Partial Acetolysis of Labeled Neopentyl Tosylate and Degradation and Analysis of Recovered Reactant.—A mixture of 998 mg (4.12 mmoles) of the labeled neopentyl tosylate and 40 ml of acetic acid, 1% in acetic anhydride, containing 4.80 mmoles of sodium acetate (0.120 *M*) was heated to reflux (*ca.* 118°) (drying tube to the atmosphere) and the progress of the reaction was followed by titrating, with standard perchloric acid in glacial acetic acid, aliquots withdrawn from a simultaneous reaction conducted with unlabeled tosylate but otherwise identical. After 67 ± 1% reaction (*ca.* 16.5 hr) the mixture was cooled in ice water, added to 400 ml of water, and extracted with three 150-ml portions of ether. The combined ether solution was washed with water, 10% sodium bicarbonate solution, and water, and was dried over anhydrous magnesium sulfate. After filtration the ether and *t*-amyl acetate were removed on a rotary evaporator with mild warming (<45°). The solid residue was crystallized from hexane with cooling to −50°, yielding 332 mg (1.37 mmoles) of crude recovered neopentyl tosylate. This material, dissolved in 5 ml of dry tetrahydrofuran, was added to a stirred solution of sodium naphthalene prepared by reaction between 0.16 g (0.0070 mole) of sodium chips and 0.90 g (0.0070 mole) of naphthalene in 15 ml of dry tetrahydrofuran for 3 hr under a dry nitrogen atmosphere.[12] After 15 min, during which the color of the solution changed from dark green to dark greenish brown, 3 ml of water was added cautiously and the mixture was then added to 150 ml of ether and 200 ml of water in a separatory funnel and thoroughly shaken. The ether layer was separated, washed several more times with water until the aqueous layer was no longer strongly basic, and dried over anhydrous magnesium sulfate. Most of the ether was removed by rotary evaporation and from a portion of the residual solution 6 mg of neopentyl alcohol was isolated by preparative gas chromatography. Comparison of the mass spectrum[9] (51 ev) of the recovered neopentyl alcohol with that of a sample of pure unlabeled material in the *m/e* 73–75 region (M-CH_3) showed ^{18}O enrichment of the former to be no greater than 0.1% and probably considerably less.

Registry No.—1a, 14128-46-2; neopentyl cation, 14128-47-3.

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The Polar Addition of Molecular Fluorine to Acetylenes[1,2]

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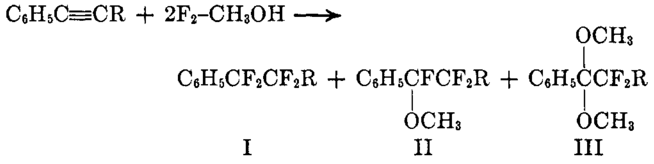
The addition of halogen to the carbon–carbon triple bond is an old and established process[3] studied by many workers. Direct low-temperature fluorine–olefin addition reactions have been examined extensively[4-6] in this laboratory and molecular complexes as well as β-fluorocarbonium ions were postulated[2,6] as intermediates for this process. It seemed of interest to complete the halogen–acetylene series for the case of fluorine as well as to provide more information on fluorine addition processes in general.

The additions were conducted at −78° and the acetylenes diluted with either Freon 11[7] or methanol. No difference in absorption (addition) rates was observed for these two solvents even though they are of widely differing polarity.

The use of CCl_3F precluded solvent intervention and the major fluorine-containing product was the tetrafluoride (I). Less than stoichiometric amounts of fluorine did not favor difluoro olefin information and only tetrafluoride and unreacted acetylene were found. However, the use of methanolic solutions of the substrate led to the formation of *gem*-fluoro ethers (II) and dimethyl ketals (III) as well as tetrafluorides. Table I below lists the product distribution for the three acetylenes studied.

TABLE I

PRODUCT DISTRIBUTION FOR FLUOROMETHANOLYSIS



$$C_6H_5C{\equiv}CR + 2F_2\text{-}CH_3OH \longrightarrow \underset{\text{I}}{C_6H_5CF_2CF_2R} + \underset{\text{II}}{C_6H_5\underset{OCH_3}{C}FCF_2R} + \underset{\text{III}}{C_6H_5\overset{OCH_3}{\underset{OCH_3}{C}}CF_2R}$$

	% composition		
	I	II	III
R = C_6H_5	23	57	20
R = CH_3	19	50	31
R = H	13	35	52

The product mixtures were analyzed by vapor phase chromatography (vpc) where appropriate and in every case by integration of the fluorine nuclear magnetic resonance (nmr) spectra. The relative position of the ether groups was easily ascertained by their nmr spectra (F^{19} and H^1) as well as acidic hydrolysis to the corresponding α,α-difluoro ketone.

