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SYNTHESES AND ISOLATION OF THE PERCHLORODIPHENYLAMINYL, AN EXCEPTIONALLY STABLE RADICAL

M. Ballester, J. Castañer and S. Olivella

Instituto de Química Orgánica, Patronato "Juan de la Cierva" (C.S.I.C.)
Zona Universitaria, Barcelona 17, Spain

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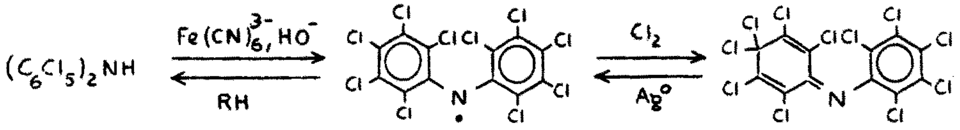
THE tetraarylhydrazines in solution, at room temperature, are either undissociated or slightly dissociated into the corresponding diarylaminyl radicals.[1] Solids have been obtained containing small amounts of 2,6-dinitrophenyl aryl aminyl radicals,[2] and it would appear that some of these have recently been isolated.[3]

The authors report here the syntheses and isolation of an exceptionally stable diphenylaminyl radical: perchlorodiphenylaminyl (PDA). It has been synthesized in different ways: a) Oxidation of NH-decachlorodiphenylamine (I)[4] with an aqueous, alkaline solution of potassium ferricyanide or with silver II oxide; b) dechlorination of perchloro-N-phenylcyclohexan-2,5-dienimine (II)[4] with molecular silver. Magnetic susceptibility measurements show that PDA obtained by the last method reaches 83% purity, the yield being 87% of theory.



(I) (PDA) (II)

PDA is a crystalline, deep-green solid melting at about 218-20° (dec.). Anal. Calcd. for $C_{12}Cl_{10}N$: C, 28.1; Cl, 69.2; N, 2,7. Found: C, 28.0; Cl, 69.2; N, 2.6. ir (KBr) $\bar{\nu}$ 1550 (w), 1480 (m), 1403 (m), 1345 (s), 1270 (s), 1110 (m), 1020 (m), 785 (s), 705 (s), 655 (m), 635 (m), 600 (m) cm^{-1} . uv-vis

(CCl_4) λ (ε) 281 (16,000; sh), 296 (16,700; max), 335 (8.220; sh), 343 (8,000; min), 363 (10,400; max), 397 (506; min), 453 (1,390; sh), 470 (2,300; max), 515 (137; min), 665 (425; max) nm. *epr* (CCl_4) g, 2.0054 $\pm$ 0.0003, triplet 1.1.1, $a_N = 22.4$ MHz; line width, 11.2 MHz.

Solid PDA can be kept in the air for months without appreciable alteration. Its half-life is about two months in carbon tetrachloride (uv-visible spectroscopic concentration), in contact with air at room temperature.

PDA can be reduced to I by means of a) iodide ion in acetic acid (80% yield); b) stannous chloride in ethyl ether-chloroform (91%); and c) sodium in benzene (88%). It readily reacts with chlorine in carbon tetrachloride to give a mixture from which a 23% yield of II can be isolated (the rest is practically pure I).

PDA at room temperature reacts rapidly with toluene and other arylmethanes by abstraction of a hydrogen giving I (64% yield).

The relative inertness of PDA is traced to the shielding of its nitrogen by the four *ortho* chlorines.[5] It is, however, more reactive than perchlorodiphenylmethyl (PDM) radical,[5] a fact which, together with the lack of dissociation of *sym*-1*H*,2*H*-icosachlorotetraphenylethane at room temperature,[6] shows clearly the importance of the shielding of a chlorine on the atom where most spin density resides.

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