form a variety of organometallic compounds has been widely used for preparative purposes. In earlier work[1,2] we employed this reaction to synthesize a number of compounds of types R_3SbY_2 and $(R_3SbY)_2O$. Thus triphenylantimony difluoride was formed when triphenylantimony dichloride was treated with 2 equiv of silver fluoride. However, when 2 equiv of silver perchlorate were used in place of the fluoride, the resulting product was oxybis(triphenylantimony) diperchlorate. We therefore anticipated that reaction between triphenylbismuth dichloride and 2 equiv of silver perchlorate would yield oxybis(triphenylbismuth) diperchlorate or possibly triphenylbismuth diperchlorate. When the filtrate from the mixture was concentrated, however, the product which crystallized proved to be *tetraphenylbismuthonium perchlorate*. That this was indeed the product was shown by: (a) elementary analysis, (b) comparison of the product with a sample of tetraphenylbismuthonium perchlorate prepared by a known method,[3] and (c) conversion of the product to the tetraphenylborate derivative and comparison of this derivative with tetraphenylbismuthonium tetraphenylborate prepared by a known method.[3] The formation of a tetraphenylbismuthonium compound from triphenylbismuth dihalide is remarkable since metathesis between triarylbismuth dihalides and silver salts has been used many times previously without this unusual structural change being observed.[4,5]

It is not easy to write, *a priori*, a mechanism for this reaction in which a phenyl–bismuth bond is broken and another phenyl–bismuth bond is formed at room temperature. The synthesis has been repeated a number of times, and a yield in the neighborhood of 65% (based on phenyl groups) was consistently obtained. This relatively large yield indicates that the tetraphenylbismuthonium perchlorate is not just a by-product of a radical-type reaction.

This reaction is of considerable interest since it represents a comparatively simple route to the preparation of the tetraphenylbismuthonium group. By analogy with the arsonium and stibonium compounds, the tetraphenylbismuthonium cation may prove to be valuable as a precipitant in analytical chemistry. Only a few bismuthonium compounds are known. It was long believed that such compounds were incapable of existence and they have been described only once previously,[3] a preparation which involved a long and difficult pathway through pentaphenylbismuth.

In a typical experiment a solution of 3.250 g (0.0156 mole) of silver perchlorate in 10 ml of absolute alcohol was added to a solution of 4.000 g (0.00782 mole) of triphenylbismuth dichloride in 50 ml of acetone. All of the chloride immediately precipitated as silver chloride. The filtrate was concentrated to 20 ml *in vacuo* at room temperature and was then allowed to stand overnight. The next morning a crystalline product had formed which was removed by filtration and washed with cold absolute alcohol. The yield of crystalline product was 1.504 g. Addition of 100 ml of water to the filtrate resulted in the precipitation of a further 0.874 g of product which had an infrared spectrum very similar to that of the first crop of crystals. The two precipitates were combined (2.378 g, 65.7% yield based on phenyl groups) and recrystallized twice from absolute ethanol.

Anal. Calcd for $C_{24}H_{20}BiClO_4$: C, 46.73; H, 3.27; Cl, 5.75. Found: C, 46.31; H, 3.35; Cl, 5.95.

The infrared spectrum of the above compound was determined in the region between 4000 and 250 cm^{-1} and found to be identical with the spectrum of tetraphenylbismuthonium perchlorate prepared by Wittig's method.[3] Infrared spectra were determined for Nujol mulls between CsBr plates with a N_2-purged Perkin-Elmer Model 521 infrared spectrophotometer. The observed bands may be divided into three groups of frequencies: (a) assigned to the phenyl: 1564 (m), 1471 (s), 1436 (s), 1328 (m), 1307 (vw), 1190 (m), 1062 (m), 1052 (m), 1012 (w), 992 (s), 734 (s), 686 (m), 609 (w), 442 (m), and 432 (m); (b) assigned to the perchlorate ion: 1090 (s) (broad), 916 (w), 624 (m), and 456 (vw); and (c) unidentified: 996 (m), 846 (vw), and 652 (w).

When a sample of the product was dissolved in absolute alcohol and warmed with an equimolar portion of sodium tetraphenylborate, a voluminous white precipitate was obtained. Recrystallization from nitromethane resulted in a material melting at 215°, which is 10° lower than the tetraphenylbismuthonium tetraphenylborate reported by Wittig.[3] However, by Wittig's method we were unable to prepare tetraphenylbismuthonium tetraphenylborate which had a melting point higher than 217°. Furthermore, the melting point of the compound prepared from our sample of tetraphenylbismuthonium perchlorate was not depressed when admixed with the material obtained by Wittig's procedure. The melting points were determined on a Fisher–Johns melting point apparatus calibrated against U.S.P. melting point standards.

