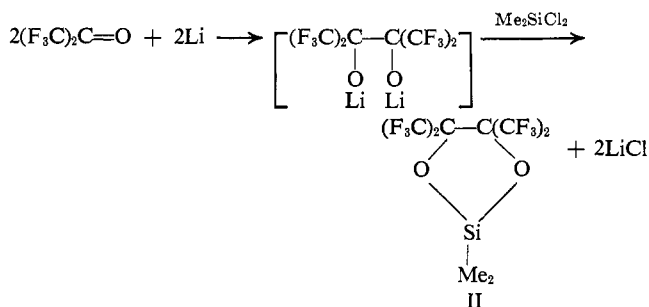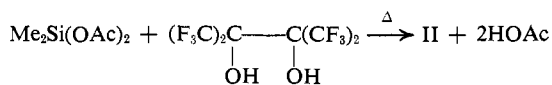to a pinacol derivative does not appear to have been considered.
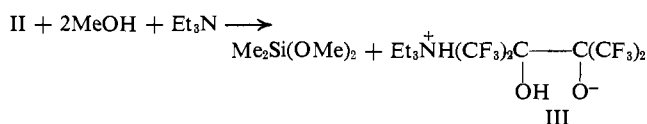
We have found the product of the above reaction to be consistent with this less exotic course and to be in fact merely the expected perfluoropinacol derivative (II) of Me_2SiCl_2; *i.e.*

$$2(F_3C)_2C=O + 2Li \longrightarrow \begin{bmatrix} (F_3C)_2C-C(CF_3)_2 \\ | \quad | \\ O \quad O \\ | \quad | \\ Li \quad Li \end{bmatrix} \xrightarrow{Me_2SiCl_2}$$

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]

$$Me_2Si(OAc)_2 + (F_3C)_2C-C(CF_3)_2 \xrightarrow{\Delta} II + 2HOAc$$
$$\quad\quad\quad\quad\quad\quad\quad | \quad\quad | $$
$$\quad\quad\quad\quad\quad\quad OH \quad OH$$

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.

$$II + 2MeOH + Et_3N \longrightarrow$$
$$Me_2Si(OMe)_2 + Et_3\overset{+}{N}H(CF_3)_2C-C(CF_3)_2$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad | $$
$$\quad\quad\quad\quad\quad\quad\quad\quad OH \quad O^-$$
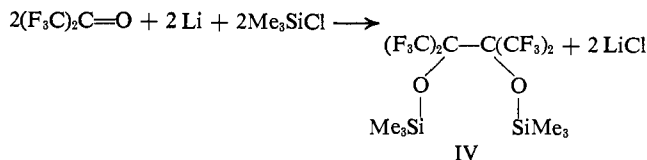$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad III$$

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.

$$2(F_3C)_2C=O + 2Li + 2Me_3SiCl \longrightarrow$$
$$\quad\quad\quad\quad\quad (F_3C)_2C-C(CF_3)_2 + 2LiCl$$
$$\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad\quad O \quad\quad\quad\quad O$$
$$\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad | $$
$$\quad\quad\quad\quad\quad Me_3Si \quad\quad SiMe_3$$
$$\quad\quad\quad\quad\quad\quad\quad\quad IV$$

$$IV + 2MeOH + Et_3N \longrightarrow 2Me_3SiOMe + III$$

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).

Table I. Solvent Dependence of Chemical Shifts and Coupling Constants (cps) for cis-1,2-Dichlorofluoroethylene

Solvent	$\delta_H^{a,b}$	$J_{C^{13}-H}{}^a$	$\phi_F{}^c$	$J_{C^{13}-F^{19}}$
Cyclohexane	362.0	195.6	4763	300.0
Benzene	323.4	198.0	...	...
Carbon disulfide	369.8	195.5	4675	300.0
Isopropyl ether	389.4	199.6	...	...
Chloroform	372.9	199.6	4746	300.0
Acetone	405.5	199.6	...	...
Acetonitrile	390.4	198.0	4798	298.6
N,N-Dimethylform-amide	424.4	202.5	4807	297.0
Dimethyl sulfoxide	428.8	201.0	4767	298.0

^{a} The proton chemical shifts are accurate to ±0.2 cps and coupling constants to ±0.1 cps. The fluorine chemical shifts and coupling constants are accurate to ±1.0 cps and ±0.5 cps, respectively. ^{b} Proton chemical shifts are for 1% solutions and are relative to internal TMS. ^{c} Fluorine chemical shifts are for 50% solutions and are given relative to external Cl_3CF.

