$\hbar\gamma_{Si^{29}}\gamma_{F^{19}})J_{Si^{29}-F^{19}}$ 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.

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DEPARTMENT OF CHEMISTRY　　　　　　STEVEN S. DANYLUK
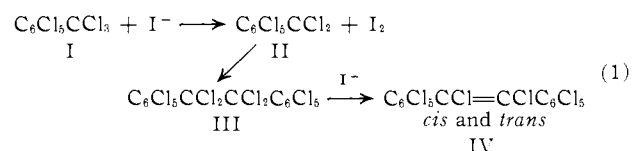UNIVERSITY OF TORONTO
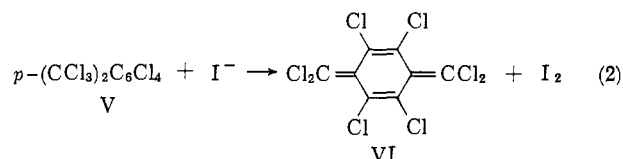TORONTO 5, CANADA

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]

$$C_6Cl_5CCl_3 + I^- \longrightarrow C_6Cl_5CCl_2 + I_2$$
$$\text{I} \qquad\qquad \text{II}$$
$$C_6Cl_5CCl_2CCl_2C_6Cl_5 \xrightarrow{\ I^-\ } C_6Cl_5CCl{=}CClC_6Cl_5 \qquad (1)$$
$$\text{III} \qquad\qquad\qquad \textit{cis} \text{ and } \textit{trans}$$
$$\text{IV}$$

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]

$$p\text{-}(CCl_3)_2C_6Cl_4 + I^- \rightarrow Cl_2C{=}\!\!\underset{\underset{\displaystyle \text{VI}}{Cl \quad Cl}}{\overset{Cl \quad Cl}{\bigcirc}}\!\!{=}CCl_2 + I_2 \qquad (2)$$

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. españ. 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 nonbenzenoid derivatives available to us. Also, the band group at 6.4–6.6 μ found in perchloro-*p*-xylylene indicates the presence of conjugated perchloroethylene groupings. These observations rule out the biradical (benzenoid) structure for perchloro-*p*-xylylene. 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.

$$(C_6Cl_5)_2CCl_2 + SnCl_2 \rightarrow (C_6Cl_5)_2CCl \qquad (3)$$
$$\text{VII} \qquad\qquad\qquad \text{VIII}$$
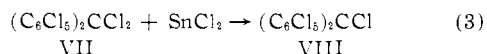
PDM consists of orange-red, paramagnetic crystals melting about 190° dec. Under certain conditions, the description of which is not pertinent to this brief preliminary note, PDM can be oxidized to perchlorobenzophenone or reduced to αH-undecachlorodiphenylmethane.

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.

DEPARTAMENTO DE QUÍMICA ORGÁNICA　　MANUEL BALLESTER
PATRONATO "JUAN DE LA CIERVA"　　　　JUAN RIERA
UNIVERSITY OF BARCELONA, SPAIN

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.