Oxidation of Ethyl 3-[Bis-(*N*-methylanilino)phosphinoyl]carbazate

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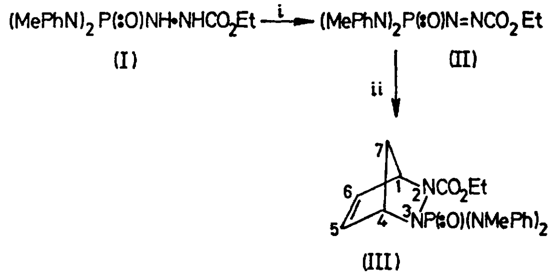
Summary Ethyl 3-[bis-(*N*-methylanilino)phosphinoyl]carbazate has been oxidized to the corresponding azo-compound by lead tetra-acetate; the product was characterised by formation of a Diels–Alder adduct with cyclopentadiene.

Bock has reported[1] the formation of several azophosphinoyl systems by oxidation of the corresponding disubstituted hydrazines with *N*-bromosuccinimide or HgO. We found that these reagents were unsatisfactory for the oxidation of compound (I) to the derivative (II), which we obtained, instead, as a red viscous oil, by use of $Pb(OAc)_4$[2] in $CHCl_3$. Its i.r. [ν_{max} ($CHCl_3$) 1765(CO) and 1230br (P = O) cm^{-1}] and n.m.r. (no doublet at τ 4·41) spectra showed the absence of N–H bonds. The azo-compound (II) was further characterized by its reaction with cyclopentadiene in CCl_4 (17 h) which gave the Diels–Alder adduct (III) as a green glass;† ν_{max} ($CHCl_3$) 1740 (CO) and 1185 (P=O) cm^{-1}; τ 2·3—3·0 (10H, m, ArH), 3·65 (1H, m, 1-H), 5·21 (2H, d, *J* 10 Hz, 5- and 6-H), 5·88 (2H, q, *J* 7 Hz, OCH_2), 6·72 and 6·87 (6H, 2 × d, J_{PNMe} 10—11 Hz, NMe), 7·79 (1H, d, *J* 9 Hz, 4-H), 8·50 (2H, d, *J* 9 Hz, 7-H), and 8·79 (3H, t, *J* 7 Hz, OCH_2Me); *m/e* 426·1811 (M^+). The absence of a u.v. band at 464 nm, which was present for compound (I), showed the absence of the azo-chromophore in (III). The carbonyl stretching frequency (1765 cm^{-1}) in the azo-compound (II) was appreciably higher than for the hydrazine (I) (double absorption at 1750, 1742 cm^{-1}) or the Diels–Alder adduct (III) (1740 cm^{-1}) (*cf.* ref. 3).

The formation of the Diels–Alder adduct is of considerable interest since this is the first reported Diels–Alder reaction with an azophosphinoyl system. Several dialkyl azodicarboxylates are, however, known[4] to undergo the reaction although it has been claimed[5] that monocarbonyl azo compounds do not react.



Reagents: i, $Pb(OAc)_4$; ii, cyclopentadiene.

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† Satisfactory elemental analytical results were obtained for C, H, N, and P.

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