The nature of the products found (*i.e.*, II and III) as well as the placement of the oxygen is a strong indication of the polar character of the fluorinating reagent. The formation of ketals and fluoro ethers may be envisioned as arising *via* path A or B (Scheme I).

To be of significance the methanolysis reaction (path B) would have to proceed exclusively to the enol ether (VI) and not continue to the unreactive (to fluorine) dimethyl ketal. It is expected that formation of the ketal under these conditions would be greatly favored over partial methanolysis to the enol ether.

The acetylenes seem to fluorinate completely (in inert solvents) to tetrafluoride which implies that difluoroolefin is more reactive to fluorine than is the parent acetylene. In methanol, no products could be found that would correspond to the intermediate olefins shown in Scheme I as IV, V, or VI. This would be consistent with the general view that olefins and enol ethers are much more receptive to electrophilic addition than are acetylenes.

The relative ratios of products are not of great significance as the magnitude of the influence of path B cannot be ascertained. Bases strong enough to scrub out all the HF are also reactive to fluorine and cannot be incorporated in the fluorination solution. The only trend which is apparent is that as the substituent becomes more bulky the amount of tetrafluoride (I) and

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[1] This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021 AMC-11536 (Z).

[2] Part IV of the Low-Temperature Fluorination Process: R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).

[3] M. L. Poutsma and J. L. Kartch, *Tetrahedron*, **22**, 2167 (1966), and references therein.

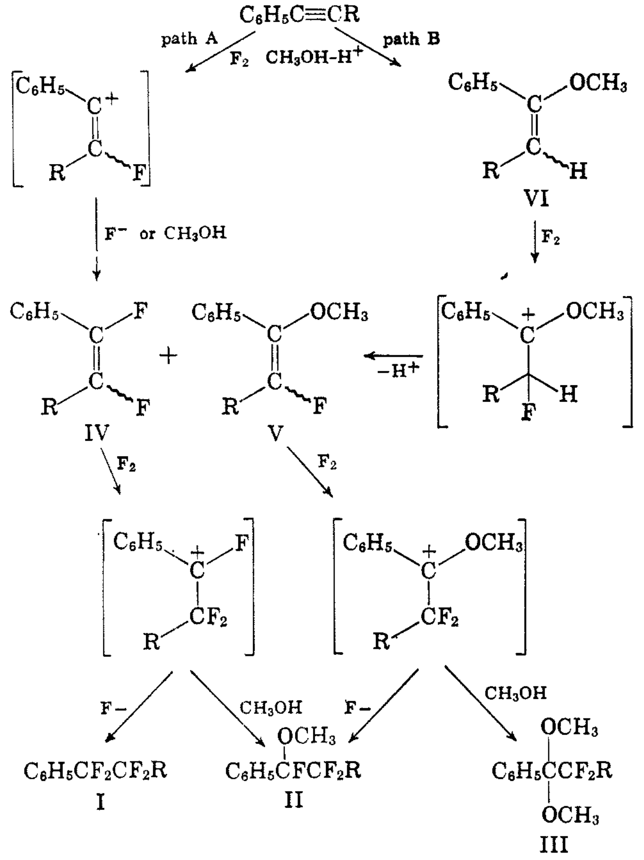
[4] R. F. Merritt and T. E. Stevens, *ibid.*, **88**, 1822 (1966).

[5] R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).

[6] R. F. Merritt, *ibid.*, 3871 (1966).

[7] Trademark of E. I. du Pont de Nemours and Co., Wilmington, Del., for CCl_3F.

Scheme I



fluoro ether (II) increases while that of ketal (III) decreases. No electronic interpretation is obvious as the substituents are rather remote from the carbon atom undergoing methanolysis.

This process proved to be of synthetic utility for preparation of certain trifluoro ethers and difluoro ketals, as well as the α,α-difluoro ketones obtained from both by hydrolysis.

Experimental Section

Materials.—The acetylenes were obtained from commercial sources and purified to conform with published physical and spectral data. The fluorine was obtained from Allied Chemical Corp. and was passed through a NaF-filled HF scrubber prior to use. The fluorine purity was checked periodically by iodometry and mass spectra in which the only detectable impurity (~0.5%) was oxygen.

