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PERCHLOROBENZYL, A STABLE CARBON FREE RADICAL

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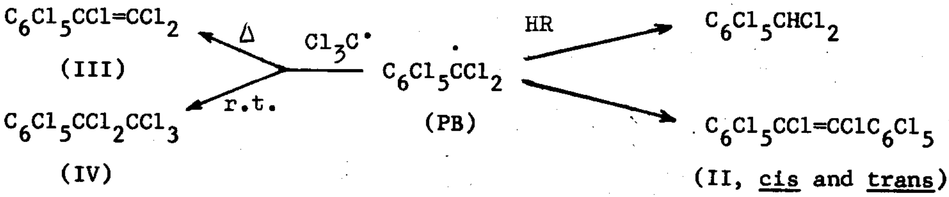
THE formation of perchlorobenzyl (PB) radical has already been postulated in order to account for a number of reactions of perchlorotoluene (I),[1] such as its reducto-dimerization to the perchlorostilbenes (II),[2] its thermolysis to a mixture of CCl_4, perchlorobenzene and perchlorostyrene (III),[3,4] and its photolysis in CCl_4 by ultraviolet light giving a mixture containing perchloroethylbenzene (IV) and other chlorocarbons.[4,5]

$$\underset{\text{(PB)}}{C_6Cl_5\dot{C}Cl_2} + Cl^- \xleftarrow{+e} \underset{\text{(I)}}{C_6Cl_5CCl_3} \xrightarrow[\text{or } h\nu]{\Delta} \underset{\text{(PB)}}{C_6Cl_5\dot{C}Cl_2} + Cl$$

No direct evidence for its existence has been reported however. It was assumed that the formation of PB is assisted by the high steric strain of I due to the strong steric interactions between the *ortho* and the *alpha* chlorines. According to the reaction conditions, PB was found to react with other free radicals such as trichloromethyl (photolysis in CCl_4),[4,5] add a hydrogen from the media (reductions in the presence of hydrogen donors),[2] or undergo dimerization with subsequent loss of chlorine.[2]



The ease of formation of II from I, even at 100º in the presence of hydrogen-donor solvents such as acetic acid[2] or DMSO,[6] infers considerable stability for PB. All attempts to isolate the dimer perchlorobibenzyl (V) were unsuccessful, a fact which was readily explained by the high steric strain in its molecule. It was found, however that reduction of 2*H*-heptachlorotoluene under the relevant reaction conditions permits the isolation of 2*H*,2'*H*-dodecachlorobibenzyl as an intermediate in the formation of 2*H*,2'*H*-decachlorostilbenes,[2] this being due to the relatively unimportant steric repulsions compared with those of V.

The authors now wish to report the detection of the perchlorobenzyl (PB) radical by means of *epr* spectroscopy, as well as its preparation in stable form. It has been found that the reaction of I with alkaline iodides in acetic acid or with $SnCl_2$ in ethers gives a strong, transient *epr* signal. An identical spectrum has been obtained by illumination of a solution of I in CCl_4 with ultraviolet light; the concentration of PB falls sharply in the dark however, because of extensive recombination with the liberated molecular chlorine. This procedure has led to the successful preparation of a stable solution of PB by treatment with copper turnings during the illumination, this destroying the chlorine formed. When the copper is removed and the light switched off, an initial second-order decay of the signal is observed, this rapidly reaching a steady concentration. The resulting solution gives a strong *epr* signal at room temperature which remains unchanged for months, and which is greatly enhanced on warming ($\sim$10 fold increase at 80°C), the original signal intensity being restored on cooling back to room temperature. These phenomena show that at room temperature PB is indeed in equilibrium with a dimer, presumably V. An alternative structure for the dimer[7] is unlikely since II is obtained.[2]

$$\underset{(PB)}{2\ C_6Cl_5CCl_2} \rightleftharpoons \underset{(V)}{C_6Cl_5CCl_2CCl_2C_6Cl_5}$$

The intermediate formation of V in the reducto-dimerization and the photolysis of I is thus confirmed.

