Fig. 1.—Plot of the rate data based on the assumption that the substituent effect changes by a constant factor per methylene group.

Based on the marked deviation of the point for 5-chloro-1-pentene from the line defined by the other rate constants, the rate of reaction of 5-chloro-1-pentene may be calculated to be seven to ten times faster than expected in the absence of chlorine participation. Since terminal and nonterminal substituents show similar rate effects,[2a,3] the per cent of 1,4-chlorine shift expected for the reaction shown in eq. 1 is 43–45.[4] The agreement with the value found, 40%, is fair.

TABLE I

RATES OF ADDITION OF TRIFLUOROACETIC ACID TO ω-CHLORO-1-ALKENES AT 60.0°[a]

Alkene	$k \times 10^6$ sec.$^{-1}$, 60°
4-Chloro-1-butene	2.85[b]
5-Chloro-1-pentene	217[c]
6-Chloro-1-hexene	160
7-Chloro-1-heptene	308
8-Chloro-1-octene	708
9-Chloro-1-nonene	868
11-Chloro-1-undecene	1283

[a] 0.125 M sodium trifluoroacetate was present to neutralize adventitious traces of strong acid. Alkene concentrations were 0.1 or 0.03 M. [b] Determined by Mr. G Thompson. [c] From ref. 3.

Previously a 1,4-chlorine shift was found in addition of trifluoroacetic acid to 5-chloro-1-pentyne[5] but not in addition of trifluoroacetic acid to 5-chloro-1-pentene. The present demonstration of a 1,4-chlorine shift in an alkene addition supports previous postulates[3,5] concerning the importance of cyclic halonium ion intermediates in alkene additions and demonstrates that halogen shifts are not a special feature associated with the possible intermediacy of vinyl cations in the reaction of alkynes.

(3) P. E. Peterson and G. Allen, J. Am. Chem. Soc., 85, 3608 (1963).

(4) Following the usual treatment for estimating anchimeric assistance, and using the averaged value, (7 + 10)/2 = 8.5, ($k_{nonassisted}$ + $k_{assisted}$)/$k_{nonassisted}$ = 8.5. The fraction of assisted reaction presumed to proceed via a chloronium ion is $k_{assisted}$/k_{total} = 7.5/8.5 = 0.88. The per cent of chlorine shift is 50% × 0.88 = 44%.

(5) P. E. Peterson and J. E. Duddey, J. Am. Chem. Soc., 85, 2865 (1963).

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The Signs of Si²⁹–H¹ and Si²⁹–F¹⁹ Coupling Constants[1]

Sir:

Although it is well established theoretically[2] and experimentally[3] that the signs of directly bonded X–H¹ coupling constants are positive (with the exception of H–F), it is less certain that directly bonded X–Y coupling constants follow the same pattern. Recent MO calculations by Pople and Santry[2a] indicate that the X–Y coupling constants for first-row elements are likely to be negative if one of the nuclei is F¹⁹ and positive in all other cases in agreement with the limited experimental data available at present.[4]

In this communication we wish to report the signs for directly bonded Si²⁹–H¹ and Si²⁹–F¹⁹ coupling constants. These have been determined by carrying out {Si²⁹}H¹ field-sweep double resonance experiments on (CH₃)₂SiHCl and (CH₃)₃SiF molecules, respectively. The procedure followed can be illustrated by considering the case of (CH₃)₃SiF in some detail. The proton spectrum for this compound, measured with a Varian DP-60 spectrometer, consists of a doublet centered at τ 9.80 ± 0.01, with $J_{H^1-C-Si-F^{19}}$ = 7.51 ± 0.05 c.p.s. Superimposed about the midpoints of the main proton signals are Si²⁹ satellite doublets[5] with $J_{H^1-C-Si^{29}}$ = 7.09 ± 0.05 c.p.s. Although the Si²⁹ spectrum was not recorded, the first-order spectrum would consist of two sets of decets ($J_{H^1-C-Si^{29}}$ = 7.09 c.p.s.) separated by $J_{Si^{29}-F^{19}}$ between their midpoints.

The Si²⁹ radiofrequency field was applied at 11.215 Mc./sec. with a Rohde and Schwarz Type XUA frequency synthesizer, and frequencies were monitored with a Rohde and Schwarz Type FKM counter. The Si²⁹ frequency was varied in small increments (5–10 c.p.s.), while repeatedly scanning the proton spectrum until the correct decoupling frequency was obtained. Since $J_{Si^{29}-F^{19}} \gg J_{Si^{29}-C-H^1}$, it is possible to irradiate near the frequency of one set of Si²⁹ multiplets without perturbing transitions of the other set. The relative signs of $J_{Si^{29}-F^{19}}$ and $J_{H^1-C-Si-F^{19}}$ can therefore be determined by irradiating one of the Si²⁹ multiplets and observing which pair of satellite lines collapses. For (CH₃)₃SiF, irradiation at the *lowest* Si²⁹ frequency collapsed the *low-field* satellite, increasing the Si²⁹ frequency by 280 c.p.s.; *i.e.*, $J_{Si^{29}-F^{19}}$ led to a collapse of the high-field satellite. Thus $J_{Si^{29}-F^{19}}$ and $J_{H^1-C-Si-F^{19}}$ have the same sign (note, γ for Si²⁹ is negative). Since it is likely that the vicinal H¹–F¹⁹ coupling constant is positive,[6] it can be concluded that $J_{Si^{29}-F^{19}}$ is also positive. However, because of the negative magnetogyric ratio of Si²⁹, the reduced coupling constant[2a] given by $K = (2\pi/$

