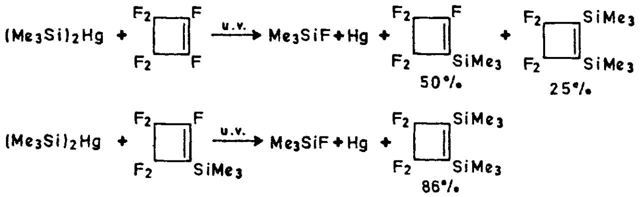
Summary Under u.v. irradiation, bis(trimethylsilyl)mercury displaces halogen from fluoro-olefins (C_2F_4, C_3F_6, cyclo-C_4F_8, $CF_2:CFCl$, $CF_2:CF{\cdot}SiMe_3$, $CF_3{\cdot}CF:CF{\cdot}SiMe_3$, $\overline{CF_2{\cdot}CF_2{\cdot}CF:C}{\cdot}SiMe_3$) to give fluorovinyltrimethylsilanes of type $Me_3Si{\cdot}\overset{|}{C}:\overset{|}{C}F$ and $Me_3Si{\cdot}\overset{|}{C}:\overset{|}{C}{\cdot}SiMe_3$; intermediate 1:1-adducts of olefins and mercurial of type $Me_3Si{\cdot}\overset{|}{\underset{|}{C}}{\cdot}\overset{|}{\underset{|}{C}}{\cdot}Hg{\cdot}SiMe_3$ have been isolated from some reactions.

THE reactions of bis(trimethylsilyl)mercury with aryl halides[1] or aryl ethers[2] appear to involve four-centre transition states. The photochemical reactions of the mercurial with some olefins leading to the formation of mono- and bis-(trimethylsilyl)olefins are now reported. The isolation for the first time of intermediate 1:1 adducts of the mercurial and the olefin demonstrates an initial net insertion of an olefin (*e.g.*, a fluoro-olefin) into the Hg–Si bond (see Scheme 1).

Thus olefins such as C_2F_4, C_3F_6, or cyclo-C_4F_8 reacted to give the mono- and bis-(trimethylsilyl)olefins and the former were shown by separate experiments to react readily with $(Me_3Si)_2Hg$ to give the bis(trimethylsilyl)olefins (see Scheme 2). There is no apparent reaction in the dark at the same temperature.

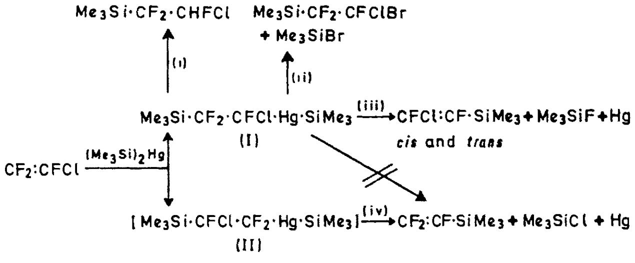


SCHEME 1



SCHEME 2

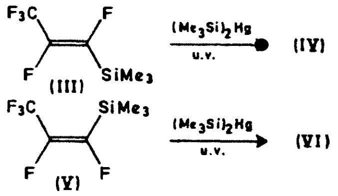
Reactions with $CF_2{\cdot}CFCl$ or with C_3F_6 gave intermediate products formed by addition of $Me_3Si{\cdot}Hg{-}SiMe_3$ to double bonds. The yield of the intermediates depended critically on irradiation time and temperature and the adducts decomposed on further irradiation or when kept at 20—50°. The reactions of the isolated 1 : 1-adduct of bis(trimethylsilyl)mercury and $CF_2:CFCl$ with alkaline sodium stannite, and with bromine, and its n.m.r. spectrum, suggest that it is (I) (see Scheme 3). Decomposition of the *isolated* 1 : 1-adduct was shown to give, quantitatively, only mercury, and equimolar amounts of fluorotrimethylsilane, and *cis*-plus *trans*-2-chloro-1,2-difluorovinyltrimethylsilane (*cis* : *trans* = 1 : 1). The fact that the reaction of $CF_2:CFCl$ with bis(trimethylsilyl)mercury gave chlorotrimethylsilane and trimethyltrifluorovinylsilane as well, suggests that another intermediate and much more transient adduct such as (II) may also be involved. The ratio of products indicates that formation of (I) is favoured over that of (II) by approximately 4 : 1.



(i) $SnCl_2$-NaOH, (ii) Br_2, -20°; (iii) u.v., or 50°; (iv) u.v., or heat,

SCHEME 3

Only one 1 : 1-adduct was detectable in the reaction between C_3F_6 and bis(trimethylsilyl)mercury, and its decomposition gave the propenyl-compounds (III) and (V) quantitatively. Further reaction of the trimethylpentafluoropropenylsilane (III) with the mercurial gave a single compound (IV) shown chemically and spectroscopically to have molecular formula $CF_3{\cdot}C(SiMe_3):CF{\cdot}SiMe_3$, and similar reaction of (V) gave (VI), the geometric isomer of (IV), but the configuration about the double bond is not yet certain. The isomer (IV) was converted into an approximately 1 : 1 mixture of (IV) and (VI) when treated with bromine and light.



The reaction of bis(trimethylsilyl)mercury with these fluoro-olefins thus appears to involve a stereospecific insertion of the olefin into one Si–Hg bond of the mercurial, followed by a stereospecific elimination of mercury and Me_3SiX where X is halogen on carbon β to mercury. Formation of Me_3SiX by elimination of X α to mercury would give a carbene, and migration of fluorine or of a trimethylsilyl group could then account for some of the products. Carbene formation, if involved at all, cannot be the exclusive decomposition route, since it cannot account for the exclusive formation of isomers (IV) and (VI).

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

[2] C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Chem. Soc.* (*C*), 1967, 2188.