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PERCHLORO-9-PHENYLFLUORENYL, A REMARKABLY STABLE CARBON FREE RADICAL

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THE chemical stability of aryl substituted methyl radicals is the result of a compromise between two main factors: steric hindrance to bonding with the trivalent carbon, and delocalization of the lone electron, *the former being the predominant*.[1,2]

By far, the highest inertness occurs in perchlorotriphenylmethyl radicals where shielding of the central carbon is almost perfect on account of the three pairs of *ortho* chlorines surrounding it in its strain-free, helicoidal array. In fact, their stability is so high that they have been termed "inert free radicals".[1,2]

However, some of these inert radicals, such as perchlorotriphenylmethyl (PTM), are light sensitive in solution.[1] Since the parent hydrocarbon, the triphenylmethyl (trityl) radical, gives readily bi-9-phenylfluorenyl when exposed to light,[3,4] it was assumed that the resulting greenish solution contained perchloro-9-phenylfluorenyl (PPF) radical. This was suggested to other researchers who, working on the hypothesis that either cyclization to PPF or bicyclization to perchlorofluoradenyl radical occurred, have found that the *alpha* ^{13}C hyperfine splitting observed was consistent with the calculated value for the formation of PPF only.[5] "Capture" of PPF with chlorine was attempted and, accordingly, among other chlorocarbons, some perchloro-9-phenylfluorene (I) was isolated.[6]

The authors now wish to report a number of high- to excellent-yield syntheses of PPF by thermolysis, at temperatures ranging from 250 to 320º, of compounds with well-established structures: perchloro-9-phenylfluorene[6,7] (I; 80% yield), αH-pentadecachloro-2-phenyldiphenylmethane[7] (II; 93%), perchloro-2-phenyldiphenylmethyl radical[7] (PODM; 84.5%), perchloro-2-phenyldiphenylmethane (III; 73%), and perchlorotriphenylmethyl radical[1,2] (PTM; 78.5%).

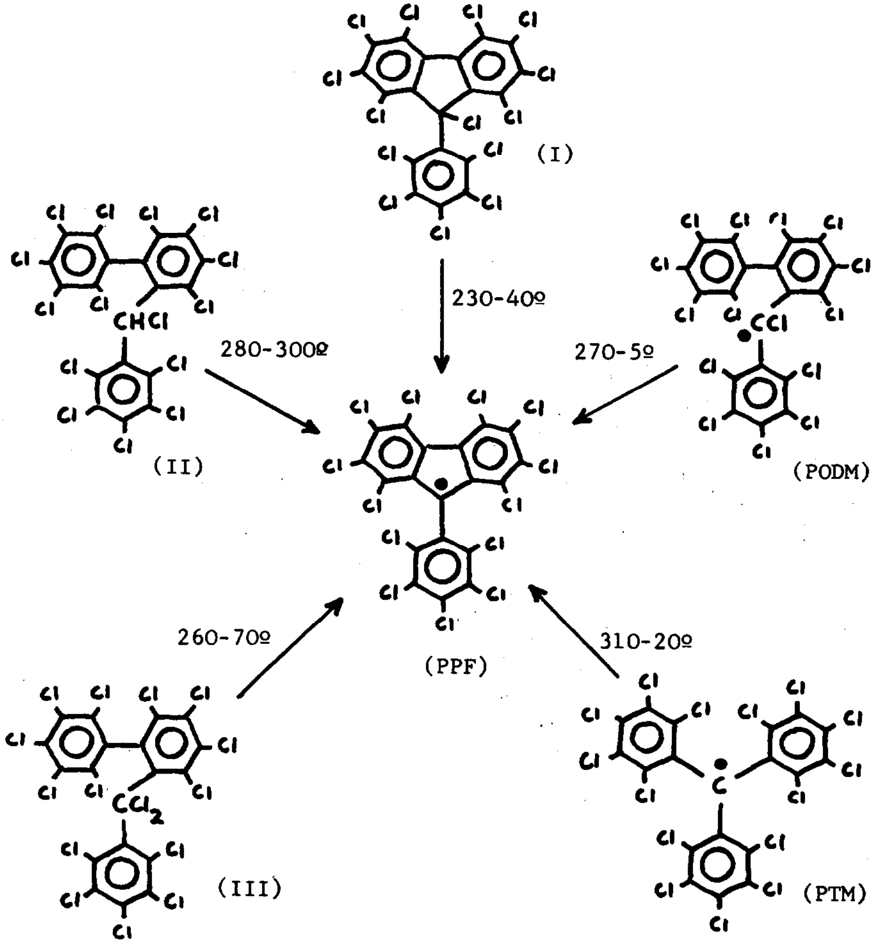
PPF is a completely disassociated, deep-green radical melting at about 300º.

