

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

The relative sign of $J_{\text{Si}^{29}\text{-H}^1}$ and $J_{\text{H}^1\text{-C-Si-H}^1}$ was obtained in a similar manner. In this case, however, the lowest Si²⁹ frequency collapsed the high-field satellite pair indicating that the signs were opposite. Since the vicinal H¹-C-Si-H¹ coupling constant is almost certainly positive, it follows that $J_{\text{Si}^{29}\text{-H}^1}$ is negative. If the negative magnetogyric ratio is taken into account, however, the reduced coupling constant $K_{\text{Si}^{29}\text{-H}^1}$ 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
UNIVERSITY OF TORONTO
TORONTO 5, CANADA

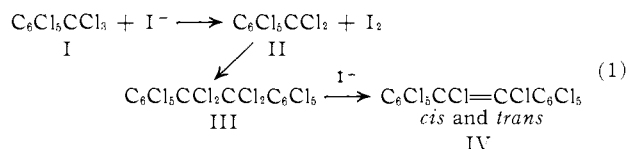
STEVEN S. DANYLUK

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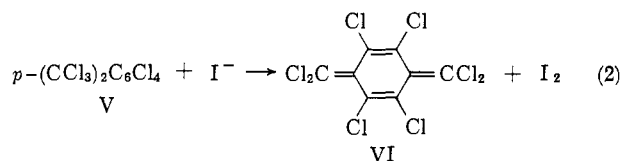
Perchlorodiphenylmethyl (PDM), a Carbon Free Radical of Remarkable Stability¹

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



The analogous reaction with perchloro-*p*-xylylene (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}



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).

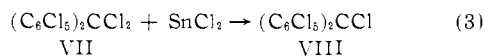
(3) M. Ballester and J. Castañer, *Anales real soc. españ. fis. y quim.*, **56B**, 207 (1960).

(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*-xylylene and all non-benzenoid 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.³ 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 C₁₂Cl₁₁: C, 28.6; Cl, 71.4; mol. wt., 546.1. Found: C, 28.6; Cl, 71.4; mol. wt., 563 \pm 25. E.s.r. data⁶ show *g*-factors of 2.0062 (solid) and 2.0057 (in chloroform); N: 3.1 \times 10²³ spin/mole (solid)⁷; hyperfine splitting: 2.5 \pm 0.1 gauss (in chloroform). No perchlorotetraphenylethylene is isolated.



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 α H-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 sp² 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 \pm 50% this datum is consistent with PDM being a 100% free radical.

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

MANUEL BALLESTER
JUAN RIERA

RECEIVED JULY 20, 1964

K_D/K_H for Base Ionization of Mono- and Dimethylamine

Sir:

The common tendency¹ to adopt the zero-point energy approximation² in discussing kinetic secondary deuterium isotope effects was shown to be inadequate for the solvolysis of isopropyl- β -*d*₅ halides and sulfonates,³ and for α -phenylethyl- β -*d*₅ chloride.⁴ For these examples $\delta_T\Delta F^* = \delta_I\Delta S^*$, 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.

et al.,³ suggested that this unexpected result could be explained if there was a decrease in the barrier to torsional motion of the methyl group on deuterium substitution in the initial state and that this barrier became small in the transition state. In a more detailed theoretical analysis, Bartell⁵ discussed the possibility that α and β secondary deuterium isotope effects could arise from changes in nonbonded interaction accompanying the change from tetrahedral to trigonal configuration.

Wolfsberg and Stern⁶ have shown that large normal temperature-independent isotope effects for such reactions can be calculated if force constants, which give rise to small frequencies (such as torsions), become larger in the transition state, and some large force constants (*e.g.*, C-H stretching) simultaneously become smaller. Since the un-ionized isopropyl halides do not interact strongly with the solvent, nucleophilic interaction could provide just such a condition in the activation process for solvolytic displacement by an SN2 mechanism. However, in addition to uncertainties with regard to the extent of such interaction and with respect to the degree of charge development, there must be added the possibility of anharmonicity, of tunnelling, and of possible variation in the transmission coefficient.

These kinetic uncertainties are in some measure removed and the position for argument and discussion of this surprising phenomena materially strengthened by the discovery that the secondary deuterium isotope effect for the thermodynamic dissociation constants in acid-base equilibria involving mono- and dimethylamine are temperature independent over 30–40° temperature range (Table I).