(1) This work was carried out while the author was a guest worker at the National Physical Laboratory, Basic Physics Division, Teddington, England.

(2) (a) J. A. Pople and D. P. Santry, Mol. Phys., 8, 1 (1964); (b) M. Karplus and D. M. Grant, Proc. Natl. Acad. Sci. U. S., 45, 1269 (1959); (c) M. Karplus, J. Am. Chem. Soc., 84, 2458 (1962); (d) N. Muller, J. Chem. Phys., 36, 359 (1962).

(3) (a) P. C. Lauterbur and R. J. Kurland, J. Am. Chem. Soc., 84, 3406 (1962); (b) F. A. L. Anet, ibid., 84, 3767 (1962); (c) S. L. Manatt, G. L. Juvinall, and D. D. Elleman, ibid., 85, 2664 (1963).

(4) (a) G. V. D. Tiers, ibid., 84, 3972 (1962); (b) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, J. Chem. Phys., 37, 182 (1962); (c) K. Brei and H. J. Bernstein, ibid., 38, 1216 (1963).

(5) Si²⁹ natural abundance, 4.7%; I = ¹/₂; μ = –0.55477 nuclear magnetons.

(6) D. P. Evans, S. L. Manatt, and D. D. Elleman, J. Am. Chem. Soc., 85, 238 (1963).

$\hbar\gamma_{Si^{49}}\gamma_{F^{19}})J_{Si^{29}-F^{19}}$ is negative in agreement with the sign predicted by Pople and Santry.[2a]

The relative sign of $J_{Si^{29}-H^1}$ and $J_{H^1-C-Si-H^1}$ was obtained in a similar manner. In this case, however, the *lowest* Si^{29} frequency collapsed the *high-field* satellite pair indicating that the signs were opposite. Since the vicinal H^1-C-Si-H^1 coupling constant is almost certainly positive, it follows that $J_{Si^{29}-H^1}$ is negative. If the negative magnetogyric ratio is taken into account, however, the reduced coupling constant $K_{Si^{29}-H^1}$ is positive in agreement with the signs observed for other X-H couplings.

Acknowledgments.—The author is indebted to Drs. D. H. Whiffen, K. A. McLauchlan, and A. D. Cohen of the Basic Physics Division for many helpful discussions and to Dr. E. A. V. Ebsworth for kindly providing the samples investigated. This paper is published with the permission of the Director of the National Physical Laboratory, Teddington, Middlesex, England.

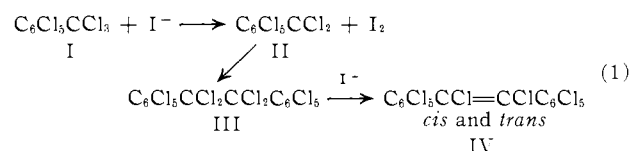DEPARTMENT OF CHEMISTRY   STEVEN S. DANYLUK
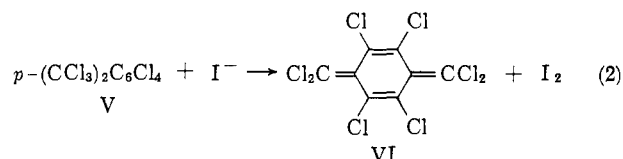UNIVERSITY OF TORONTO
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Perchlorodiphenylmethyl (PDM), a Carbon Free Radical of Remarkable Stability[1]

Sir:

Within our program on aromatic and alkaromatic chlorocarbons, we showed a few years ago the formation of perchlorobenzyl radical (II) in the reaction of perchlorotoluene (I) with iodide ion. This radical dimerizes to perchlorobibenzyl (III) which undergoes immediate dechlorination to *cis*- and *trans*-perchlorostilbene (IV).[2]

$$C_6Cl_5CCl_3 + I^- \longrightarrow C_6Cl_5CCl_2 + I_2$$

$$\text{I} \qquad\qquad\qquad \text{II}$$

$$C_6Cl_5CCl_2CCl_2C_6Cl_5 \xrightarrow{I^-} C_6Cl_5CCl=CClC_6Cl_5 \qquad (1)$$

$$\text{III} \qquad\qquad\qquad\qquad \text{cis and trans}$$

$$\text{IV}$$

The analogous reaction with perchloro-*p*-xylene (V) gives perchloro-*p*-xylylene (VI).[3] The ultraviolet and infrared spectra of this chlorocarbon in solution ruled out the alternative biradical structure.[4,5]

$$p\text{-}(CCl_3)_2C_6Cl_4 + I^- \longrightarrow Cl_2C=\!\!\!\begin{array}{c} Cl \quad Cl \\ \bigcirc \\ Cl \quad Cl \end{array}\!\!\!=CCl_2 + I_2 \qquad (2)$$

$$\text{V} \qquad\qquad\qquad\qquad\qquad \text{VI}$$

We now report the preparation of a stable, remarkably inert, carbon free radical, the perchlorodiphenyl-

(1) This work has been sponsored by the Office of Aerospace Research, United States Air Force, through contract AF 61(052)-749.