As far as the authors know, PB is the only known benzyl radical which is partly disassociated at low temperatures. This remarkable fact is traced to the very high frontal strain of the dimer; *i.e.*, the repulsions between α- and α'-chlorines, buttressed by the *ortho* chlorines, which greatly weaken the central carbon-carbon bond. The steric strain of I has been estimated to be of the order of twenty kcal/mol.[1,8] Substitution of a chlorine by a perchlorobenzyl group to give V should increase this strain greatly. Furthermore, it is well known that benzyl radicals are stabilized by odd-electron delocalization, and that the chlorine has a stabilising effect on carbon free radicals.

When the distances between two chlorine atoms are smaller than 3.0 Å there is significant steric compression (and molecular distortion). The distance between the nuclei of an *ortho* and an *alpha* chlorine in the planar conformation of PB (maximum resonance energy) is about 2.5 Å. Therefore, such a conformation would be highly strained. In the actual conformation, however, relief is obtained by rotation of the dichloromethylene group about its bond until a balance between the force tending to restore that planar conformation, and the steric repulsions is reached. The angle θ between the planes of the groups has been estimated by the "proton homomorph" method devised by the authors, which is based on the assumption that this balance is about the same for PB and for its homomorph 4*H*-hexachlorobenzyl radical (VII). Consequently, θ should also be about the same.

4*H*-Heptachlorotoluene forms VII in the same fashion as I yields PB; *i.e.*, by reduction with iodide ion in acetic acid[9] or $SnCl_2$ in dioxane, or by illumination with ultraviolet light in CCl_4. Its *epr* spectrum shows no splitting due to the proton. This unexpected result indicates that the spin density at the *para* carbon atom is nearly zero. (4*H*-Tetradecachlorotriphenylmethyl and 4*H*,4'*H*,4"*H*-dodecachlorotriphenylmethyl radicals show definite splittings due to the protons ($\sim$ 5.5 MHz)).[6]

McLachlan's approximation[10] has been used to calculate the spin density distribution at carbon or chlorine atoms.

The spin densities at the *para* carbon are calculated as a function of θ. For a tilting angle of about 60° the spin density becomes zero, and consequently, the tilting in PB should be close to this value.

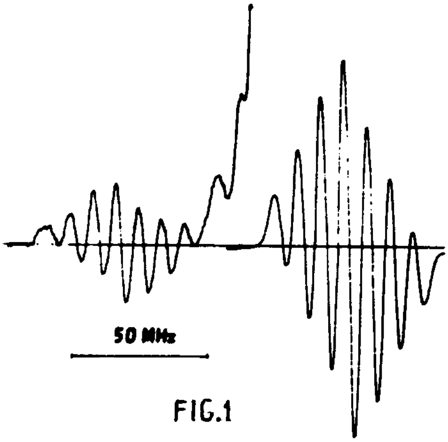


FIG.1

Epr spectrum PB possesses two chlorines attached to the *alpha* carbon. Accordingly, 7 lines with the expected intensity ratios are observed (Fig. 1). Because of the angle of tilting θ , and the attachment of only one benzene ring to the *alpha* carbon, the odd-electron localization on that carbon is high and so the coupling constant with the *alpha* ^{13}C satellite peaks (166 MHz) (perchlorodiphenylmethyl (PDM) radical, 102; perchlorotriphenylmethyl (PTM) radical, 82.5 MHz).[11] The coupling constant with the chlorine bonded to that carbon is, accordingly, significantly higher (8.4 MHz) than that of PDM (6.1 MHz).[14] Landé's g value is unusually high (2.0072 ± 0.0003) (PDM, 2.0055 ± 0.0003; PTM, 2.0026 ± 0.0003)[11] indicating important spin-orbit coupling with the chlorines. The broadness of the *epr* peaks, found also in other perchlorinated radicals,[11] is traced to interaction with the ring chlorines.

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