Preparation of a Dibenzo[*b*,*e*]phosphorin. Selective Phosphine Oxide Reduction by Trichlorosilane.

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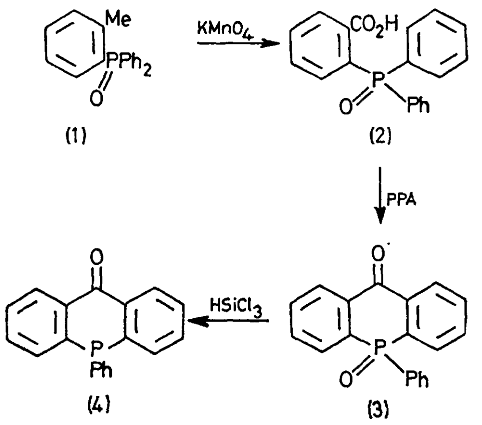
Summary 5,10-Dihydro-5-phenyldibenzo[*b*,*e*]phosphorin-10-one 5-oxide (**3**) has been prepared by the action of polyphosphoric acid on *o*-diphenylphosphinylbenzoic acid, and has been selectively reduced by trichlorosilane to the ketophosphine (**4**).

THE growing interest in potentially aromatic phosphorus heterocycles[1,2] has led to two syntheses of the dibenzo[*b*,*e*]-phosphorin skeleton.[3,4] These multi-step procedures have also been the major approaches to the syntheses of polynuclear C–P heterocycles,[5] using C–P bond formation for the cyclisation reaction. We now report a novel approach exemplified by the preparation of 5,10-dihydro-5-phenyldibenzo[*b,e*]phosphorin-10-one 5-oxide (**3**) (Scheme).



Scheme

Diphenyl(*o*-tolyl)phosphine oxide (**1**) (m.p. 124—125°) was prepared[6] by the reaction of *o*-tolylmagnesium bromide and diphenylphosphonous chloride followed by H_2O_2 oxidation (73%). It was converted with potassium permanganate into *o*-diphenylphosphinylbenzoic acid (**2**) (m.p. 274—275°) (75%). Finally the phosphorin (**3**) was obtained by heating (**2**) with freshly prepared polyphosphoric acid (PPA) for 3 h at 175° (50%), and treating the mixture with crushed ice. M.p. 222—223° (from ethanol); λ_{max} (EtOH) 240 sh ($\log \epsilon$ 5·26), 261 (4·93), and 284 nm (4·96). The mass spectrum showed a parent peak at *m/e* 304.

Further derivatives of (**3**) can be synthesised by this method and the carbonyl function in (**3**) is accessible to further transformations. Our "acylation–cyclisation" technique forms a rare example of electrophilic substitution in aromatic phosphine oxides. The temperature of the cyclisation reaction, apparently plays a specific role, as only starting material and a polymeric product were obtained at 130—140°. This failure recalls previous unsuccessful attempts[7,8] at the synthesis of the benzo[*b*]phosphorin skeleton.

Phosphine oxides[9] and ketones[10] are reduced by various silicon compounds. However, heating (**3**) and an excess of trichlorosilane in benzene at reflux, yielded, after the usual[9] work-up, the keto-phosphine (**4**), m.p. 135° (ethanol) (90%). Thus, the phosphine oxide (**3**) has been selectively reduced.

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