Apparatus.—The equipment and general operation have been amply described in previous articles.[4,5]

CAUTION: Proper safety precautions such as safety shields and adequate ventilation must be observed as fluorine leaks inevitably occur.

Fluorination of Diphenylacetylene.—A solution of 3.9 g (22 mmoles) of diphenylacetylene in 75 ml of methanol was cooled to −78° and thoroughly degassed. The fluorine (44 mmoles) was slowly admitted above the well-stirred solution at such a rate that the pressure of fluorine in the reactor never exceeded 5 mm. After completion of the fluorine uptake (~1.5 hr) the solvent was vacuum distilled and replaced with 50 ml of methylene chloride. This solution was washed with two (50-ml portions) 1% NaOH solution and (two 50-ml portions) H_2O, and finally dried over magnesium sulfate. After removal of the methylene chloride a portion of the crude product (5.1 g) was analyzed by F^{19} nmr and the remainder (4.06 g) was immediately rectified by elution chromatography on silica gel. A jacketed (20 × 300 mm) column was used with a pentane–methylene chloride (60:1) solvent mixture. The products will be discussed in order of their elution from this column.

Peak A consisted of 0.36 g (yield 23%) of tetrafluorobibenzyl (I) [mp 119.3–120.5° (lit.[8] mp 122–123°)] after sublimation at 45° (0.01 mm). The fluorine nmr spectrum consisted of a single peak at ϕ +112.7.[9]

Peak B contained 2.0 g (50% recovery) of diphenylacetylene identified by comparison of infrared spectra with that of the starting material and mixture melting point.

Peak C proved to be 0.870 g (57% yield) of 1-methoxy-1,2-diphenyl-1,2,2-trifluoroethane (II) which was a colorless crystalline solid, mp 71.5–73°. The fluorine nmr spectrum contained peaks at ϕ +131.8 and 109.8 in a ratio of 1:2. Proton nmr and infrared spectra were consistent with the structure as II.

Anal. Calcd for $C_{15}H_{13}F_3O$: C, 67.66; H, 4.92. Found: C, 68.06; H, 4.99.

Peak D.—The dimethyl ketal of α-phenyl-α,α-difluoroacetophenone (III) (0.650 g, 20%) as a colorless liquid, bp 70° (0.4 mm). The F^{19} nmr spectrum contained a single peak at ϕ +106.4. The proton nmr showed the methoxyl to phenyl ratio of 3:5. Satisfactory analytical data could not be obtained as the sample could not be completely separated from the α-difluoro ketone hydrolysis product.

When Freon 11 (CCl_3F) was employed as the fluorination solvent, the single product isolated was the tetrafluoride (I) with properties identical with those of peak A above.

Fluorination of Phenylacetylene.—The fluorination and elution work-up were essentially the same as described above and product distribution (given in Table I) was determined by integration of the F^{19} nmr spectrum of the crude mixture. The components were of marginal stability and could not be vacuum distilled.

Component A.—1,1,2,2-Tetrafluoroethylbenzene (13%) could be isolated in analytical purity by vpc (didecylphthalate 6 ft × 0.25 in. at 57°). The fluorine nmr spectrum consisted of a doublet (J_{HF} = 56 cps, CF_2H) centered at ϕ +134.8 and a singlet at ϕ +114.3 in a 1:1 ratio. The proton spectrum of the aliphatic proton consisted of a triplet (J_{HF} = 56 cps) of triplets (J_{HF} = 3 cps) centered at δ 5.87 (tetramethylsilane) as well as the singlet phenyl peak at δ 7.53 (ratio 1:5).

Anal. Calcd for $C_8H_6F_4$: C, 53.94; H, 3.40. Found: C, 53.71; H, 3.39.

Component B.—1-Methoxy-1-phenyl-1,2,2-trifluoroethane (35%) was purified by elution chromatography (silica gel–CH_2Cl_2 eluent) to a colorless unstable liquid. The fluorine nmr spectrum consisted of a doublet (J_{HF} = 56 cps) of doublets (J_{FF} = 6 cps) centered at ϕ +133.1 in a ratio of 2:1, respectively. The single proton appeared as a triplet (J_{HF} = 56 cps) of doublets (J_{HF} = 3 cps) centered at δ 5.70, with the methoxy protons at δ 3.33 (singlet) and phenyl protons at δ 7.48 in the ratio of 1:3:5, respectively. The infrared spectrum is consistent with this structure and confirms the absence of a carbonyl group.