TABLE I
 K_D/K_H FOR BASE IONIZATION OF MONO- AND DIMETHYLAMINES IN WATER

| T, °C. | K_D/K_H | |
|--------|-----------------|---------------|
| | Monomethylamine | Dimethylamine |
| 5 | 1.14 | |
| 10 | | 1.32 |
| 15 | 1.16 | 1.32 |
| 20 | | 1.31 |
| 25 | 1.12, 1.13 | 1.31 |
| 30 | | 1.31 |
| 35 | 1.14 | 1.32 |
| 40 | | 1.33 |
| 45 | 1.13 | |

The deuterated compounds were better than 97% $-d_3$ and $-d_6$, respectively. Equilibrium values were obtained by a conductance method adapted from that described by Ives and Pryor.⁷ The concentration of amine was in the range 0.003–0.007 mole/l.

Everett and Wynn-Jones⁸ report $K_B = 0.0004246$ for monomethylamine at 25°. We found 0.0004517. For dimethylamine the corresponding values are 0.0005954 and 0.000604. Since the potentiometric method is expected to give low values of K_B ,⁷ the difference is probably not important.

The solvated methylammonium ion is not a good model for the transition state in the solvolysis of second-

ary halides but it will be obvious that the same type of calculation proposed by Wolfsberg and Stern⁶ will be expected to yield similar temperature-independent isotope effects for amine equilibria provided suitable changes in force constants are assumed.⁹

In this connection it is significant that MacLean and Leffek¹⁰ have recently reported that the *inverse* isotope effect associated with the displacement of I⁻ from methyl iodide by amines in benzene is temperature independent.

(9) M. Wolfsberg, private communication.

(10) J. W. MacLean and K. T. Leffek, Spring Meeting, C. I. C. Kingston, 1964.

(11) National Research Council of Canada Postdoctoral Fellow 1961–1963.

N.R.C. No. 8182
DIVISION OF PURE CHEMISTRY
NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

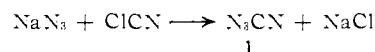
WM. VAN DER LINDE¹¹
R. E. ROBERTSON

RECEIVED MAY 13, 1964

Cyanogen Azide

Sir:

Cyanogen azide (1) has been synthesized in virtually quantitative yield from the reaction of sodium azide with cyanogen chloride in aprotic media.¹ This new



azide has a versatility and scope of chemical reactivity that is very broad and useful.

Cyanogen azide, a colorless oil, detonates with great violence when subjected to mechanical or thermal shock, and *great care should be taken in any work with this compound*. It can be handled relatively safely in solvents where most of its properties have been studied. The half-life of a 27% solution of the azide in acetonitrile is 15 days at room temperature, but this solution can be stored indefinitely without change at 0 to –20°. The pure azide is too sensitive for combustion analysis; however, its molecular weight (freezing point in benzene) is 69 (calcd. 68).

The infrared spectrum of 1 in carbon tetrachloride shows absorptions at 2240 (s), 2199 (vs), 2143 (s), and 2090 (s) cm^{-1} (associated with the nitrile and azide stretching vibrations) and at 1245 (vs) cm^{-1} (C–N stretching). In cyclohexane, 1 has two resolved absorptions at 275 (ϵ 103) and 220 $\text{m}\mu$ (ϵ 2157). The mass spectrometric cracking pattern of 1 shows a peak of 48% relative abundance for the parent and is entirely consistent with the formulated structure.

The synthesis of cyanogen azide is carried out by adding cyanogen chloride to sodium azide. Excess cyanogen chloride or anhydrous aprotic solvents may be used as reaction media. In a typical preparation, sodium azide was suspended in dry acetonitrile, and cyanogen chloride was distilled into the mixture at a rate to maintain the temperature below 12°. The solution was allowed to warm to room temperature and filtered to remove sodium chloride. The use of dry solvents is important to avoid the formation of explosive, solid by-products, and care also must be taken

(1) There are several references to cyanogen azide in the older literature, none of which appear correct. For example, M. G. Darzens (*Compt. rend.*, **154**, 1232 (1912)) obtained a crystalline product incorrectly characterized as N_3CN , which was later suggested by C. V. Hart [*J. Am. Chem. Soc.*, **50**, 1922 (1928)] to be guanyl azide, a result we have now confirmed.

(5) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).

(6) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).

(7) D. I. G. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955).

(8) D. D. Everett and W. F. R. Wynne-Jones, *Proc. Roy. Soc. (London)*, **A177**, 499 (1941).