and is, in fact, identical with the observed intermediate having an absorption maximum at 356 mμ. However, these results do not exclude other compounds, such as the hypothetical formiminotetrahydrofolic acid,[12] as intermediates which could give rise to 10-formyl-THF directly or by way of 5,10-formyl-THF.

(12) R. D. Sagers, J. V. Beck, W. Gruber and I. C. Gunsalus, THIS JOURNAL, **78**, 694 (1956).

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RECEIVED JUNE 25, 1956

THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF F^{19} IN METHYL- AND ETHYLFLUOROSILANES

Sir:

It has been suggested that the chemical shift of F^{19} atoms in binary fluorides has a direct relationship with the electronegativity of the atom bound to fluorine.[1] The extent of magnetic shielding of fluorine in the fluorosilanes is reported here. As would be expected the chemical shift differs from one compound to another.

Figure 1 shows the relative shifts of the methyl- and ethylfluorosilanes and silicon tetrafluoride in cycles per second in a magnetic field of approximately 9,989 gauss.[2] We used diethyldifluorosilane as reference substance. All the values given correspond to the pure liquids at room temperature. Extrapolation of values for an infinitely dilute solution in carbon tetrachloride from data obtained at various concentrations does not change the sequence of the shifts, nor does it affect the qualitative interpretation of the results. The probable error with the applied technique is within 2%.

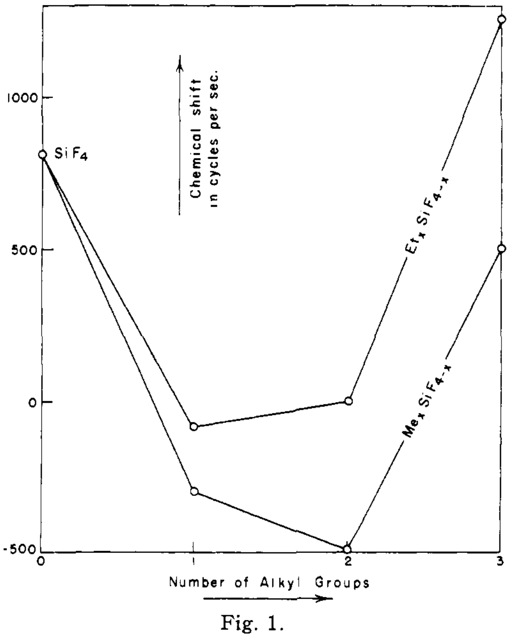

Fig. 1.

The values for silicon tetrafluoride were obtained from measurements at various concentrations in carbon tetrachloride and in *n*-hexane, and extrapolation of the value for the pure compound. For this particular measurement we believe that the maximum probable error does not exceed ±30 cycles per second.

The fluorine resonance of our reference substance is shifted 2,665 cycles per second toward higher fields from that of trifluoroacetic acid, and thus the F^{19} resonance of silicon tetrafluoride is 3,479 cycles per second higher than that of trifluoroacetic acid. (This would correspond to 0.554 gauss at 25.46 mc., which is the frequency used by Gutowsky and Hoffman[1] when they found 0.611.)

The shielding of the fluorine atoms in the fluorosilanes may well be controlled by a number of effects the most important of which are probably an inductive effect, and a π-bonding effect. Substitution of electron-releasing alkyl groups on silicon should result in an increase in shielding of the fluorine atoms. An opposing effect leading to a reduction in the fluoride shielding would be the occurrence of Si-F *dπ-pπ*-bonding.[3] From our present knowledge of chemical bonding it is not possible to quantitatively predict the extent of these two opposing effects. Certainly the electron-releasing effect would be increased by substituting ethyl groups for methyl.[4]

Extensive study of the proton resonance in methyl derivatives of silicon and the other group IV elements is now being conducted by Mr. A. L. Allred of this laboratory, and it is hoped that this will shed further light on the shifts of fluorine resonance noted above.

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(1) H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, **80**, 110 (1950); *J. Chem. Phys.*, **19**, 1295 (1951), and **20**, 200 (1952), who have measured a large number of fluorine compounds including silicon tetrafluoride.

(2) Measurements were made on a Varian N–M–R Spectrometer at 40 megacycles using a 5-mm. spinning sample tube containing a 1-mm. sealed capillary of reference substance as described by Aksel A. Bothner-By and Richard E. Glick, THIS JOURNAL, **78**, 1071 (1956).

(3) F. G. A. Stone and D. Seyferth, *J. Inorg. and Nuclear Chem.*, **1**, 112 (1955).

(4) J. W. Baker, "Hyperconjugation," Oxford at the Clarendon Press, p. 5.

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RECEIVED JULY 11, 1956

CYCLOHEXADECA-1,3,9,11-TETRAYNE, A CYCLIC TETRA-ACETYLENE

Sir:

We have prepared the cyclic tetra-acetylene, cyclohexadeca-1,3,9,11-tetrayne (II), in one step from octa-1,7-diyne (Ia) by a novel cyclization reaction.

In the course of a general investigation into the oxidative coupling of terminal diacetylenes, the aerial oxidation of octa-1,7-diyne (Ia) in the presence of cuprous chloride and ammonium chloride was studied. When the reaction mixture in water was shaken in air at 20°, the ordinary dimer,[1] hexadeca-1,7,9,15-tetrayne (Ib) (m.p. 21–22°, b.p. 119–120° (0.1 mm.), n^{23}_D 1.5205, $\lambda_{max.}$ 226, 238 and 253 mμ, log ε, 700, 620 and 430 respectively, $\nu_{max.}$ 3300 and 2235 cm.$^{-1}$, found: C, 91.32; H, 8.80)

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(1) The terms "dimer" and "tetramer" are used to denote products derived respectively from two and four molecules of monomer, although their empirical formulas are of course not exact multiples of the monomer.