Table II. Solvent Dependence of Chemical Shifts and Coupling Constants (cps) for trans-1,2-Dichlorofluoroethylene

Solvent	$\delta_H{}^a$	$J_{C^{13}-H}$	ϕ_F	$J_{C^{13}-F^{19}}$
Cyclohexane	325.2	201.7	4501	306.9
Benzene	286.3	204.0	...	...
Carbon disulfide	333.6	201.8	4468	306.6
Isopropyl ether	352.6	205.2	...	...
Chloroform	336.2	203.8	4491	306.2
Acetone	377.3	205.9	...	...
Acetonitrile	355.7	204.5	4558	304.5
N,N-Dimethylformamide	390.7	208.6	4565	302.9
Dimethyl sulfoxide	394.7	207.1	4518	304.2

^{a} Experimental conditions are the same as for the cis isomer, Table I.

those observed in different solvents. The proton and fluorine chemical shifts for both isomers show a marked *decrease* in solvents of higher dielectric constant. In contrast the $C^{13}-H$ coupling constants *increase* in magnitude while the $C^{13}-F^{19}$ coupling constants *decrease* in the more polar solvents. Both the proton and fluorine chemical shifts vary linearly[7] with the respective $J_{C^{13}-H}$ and $J_{C^{13}-F^{19}}$ coupling constants in different solvents. A linear correlation is also noted between the directly bonded couplings and J_{H-F}, over the same range of solvents. These observations indicate that the medium effect acts to change the shieldings and coupling constants by a similar mechanism. Since the chemical shifts follow the trend expected if the reaction field of the solvent is the dominant influence,[8] it is likely that the changes in coupling constants are also largely due to this effect.[9]

The solvent-induced changes in magnitude of $J_{C^{13}-H}$ and $J_{C^{13}-F^{19}}$ can be rationalized in terms of the MO theory of Pople and Santry[10] for directly bonded coupling constants. Considering the $C^{13}-H$ coupling constant, an increase in the magnitude of the reaction

(6) The high solute concentration (50%) required in order to observe the $J_{C^{13}-F^{19}}$ satellites precluded the observation of any concentration dependence for this coupling constant.
(7) The pronounced high-field shift in benzene is due to the anisotropic diamagnetic susceptibility of the solvent molecules.
(8) F. Hruska, E. Bock, and T. Schaefer, *Can. J. Chem.*, **41**, 3034 (1963).
(9) Watts and co-workers[21] have suggested that the medium effect on $J_{C^{13}-H}$ in some dihaloethylenes is due in part to a specific interaction between a solvent molecule and the halogen substituent. Such a possibility cannot be completely ruled out in the present systems; however, it is not expected to be the predominant factor.
(10) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

field acting in the region of the C–H bond will tend to increase the s character[11] of the C-hybrid bonding orbital and hence will lead to a more positive value for $J_{C^{13}-H}$; if the sign of $J_{C^{13}-H}$ is positive,[12] then $J_{C^{13}-H}$ will increase in more polar solvents as is observed. For the $C^{13}-F^{19}$ coupling, the reaction field acting in the region of the C–F bond will tend to draw the bonding electrons closer to the F atom. The increased polarity of the bond results in a trend of the $C^{13}-F^{19}$ coupling constant to more positive values; since the sign of $J_{C^{13}-F^{19}}$ is most likely negative,[13] the observed coupling constant decreases in magnitude.

The present results show the possibility of obtaining evidence about the signs of directly bonded coupling constants from their solvent dependence without recourse to double resonance techniques. A similar suggestion was made recently[2j] in connection with the solvent dependence of the geminal and vicinal couplings in styrene oxide. The usefulness of solvent effects for sign determination is limited, however, to simple systems in which solute–solute and solute–solvent interactions are easily characterized.

(11) Electrostatic repulsion between the bonding electron and the negatively charged reaction field will force the electron closer to the C atom; cf. Evans.[2a]
(12) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3406 (1962).
(13) G. V. D. Tiers, *ibid.*, **84**, 3972 (1962).
(14) Visiting summer scientist, 1965.

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An Explanation for the Predominance of cis-2-ene over trans-2-ene in p-Toluenesulfonate Eliminations

Sir:

A recent communication[1] reports that cis-2-ene is formed more rapidly than trans-2-ene when secondary tosylates undergo base-promoted eliminations with potassium t-butoxide in t-butyl alcohol. It was suggested[1] that these data could be rationalized in terms of a steric model involving the steric requirements of both the attacking base and the leaving group.

We have studied the products formed from 2-butyl and 2-pentyl tosylates using various solvents and two alkoxide bases and have also observed this unusual effect when reactions were carried out in t-butyl alcohol with both bases. The reaction conditions were the same as previously reported.[2] The data are summarized in Table I.

Examination of these and the previous[1,2] data suggests that: (1) the predominance of cis-2-ene over trans-2-ene is the result of a solvent effect since it is peculiar to t-butyl alcohol and not to the identity of the base, and (2) contrary to previous hypotheses[1,3] the steric requirements of alkoxide bases in general are relatively unimportant in tosylate eliminations.

Any consideration of the proposed steric requirements[1,3] of attacking base must take into account the degree of β-C–H bond stretching in the transition

(1) H. C. Brown and R. L. Klimish, *J. Am. Chem. Soc.*, **87**, 5517 (1965).
(2) D. H. Froemsdorf and M. E. McCain, *ibid.*, **87**, 3983 (1965).
(3) H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956).