Anal. Calcd for $C_9H_9F_3O$: C, 56.84; H, 4.77. Found: C, 57.85; H, 5.17.

Component C.—1-Phenyl-1,1-dimethoxy-2,2-difluoroethane (52%) was purified by elution chromatography (silica gel–CH_2Cl_2) to a colorless nondistillable liquid. The proton nmr spectrum consisted of a triplet (J_{HF} = 56 cps) centered at δ 5.83 for the CHF_2 group, a singlet at δ 3.39 (OCH_3) and the phenyl complex at δ 7.50 in a ratio of 1:6:5.2, respectively. The fluorine nmr spectrum consisted of the expected doublet (J_{HF} = 56 cps) centered at ϕ 131.9.

Anal. Calcd for $C_{10}H_{12}F_2O_2$: C, 59.40; H, 5.98. Found: C, 59.21; H, 6.07.

The addition of fluorine conducted in Freon 11 produced the tetrafluoride (component A) with traces of $C_6H_5CF_2CF_3$.

Fluorination of Methylphenylacetylene.—The acetylene was fluorinated and worked up in a manner described above and relative yields calculated by integration of the F^{19} nmr spectrum of the product mixture.

Component A.—1-Phenyl-1,1,2,2-tetrafluoropropane could be effectively purified by vpc (4 × 0.25 in. diisodecylphthalate/125°) to a colorless stable liquid. The fluorine nmr spectrum contained a complex quartet (J_{HF} = 18 cps) (centered at ϕ +107.5) and a broadened singlet at ϕ +112.7 in a 1:1 ratio. The methyl group appears as a triplet (J_{HF} = 18 cps) centered at δ 1.77 in a ratio of 3:5 with the phenyl protons.

Anal. Calcd for $C_9H_8F_4$: C, 56.25; H, 4.20. Found: C, 56.50; H, 4.23.

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[8] W. R. Hasek, W. G. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[9] Fluorine nmr spectra are reported in units of ϕ (parts per million from CCl_3F) as 10% solutions in $CDCl_3$ with a Varian HR-40 spectrometer.

Component B.—1-Methoxy-1-phenyl-1,2,2-trifluoropropane was purified by elution chromatography (silica gel/CH_2Cl_2 eluent) to an unstable, nondistillable colorless liquid. The fluorine nmr spectrum contained a quartet (J_{HP} ~19 cps) centered at ϕ +104.6 and a singlet at ϕ +131.4 in a 2:1 ratio. The proton nmr spectrum consisted of a triplet (J_{HF} = 19 cps) of doublets (J_{HF} = 1.5 cps) centered at δ 1.69, a singlet methoxyl at δ 3.30, and the phenyl protons at δ 7.61 in a 3:3:5 ratio.

Anal. Calcd for $C_{10}H_{11}F_3O$: C, 58.82; H, 5.43; F, 27.92. Found: C, 59.26; H, 5.39; F, 30.90.

Component C.—The 1-phenyl-1,1-dimethoxy-2,2-difluoropropane could not be adequately purified for an elemental analysis but its structure can be indicated by nmr and its hydrolysis to α,α-difluoropropiophenone. The fluorine nmr spectrum of the difluoro ketal consisted of a quartet (J_{HF} = 16 cps) centered at ϕ +102.

Hydrolysis of Trifluoro Ethers (II) and Difluoro Acetals (III).—Both types were readily hydrolyzed by 10% H_2SO_4 at 50° for 3 hr, to the same α,α-difluoro ketone whose properties are listed in Table II.

TABLE II

NMR DATA FOR α,α-DIFLUORO KETONES

Compound	C=O, μ	ϕ (CF_2)	J_{HF}, cps	Ref
$C_6H_5C(=O)CF_2H$	5.83	+131.9 (doublet)	54	*a*
$C_6H_5C(=O)CF_2CH_3$	5.88	+93 (quartet)	19	*b*
$C_6H_5C(=O)CF_2C_6H_5$	5.90	+99.3 (singlet)	...	*c*

[a] M. Prober, *J. Am. Chem. Soc.*, **75**, 968 (1953). [b] R. M. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965). [c] J. Bornstein and M. R. Borden, *Chem. Ind.* (London), 441 (1958).

