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A NOVEL CYCLIZATION TO A BENZIMIDAZOLE

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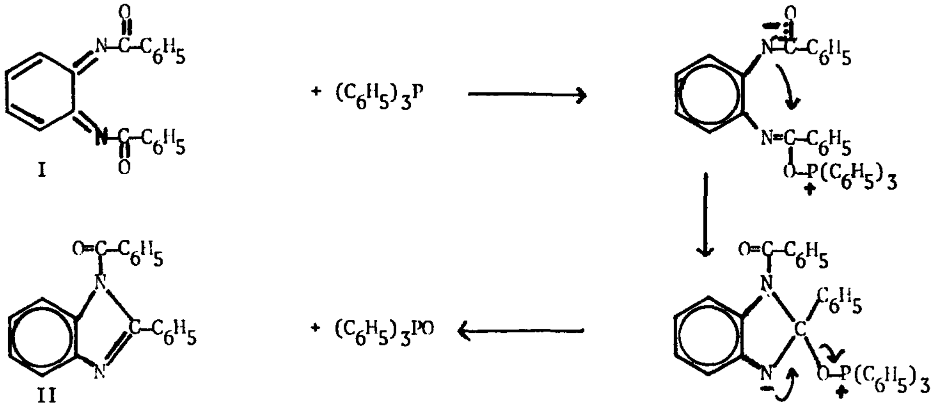
The reactions of trivalent phosphorus compounds with ortho and para quinones and their derivatives present a variegated pattern of pathways which has been the subject of many recent studies,[2] but in which analogy is often a treacherous guide. We now add to this variety by reporting the novel reductive cyclization of o-benzoquinonedibenzimide (I) by triphenylphosphine under neutral conditions at ambient temperatures.

The addition of triphenylphosphine (1.3 g) to a solution of I (1.57 g) in carefully dried benzene (100 ml) under nitrogen, caused the discharge of the yellow color of the quinoneimide. Removal of solvent and crystallization from hexane yielded a solid. Spectral data and t. l. c. (silica gel;hexane-ethyl acetate 2/1, $^{v}/v$) showed it to be a mixture of triphenylphosphine oxide and 1-benzoyl-2-phenylbenzimidazole (II) only. These were separated by column chromatography (silica gel 0.05-0.2 mm; chloroform eluent). Compound II eluted first and was recrystallized from hexane, m.p. 145-146°;u.v. (95% ethanol) λ_{max} 271 mμ (ε 34,000);i.r. (KBr)$\bar{\nu}_{max}$ 1700 cm^{-1} (amide carbonyl); nmr ($CDCl_3$) complex of aromatic hydrogens only, δ 7.10-7.93. In the mass spectrum the two most intense peaks were those of the molecular ion,m/e 298 (base peak) and the benzoyl ion, m/e 105 (rel. abund. 68%). The only other ions appearing in relative abundance greater than 1% were those characteristic of 2-phenylbenzimidazole,[3] m/e 194 (1.2%), m/e 193 (1.8%),m/e 192 (1.2%), m/e 166 (1.1%). Elemental analysis of II: Calc. for $C_{20}H_{14}N_2O$; C, 80.52; H, 4.73; N, 9.39; Found: C, 80.42; H, 4.78; N, 9.28%.

The structure of II was further confirmed by acid hydrolysis (0.5 hydrochloric acid, reflux 4 hrs.) which yielded benzoic acid, minor amounts of o-phenylene dibenzamide (III), and the known 2-phenylbenzimidazole as principal product. These were separated by column chromatography on silica gel and the imidazole was identified by m.p., u.v.,[4] i.r.,[5] mass spectrum[3] and elemental analysis.

We propose the mechanism illustrated in the figure for the cyclization in question. Alternatively, an attack of the phosphine on the nitrogen of the imide may be envisaged, with appropriate modification of subsequent steps. In view of the proclivity of trivalent phosphorus to form the very stable P-O bond, the pathway shown in the figure seems more likely.



Replacement of triphenylphosphine by trimethyl phosphite in the reaction with I resulted in a mixture of II with lesser amounts of III and an unidentified yellow oil.

The cyclization reported for I is of course precluded in the case of its para isomer, p-benzoquinonedibenzimide. The reactions of the latter with triphenylphosphine and with trialkyl phosphite yielded multicomponent mixtures which defied our attempts at separation and characterization. It is mentionable that Mustafa et al.[2b] recently reported that the action of dialkyl phosphite on this *p*-diimide resulted essentially only in its reduction to *p*-phenylene dibenzamide.

FOOTNOTES AND REFERENCES

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