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(4) H. Gilman and H. L. Yale, *Chem. Rev.*, **30**, 281 (1942).
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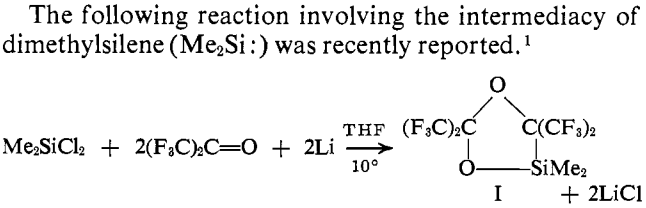
Alkoxysilanes Derived from Hexafluoroacetone. The Purported Intermediacy of Dimethylsilene

Sir:

The following reaction involving the intermediacy of dimethylsilene ($Me_2Si:$) was recently reported.[1]

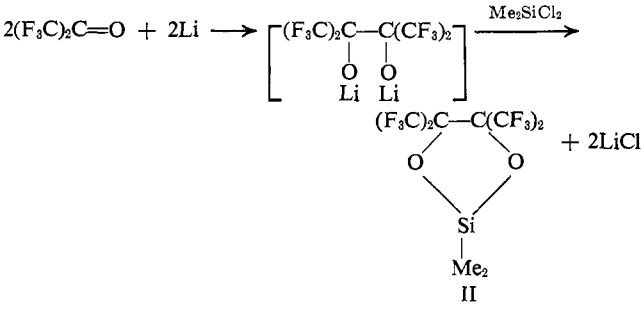


The possibility of an alternative structure *via* the relatively conventional bimolecular reduction[2] of the ketone

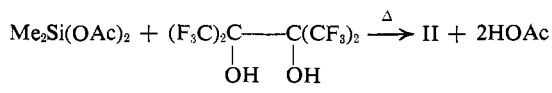
(1) R. A. Braun, *J. Am. Chem. Soc.*, **87**, 5516 (1965).
(2) R. Adams and E. W. Adams in "Organic Syntheses," Coll. Vol. 1, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1941, p 459.

to a pinacol derivative does not appear to have been considered.

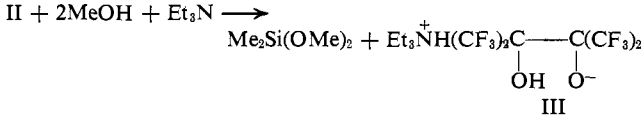
We have found the product of the above reaction to be consistent with this less exotic course and to be in fact merely the expected perfluoropinacol derivative (II) of Me_2SiCl_2; *i.e.*



Thus, addition of a hexane dispersion of lithium (0.50 equiv) to an ice-cold THF solution of Me_2SiCl_2 (0.25 mole) and hexafluoroacetone (0.50 mole) afforded upon distillation a 35% yield of 4,4,5,5-tetrakis(trifluoromethyl)-2,2-dimethyl-1,3-dioxa-2-silacyclopentane (II) [bp 150–152°; mp −7 to −4°; $n^{25.8}D$ 1.3314. *Anal.* Calcd for $C_8H_6F_{12}O_2Si$: C, 24.6; H, 1.54; F, 58.7. Found: C, 24.9; H, 1.69; F, 59.6] whose infrared and nmr (H^1 and F^{19}) spectra were identical with those obtained from authentic material prepared by the unequivocal condensation of dimethyldiacetoxysilane with perfluoropinacol.[3]



The nmr data are in complete accord with structure II, consisting of single absorptions in both the proton (τ 9.44)[4] and the F^{19} (69.58 ppm)[5] spectra. Additional evidence in support of our structural assignment was provided by the following solvolysis reaction of II.



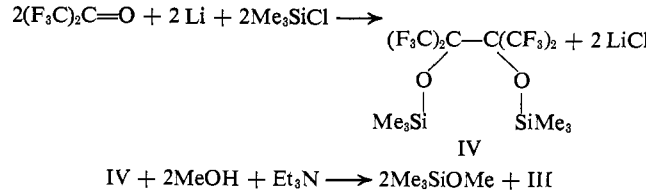
Thus, when the stoichiometric amounts of the indicated reactants were combined, an exothermal reaction occurred immediately, affording a 92% yield of the expected triethylammonium perfluoropinacolate (III) [neut equiv, calcd, 435; found, 438] whose infrared spectrum was identical with that of an authentic sample of the salt prepared directly from perfluoropinacol and triethylamine.