(2) M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959).

(3) M. Ballester and J. Castañer, *Anales real soc. español. fís. y quím.*, **56B**, 207 (1960).

(4) Its inertness contrasts with the high reactivity of the parent hydrocarbon (*p*-xylylene) which oxidizes and polymerizes very readily.

(5) Over 100 highly chlorinated and perchlorinated benzene derivatives synthesized by us, *including PDM*, show the intense characteristic benzenoid band group at 7.5 μ which is absent in perchloro-*p*-xylene and all non-benzenoid derivatives available to us. Also, the band group at 6.4–6.6 μ found in perchloro-*p*-xylene indicates the presence of conjugated perchloroethylene groupings. These observations rule out the biradical (benzenoid) structure for perchloro-*p*-xylene. Its ultraviolet spectrum is also consistent with a polyene structure of quinoid type.[4] Furthermore, perchloro-*p*-xylylene is not paramagnetic in solid form.

We are indebted to a referee for suggesting this explanatory footnote.

methyl (PDM, VIII). This can be obtained in good yield by the reaction between perchlorodiphenylmethane (VII) and stannous chloride in ethyl ether or chloroform. *Anal.* Calcd. for $C_{13}Cl_{11}$: C, 28.6; Cl, 71.4; mol. wt., 546.1. Found: C, 28.6; Cl, 71.4; mol. wt., 563 ± 25. E.s.r. data[6] show g-factors of 2.0062 (solid) and 2.0057 (in chloroform); N: 3.1 × 10^{23} spin/mole (solid)[7]; hyperfine splitting: 2.5 ± 0.1 gauss (in chloroform). No perchlorotetraphenylethylene is isolated.

$$(C_6Cl_5)_2CCl_2 + SnCl_2 \rightarrow (C_6Cl_5)_2CCl \qquad (3)$$

$$\text{VII} \qquad\qquad\qquad \text{VIII}$$
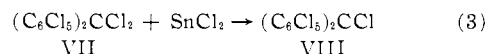
PDM consists of orange-red, paramagnetic crystals melting about 190° dec. Under certain conditions, the description of which is not pertinent to this brief preliminary note, PDM can be oxidized to perchlorobenzophenone or reduced to αH-undecachlorodiphenylmethane.

The facts given above show PDM's structure as well as its being a true free radical even in solid form. This is not unexpected for the following reasons.

On account of the steric interactions among the atoms around the α-carbon, VII is an extremely strained chlorocarbon. The formation of PDM occurs, therefore, with a great release of strain. Perchlorotetraphenylethane would be, consequently, prohibitively strained since it would result from VII by substitution of the huge PDM group for a chlorine.

A remarkable property of PDM in solid form is its stability toward oxygen. It can be left for months in the air without appreciable alteration, as ascertained by analyses and spectra. There is no question that this unique chemical inertness is due, at least to a great extent, to shielding of the central carbon atom and its lone electron by the surrounding atoms (two sp^2 carbons and five chlorines).

In forthcoming publications we shall describe and discuss in detail the preparation and properties of this and other stable free radicals.

(6) The authors are indebted to Dr. A. Horsfield, Varian A.G., Zurich, Switzerland, for the e.s.r. data and comments.

(7) Since the accuracy of absolute radical concentration determinations is probably not better than ±50% this datum is consistent with PDM being a 100% free radical.

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K_D/K_H for Base Ionization of Mono- and Dimethylamine

Sir:

The common tendency[1] to adopt the zero-point energy approximation[2] in discussing kinetic secondary deuterium isotope effects was shown to be inadequate for the solvolysis of isopropyl-β-d_6 halides and sulfonates,[3] and for α-phenylethyl-β-d_6 chloride.[4] For these examples $\delta_I\Delta F^* = \delta_I\Delta S^*$, approximately. Leffek,

(1) (a) E. A. Halevi, "Progress in Physical Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 2; (b) L. Melander, "Isotope Effects on Reaction Rates" The Ronald Press, New York, N. Y., 1960, pp. 43, 87.

(2) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(3) K. T. Leffek, R. E. Robertson, and S. Sugamori, *Can. J. Chem.*, **39**, 1989 (1961).

(4) P. Pacey, R. E. Robertson, and S. Sugamori, unpublished work.