Registry No.—Ia, 425-32-1; Ib, 14210-87-8; Ic, 383-18-6; IIa, 14210-88-9; IIb, 14210-89-0; IIc, 14210-90-3; IIIa, 14210-91-4; IIIb, 14320-36-6; IIIc, 14210-92-5.

Acknowledgment.—I am grateful to Mrs. Carolyn Haney for infrared and nmr spectra and to Mr. Morris Howard for technical assistance.

Some Reactions of Silanes and Sulfides with Strong Bases in Dimethyl Sulfoxide

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In this paper we show by studies of nmr spectra that diethyl sulfide exchanges α hydrogens readily with dimethyl-d_6 sulfoxide in the presence of sodium dimsyl at 100°, while tetramethylsilane is unaffected. With potassium *t*-butoxide in dimethyl sulfoxide tetramethylsilane reacts rapidly at 25° to form methane and *t*-butyl trimethylsilyl ether.

Some years ago, Doering and Hoffman[2] showed that hydrogens α to sulfonium and phosphonium groups were much more readily exchangeable in base than those α to ammonium groups. This was interpreted in terms of possible 3d–π bonding in the intermediate carbanions of the reactive salts. In an effort to extend such possible interactions to a carbanion adjacent to uncharged silicon, using strong bases in dimethyl sulfoxide (DMSO), the reactivity of α-hydrogens in silanes has been compared to those in sulfides and amines.

Many physical and chemical properties of organosilicon compounds have been attributed to 3d–2p–π bonding between silicon and carbon, oxygen, or nitrogen.[3] An example is the weak base strength of trisilylamine, ascribed to delocalization of the unshared pair on nitrogen into the 3d orbitals of the silicon atoms.[4] If indeed this delocalization depicted for

$$(H_3Si)_3\ddot{N} \longleftrightarrow (H_3Si)_2\overset{+}{N}{=}\overset{-}{Si}H_3$$

silylamine is as significant as the very weak basicity for this amine indicates, a similar interaction might influence the acidity of silanes through a stabilization of a carbanion. We have, therefore, made a search for this

$$(CH_3)_4Si \xrightarrow[?]{\text{base}} \left[(CH_3)_3Si\bar{C}H_2 \longleftrightarrow (CH_3)_3\bar{Si}{=}CH_2\right]$$

reaction using strong bases in DMSO. These have included not only potassium *t*-butoxide in DMSO, which has been shown to be many orders of magnitude stronger than alkoxides in conventional solvents,[5,6] but also sodium dimsyl,[7] shown to be 10^7 times stronger than potassium *t*-butoxide.[8]

It was quickly discovered that *t*-butoxide ion would not be suitable for this purpose, as it led to rapid C–Si bond cleavage. For example, potassium *t*-butoxide in DMSO reacted almost immediately with tetramethylsilane to give methane and *t*-butyl trimethylsilyl ether. The latter was also formed from benzyltrimethylsilane, along with toluene. A similar cleavage of the benzyl bond was observed with sodium methoxide in dimethylformmamide (DMF).

$$\underset{\text{TMS}}{Si(CH_3)_4} + t\text{-BuO}^- \xrightarrow[25°]{\text{DMSO}} \underset{\text{I}}{t\text{-BuOSi}(CH_3)_3} + CH_4\uparrow$$

$$\begin{tikzcd} C_6H_5CH_2Si(CH_3)_3 + t\text{-BuO}^- \arrow[r, "\text{DMSO}", "25°"'] \arrow[d, "NaOCH_3"', "\text{DMF}"] & \text{I} + C_6H_5CH_3 \\ CH_3OSi(CH_3)_3 & \end{tikzcd}$$

Despite the much greater base strength of dimsyl anion, it was found to give no detectable reaction with tetramethylsilane (TMS), not even proton exchange with deuterated DMSO. Triethylamine was also inert, but dimethyl and diethyl sulfides exchanged α-protons for deuterium on warming in DMSO-d_6 containing dimsyl anion.

$$(CH_3)_2S + (CD_3)_2SO \xrightarrow[95°,\ 60\ \text{min}]{\text{dimsyl}^-} 66\%\ \text{exchange}$$

The exchange was observed by increase of the nmr absorbance at τ 7.38 (DMSO) and corresponding decrease at τ 7.88 (DMS). When diethyl sulfide was studied, the methylene quadruplet (τ 7.42) overlapped the DMSO band. However, two approaches led to estimates of exchange. As methylene was deuter-

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