A related reaction involving Me_3SiCl, in which a divalent silicon species could not possibly be involved, afforded the anticipated 1,2-bis(trimethylsiloxy)tetrakis(trifluoromethyl)ethane (IV) [bp 201–202°; H^1 nmr, singlet at τ 9.77. *Anal.* Calcd for $C_{12}H_{18}F_{12}O_2Si$: C, 30.1; H, 3.77; F, 47.8. Found: C, 31.3; H, 4.11; F, 48.0] which, upon methanolysis in the presence of triethylamine, gave III in nearly quantitative yield.

(3) Perfluoropinacol was prepared by the method of W. J. Middleton and R. V. Lindsey, Jr., *J Am. Chem. Soc.*, **86**, 4948 (1964).

(4) Determined with a Varian **A-60** instrument.

(5) Thirty per cent in $CFCl_3$ at 94.1 Mc. We are indebted to Dr. J. P. Heeschen of The Dow Chemical Co. for this measurement.



While nothing in this paper absolutely precludes a divalent silicon intermediate in the Me_2SiCl_2 reaction, the latter experiment clearly demonstrates the feasibility of a reasonable mechanistic alternative.

The structures reported[1] for the hexafluoroacetone derivatives of various orthoformates do not appear to rest on evidence any firmer than that leading to the incorrect assignment of I and should, perhaps, also be reappraised.

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Solvent Dependence of C^{13}–H and C^{13}–F^{19} Coupling Constants[1]

Sir:

Although the solvent and concentration dependence of spin–spin coupling constants is now well established,[2] the nature of the interactions giving rise to this medium effect is still not clear. Part of the difficulty arises because of the variety of intermolecular interactions possible in the systems studied, *e.g.*, H-bonding,[2a] self-association,[2e,3] electric field effects.[2k] A further complicating factor is the influence of the sign of the coupling constant upon the direction of change in the coupling constant in solvents of increasing polarity. In order to assess this relationship more carefully, we have studied the solvent dependence of the directly bonded C^{13}–H and C^{13}–F^{19} coupling constants in *cis*- and *trans*-1,2-dichlorofluoroethylene in a variety of polar and nonpolar solvents.

The spectra for the two isomers are of the simple AX type[4] and the C^{13}–H and C^{13}–F^{19} coupling constants are obtained directly from the satellite lines in the proton and fluorine spectra, respectively. A summary of the parameters is given in Table I (*cis* isomer) and Table II (*trans* isomer). All of the chemical shifts and observable coupling constants[5] show a strong solvent dependence (Tables I and II). A slight concentration dependence was also noted for δ_H, ϕ_F, and $J_{C^{13}-H}$;[6] however, the changes were much less than

(1) Work supported by the Atomic Energy Commission.

(2) (a) D. F. Evans, *J. Chem. Soc.*, 5575 (1963); (b) V. S. Watts, G. S. Reddy, and J. H. Goldstein, *J. Mol. Spectry.*, **11**, 325 (1963); (c) B. L. Shapiro, R. M. Kopchik, and S. J. Ebersole, *ibid.*, **11**, 326 (1963); (d) *J. Chem. Phys.*, **39**, 3154 (1963); (e) P. Bates, S. Cawley, and S. S. Danyluk, *ibid.*, **40**, 2415 (1964); (f) M. Gordon and C. E. Griffin, *ibid.*, **41**, 2570 (1964); (g) G. J. Martin and M. L. Martin, *J. Chim. Phys.*, **61**, 1222 (1964); (h) S. Ng, J. Tang, and C. H. Sederholm, *J. Chem. Phys.*, **42**, 79 (1965); (i) V. S. Watts, J. Loemker, and J. H. Goldstein, *J. Mol. Spectry.*, **17**, 348 (1965); (j) S. L. Smith and R. H. Cox, *ibid.*, **16**, 216 (1965); Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J. Sept 1965, p 33S; (k) V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, **42**, 228 (1965).

(3) D. Blears, S. Cawley, and S. S. Danyluk, to be published.

(4) Spectra were measured at room temperature, 25 ± 2°, using Varian DA-60 and A56-60 spectrometers. The sweep ranges were carefully calibrated several times.

(5) A strong solvent dependence was also noted for the C^{13}≡C—H and C^{13}≡C—F coupling constants (unpublished results).