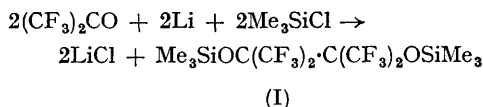


## Electrophilic Reactions of Hexafluoroacetone

By A. F. JANZEN, P. F. RODESILER, and C. J. WILLIS

(Department of Chemistry, University of Western Ontario, London, Canada)

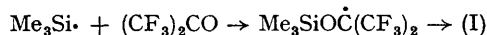
THE reaction of certain ketones with alkali metals is known to yield ketyls,  $M^+[R_2CO^-]$ , which by subsequent dimerisation give pinacols. Frye *et al.*<sup>1</sup> have recently postulated that the dilithium alkoxide of perfluoropinacol is an intermediate in the reaction of hexafluoroacetone with trimethylchlorosilane and dimethyldichlorosilane in the presence of lithium, the product in the former case being 1,2-bis(trimethylsiloxy)tetrakis(trifluoromethyl)ethane (I):



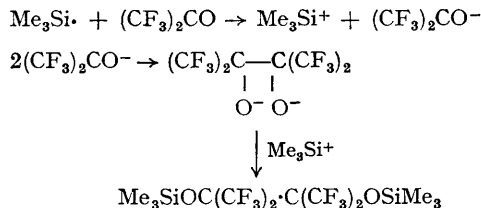
Our own work has confirmed this result, and we find that the disodium alkoxide of perfluoropinacol, readily formed by the reaction of hexafluoroacetone with sodium in donor solvent, may be isolated as a stable white solid giving an orange solution in, *e.g.*, tetrahydrofuran.

More surprisingly, however, we now find that compound (I) is also produced by the reaction of hexafluoroacetone with bis(trimethylsilyl)mercury,  $(Me_3Si)_2Hg$ . The reaction occurs under mild

conditions (dark, 24 hr. at 20°, sealed tube using an excess of ketone as solvent) but is markedly speeded up by ultraviolet irradiation. Assuming that the first step is the production of trimethylsilyl radicals, a known reaction of the mercurial,<sup>2</sup> the observed product could come from radical attack on hexafluoroacetone, followed by dimerisation:

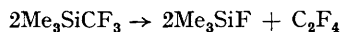
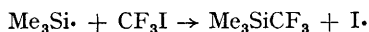


While such a process cannot be ruled out on present evidence, we prefer a scheme involving electron transfer to give an intermediate hexafluoroacetone ketyl, which by its ready dimerisation would give the product system:



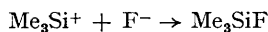
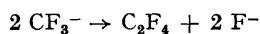
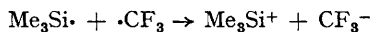
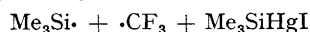
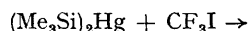
In support of an electron-transfer mechanism of

this type, we find that the mercurial reacts very rapidly with trifluoroiodomethane (dark, < 5 min. at 20°, sealed tube, in an excess of CF<sub>3</sub>I) the main products being trimethylfluorosilane and tetrafluoroethylene. One possible route to these compounds would be through the intermediate trimethyltrifluoromethylsilane:



Such ready decomposition of this intermediate must be regarded as extremely unlikely, however. The corresponding tin compound, Me<sub>3</sub>SnCF<sub>3</sub>, is known to be stable at its boiling point of 101° and to decompose slowly at 150°,<sup>3</sup> while the germanium analogue, Me<sub>3</sub>GeCF<sub>3</sub>, is stable above 200°.<sup>4</sup> It is improbable, therefore, that the silicon compound would decompose rapidly at 20°.

If, however, an electron-transfer mechanism is postulated, the observed products may readily be accounted for through decomposition of the unstable intermediate CF<sub>3</sub><sup>-</sup> ion:



Consistent with this theory, we find that reaction of bis(trimethylsilyl)mercury with pentafluorobromobenzene (dark, 7 days at 20°) gives trimethylpentafluorophenylsilane (67% yield, identified by spectroscopic comparison with previous reports<sup>5</sup>). In this case, any electron-transfer reaction would give the pentafluorophenyl ion, and the greater stability of this, compared with the trifluoromethyl ion, would reduce the possibility of fluoride elimination and subsequent decomposition.

We suggest, therefore, that the extremely electrophilic nature of hexafluoroacetone, associated with the presence of two trifluoromethyl groups, may be a dominant feature of the chemistry of this reactive compound. In reactions where the products are derivatives of perfluoropinacol, the possibility of an intermediate ketyl may warrant consideration.

(Received, August 15th, 1966; Com. 599.)

<sup>1</sup> C. L. Frye, R. M. Salinger, and T. J. Patin, *J. Amer. Chem. Soc.*, **1966**, **88**, 2343.

<sup>2</sup> C. Eaborn, "Abstracts 2nd International Symposium on Organometallic Chemistry", Madison, Wis., 1965, p. 25.

<sup>3</sup> H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, **1960**, **82**, 1888.

<sup>4</sup> N. K. Hota and C. J. Willis, unpublished observations.

<sup>5</sup> M. Feld, O. Glemser, and G. Christoph, *Angew. Chem.*, **1964**, **76**, 953.