Anal Calcd. for $C_{19}Cl_{13}$: C, 33.1; Cl, 66.9. Found: C, 33.1; Cl, 66.9. *Mol. weight* Calcd.: 689.10. Found: mass spectr., 689.10; magnetic suscept. (solid), 693. *ir* (KBr) 1486 (w), 1380 (s), 1342 (s), 1305 (w), 1298 (s), 1260 (s), 1090 (s), 815 (s), 698 (m), 640 (s), 516 (m), 500 (m) cm^{-1}. *uv-vis* (cyclohexane) λ (ε) 217 (73,500) (max), 230 (47,000) (sh), 293 (45,500) (max), 320 (13,600) (sh), 373 (5180) (max), 388 (6150) (max), 408 (3790) (max), 460 (1330) (max), 498 (1170) (max), 530 (645) (max), 573 (2030) (max), 622 (5080) (max) nm. *epr* (CCl_4) Principal line: g, 2.0043; half-width, 13.2 MHz. Overlapping $\alpha^{13}C$ satellite pair: a 58 MHz.

Photolysis of PTM with white incandescent light, in carbon tetrachloride, has been performed, the epr of the resulting solution being identical to that of pure PPF. The epr data is close to those reported by Luckhurst and Ockwell,[5] *i.e.*, half-width and $\alpha^{13}C$ splitting. (They omitted to report the g-value.) Uv-vis absorptivity indicates yields of PPF up to 15% of theory.

PPF is perfectly stable towards oxygen in solid form. Very dilute solutions in the dark, at room temperature, are not appreciably affected after months either (uv-vis absorptivity). The chemical stability of PPF is remarkable since it withstands well a number of aggressive chemicals such as sodium hydroxide, concentrated sulfuric or nitric acids, bromine, and chlorine, as well as some radical reagents (hydroquinone, and *p*-quinone). However, its stability is not so high as that of radicals of the PTM series,[1,2] for it reacts with nitric oxide and with boiling toluene. This can be accounted for as follows:

The process of going from trityl to 9-phenylfluorenyl radical causes deep changes in the molecular steric characteristics: The propeller-like configuration is lost and, consequently, although delocalization of the lone electron is substantially increased,[8,9] steric protection afforded by the three benzene rings collapses. Accordingly, at low temperature trityl is in equilibrium in a relatively significant amount with its dimer[10,11] whereas 9-phenylfluorenyl is almost completely associated. The latter is regarded as a much more reactive species.



A definite parallelism exists with the corresponding perchloro radicals. Cyclization of PTM to PPF results in a diminished shielding of the trivalent carbon. Of the three pairs of <u>ortho</u> chlorines in PTM, one disappears, another becomes less protective because of its moving away from the trivalent carbon, while the third stays as effective.

As far as the thermal stability of PPF is concerned, the fact that this radical is prepared by heating around and even above 300º, speaks for itself.

The chemistry of this radical and related compounds will be described in detail in forthcoming papers.

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References

1) M. Ballester, Pure and Appld. Chem., 15, 123 (1967).
2) M. Ballester, J. Riera-Figueras, J. Castañer, C. Badía and J. M. Monsó, J. Amer. Chem. Soc., in press.
3) M. Gomberg and L. H. Cone, Ber., 37, 3545 (1904).
4) J. Schmidlin and A. García-Banús, Ber., 45, 1344 (1912).
5) G. R. Luckhurst and J. N. Ockwell, Tetrahedron Letters, 1968, 4123.
6) C. Badía, Doctoral Thesis, University of Barcelona (1968).
7) M. Ballester, J. Castañer and J. Riera-Figueras, "Synthesis and Properties of Alkaromatic Chlorocarbons", US Clearinghouse Fed. Sci. Tech. Inform., 1968, AD 672319. (Chem. Abstrs., 70, 46980t (1969).)
8) G. W. Wheland, "Resonance in Organic Chemistry", Wiley (1955), p. 384.
9) A. Streitwieser, "Molecular Orbital Theory", Wiley (1961), p. 394.
10) H. Lankamp, W. Th. Nauta and C. MacLean, Tetrahedron Letters, 1968, 249.
11) H. Lankamp, Doctoral Thesis, Free University of Amsterdam (1970).