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PERCHLORODIPHENYLNITROXIDE, A REMARKABLY STABLE, ISOLABLE FREE RADICAL

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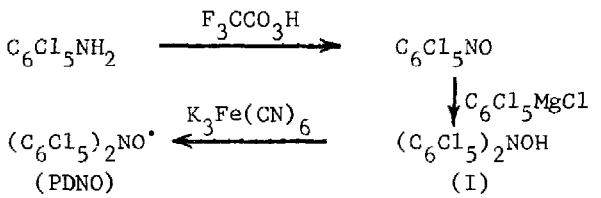
The extreme inertness of perchloropolyarylmethyls[1] and perchloro-9-phenylfluorenyl[2] and the exceptional stability of perchlorodiphenylaminyl[3] radicals are traced to steric shielding of the atom with abnormal valence. We report here the synthesis, isolation and some properties of the first example of a new type of shielded radicals: the perchlorodiphenylnitroxide (PDNO). In this connection it is mentioned that the most stable diarylnitroxides have "inactive" blocking substituents in the para-positions.[4]

PDNO has been synthesized by oxidation of 2,3,4,5,6-pentachloroaniline with peroxytrifluoroacetic acid to pentachloronitrosobenzene (78% yield) in chloroform-water (room temp.), followed by reaction with a great excess of pentachlorophenylmagnesium chloride in THF (-15°, dark) to bis(pentachlorophenyl)hydroxylamine (I; 51%), m.p. 225-7°(dec.), and finally oxidation with potassium ferricyanide in benzene-water (room temp., dark; 98%).



Anal. Calcd. for $C_{12}HCl_{10}NO$ (I): C, 27.2; H, 0.2; Cl, 66.9; N, 2.6. Found: C, 27.1; H, 0.2; Cl, 67.1; N, 2.6. ir (KBr) ν 3460 (w), 1515 (vw), 1410 (s), 1389 (s), 1341 (s), 1330 (m), 1300 (m), 1280 (m), 798 (s), 735 (m), 690 (s), 640 (m), 633 (m), 532 (s), 428 (s) cm^{-1}. uv (C_6H_{12}) λ (ε) 222 (42,200; max), 245 (21,200; sh), 332 (14,800; max) nm. nmr ($CDCl_3$) τ 2.89 (s).

PDNO forms red-brown needles (from chloroform), m.p. 185-7° (dec.). In solid it is a completely disassociated radical (magnetic susceptibility).

Anal. Calcd. for $C_{12}Cl_{10}NO$: C, 27.3; Cl, 67.1; N, 2.7. Found: C, 27.3; Cl,

67.0; N, 2.7. ir (KBr) ν 1517 (vw), 1371 (m), 1352 (s), 1341 (s), 1260 (m), 813 (m), 752 (m), 712 (m), 700 (m), 650 (m) cm^{-1}. uv (C_6H_{12})-visible ($CHCl_3$) λ (ε) 222 (45,000; max), 243 (19,850; sh), 266 (3580; sh), 304 (3900; sh), 330 (6150; sh), 339 (7710; max), 400 (530; sh), 550 (68; sh) nm. Magn. suscept. χ_{dia} $-0.485 \cdot 10^{-6}$, θ 0.5°K, Bohr magnetons 1.71, spins/mole $5.92 \cdot 10^{23}$ (97.7%). epr (benzene) g 2.0060 ± 0.0003, triplet 1,1,1, a_N 8.4 gauss, width 1.4; a(^{13}C) 7.3 gauss. The fact that a_N is lower than that of diphenylnitroxide (9.9 gauss, same solvent[5]) is regarded as due to the acummulated electron-withdrawing effect of the chlorines.[6]

PDNO is moderately soluble in chloroform, carbon tetrachloride or benzene and slightly soluble in cyclohexane. In solid, in the dark, it remains unchanged for months. In damp THF it decomposes slowly. By illumination with incandescent light (5 days; chloroform) it gives a complex mixture containing bis(pentachlorophenyl)amine;[7] no change is observed in the dark. It reacts instantaneously with ascorbic acid (damp THF);[8] other acids (benzoic acid, tartaric acid) have no significant effect.

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