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%.

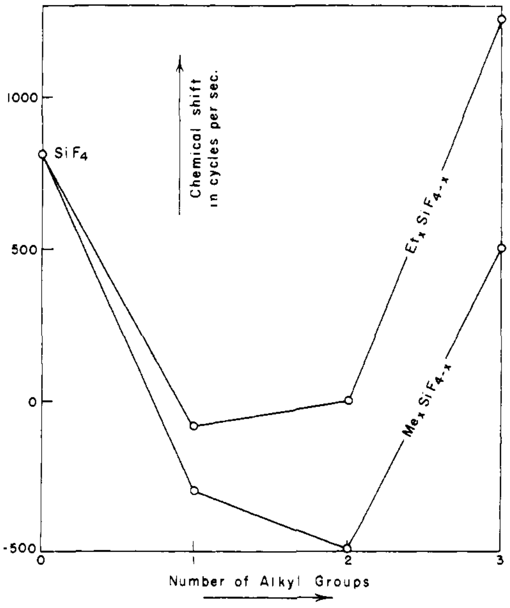

Fig. 1.

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 $d\pi$-$p\pi$-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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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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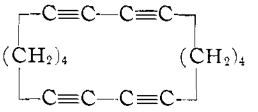
[1] The terms "dimer" and "tetramer" are used to denote products derived respectively from two and four molecules of monomer, although their empirical formulas are of course not exact multiples of the monomer.

was essentially the only product formed. However when the reaction was carried out in aqueous ethanol at 55°, air being bubbled through the mixture, three substances were formed. The first (*ca.* 40% yield) was the dimer Ib, which on hydrogenation gave hexadecane. The second (*ca.* 20% yield) was the tetramer, dotriaconta-1,7,9,15,17,23,25,31-octayne (Ic) (m.p. 92–93°, $\lambda_{\max.}$ 226, 240 and 254 mμ, log ϵ 1190, 1140 and 720, respectively, $\nu_{\max.}$ 3310 and 2235 cm.$^{-1}$, found: C, 92.11; H, 7.93), the structure of which was confirmed by hydrogenation to dotriacontane. The third (*ca.* 10% yield) was the cyclic dimer II [m.p. 158–160° (dec.), $\lambda_{\max.}$ 227, 239 and 254 mμ, log ϵ, 580, 600 and 360, respectively, $\nu_{\max.}$ 2235 cm.$^{-1}$ (–C≡C–) but not at *ca.* 3330 cm.$^{-1}$ (no ≡C–H), found: C, 92.48; H, 7.62]. The structure was confirmed by the infrared spectrum, the absence of a precipitate with alcoholic silver nitrate and by full hydrogenation to cyclohexadecane, identified by direct comparison with an authentic sample.

$H[-C{\equiv}C-(CH_2)_4-C{\equiv}C-]_nH$

Ia, $n = 1$
b, $n = 2$
c, $n = 4$



(II)

The cyclic dimer II must have been formed directly from two molecules of the monomer by coupling at both ends, rather than via the dimer Ib which cyclizes internally, for separate oxidative coupling of the dimer Ib yielded only the tetramer Ic and none of the cyclic dimer II.

The cyclic tetra-acetylene II, the first carbocyclic compound incorporating more than two acetylenic linkages,[2] contains two parallel straight α-diacetylene chains bound together on both sides by a tetramethylene bridge. As in the compounds studied by Cram, *et al.*, in which two parallel groups ( or -C≡C–) are joined by two tetramethylene bridges,[2,3] the chromophoric systems in II are too far apart for appreciable interaction to occur, as judged by the normal ultraviolet spectrum.

The scope of the new cyclization reaction and the properties and transformations of II are now being investigated. We are indebted to Prof. V. Prelog for a sample of cyclohexadecane.

(2) D. J. Cram and N. L. Allinger (This Journal, **78**, 2518 (1956)) have recently described the preparation of cyclododeca-1,7-diyne via an acyloin type cyclization. Moreover G. Eglinton and A. R. Galbraith have privately communicated to us that they have prepared cyclic polyacetylenes by the coupling of terminal diacetylenes.

(3) D. J. Cram, *et al.*, *ibid.*, **76**, 6132 (1954); **77**, 4090 (1955).

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RECEIVED JUNE 28, 1956

ACTION OF GAMMA RAYS ON FERROUS ION SOLUTIONS IN HEAVY WATER

Sir:

The action of cobalt 60 gamma radiation on solutions of ferrous ammonium sulfate in light and heavy water mixtures has been investigated. Irradiations were carried out in six cylindrical sample holders rotating about their own axes and around two central 2-Curie Co^{60} sources. Ferric ion concentrations were determined colorimetrically using the ferric thiocyanate complex. We found extinction curves to be dependent on the concentration of heavy water and have determined these curves experimentally for all water compositions used. The solutions irradiated were 0.8 *N* in H_2SO_4 and 1 mM. in ferrous ammonium sulfate and contained oxygen. Radiation doses varied from 1 to 20 × 10^{20} ev./liter. Results of our experiments are shown in Table I:

TABLE I

FERRIC ION YIELDS FOR H_2O–D_2O MIXTURES

Atom % D in solvent hydrogen	$G_{Fe^{+++}}$
0	15.5 (assumed)
55	16.1 ± 0.2
85	17.0 ± 0.5
98	18.6 ± 0.8

It is reported by Hart[1] that the primary yield for molecular hydrogen is higher in light than in heavy water. Probably this means that the radical DO_2 is formed with a higher yield than HO_2 and this difference may play an important role in the differences we have observed. He also indicates that the difference between the yield of free radicals in heavy water and in light water is more than equivalent to the first difference. If this excess is real it is reasonable to ascribe it to a higher recombination rate of hydroxyl radicals with free atoms of light hydrogen than of deuterium. For both these reasons it is of interest to consider our *G*-values as a function of the ratio of light hydrogen to deuterium in the free hydrogen radicals in the solution. If we calculate the light hydrogen to deuterium ratio in the free atoms from the figures given by Topley and Eyring,[2] we find that our *G*-values depend on the isotope ratio in the free atoms in a way which is not far from linear. It should be kept in mind, however, that representations of similar simplicity of the value of *G* can be obtained as a function of other quantities such as the mole fraction of DOD molecules in the liquid. These considerations seem to make it important to compare by direct measurement the G-values of molecular H_2, HD and D_2 in solutions of ferrous sulfate in various concentrations of light and heavy water.

Thanks are due to the Foundation for Fundamental Research of Matter (F.O.M.) and the Organization for Pure Research (Z.W.O.) who supported this work. C.N.T. is indebted to the U.S.E.F. Neth. for a Fulbright Grant.

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RECEIVED JULY 5, 1956

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(1) E. J. Hart, W. R. McDonell, and S. Gordon Proceedings of the Geneva Conference on Peaceful Uses of Atomic Energy (United Nations, New York, 1956) Volume 7, p. 593 (1955).

(2) B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934).