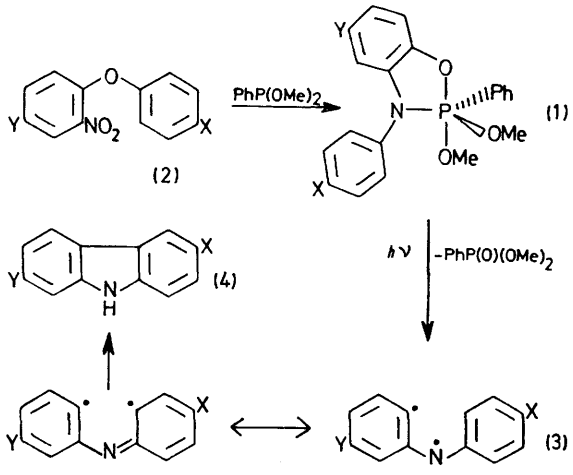
Formation of Carbazoles by Photolytic Extrusion of Dimethyl Phenylphosphonate from Oxazaphosphoranes. A Phosphorus Analogue of the Graebe-Ullmann Reaction

By J. I. G. CADOGAN,* BRIAN S. TAIT, and NEIL J. TWEDDLE
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary A phosphorus analogue of the Graebe-Ullmann reaction is described in which the carbazoles (**4**) are formed by photolytic extrusion of $PhP(O)(OMe)_2$ from the oxazaphosphoranes (**1**); this provides a two-step, complete deoxygenation of the readily available ethers (**2**) to the carbazoles.

THE ready accessibility[1] of a new series of oxazaphosphoranes (**1**) *via* deoxygenation of 2-nitroaryl aryl ethers (**2**) by tervalent phosphorus reagents, has allowed us to investigate their extrusion reactions, which would be expected to produce esters containing the strong P=O bond and a diradical species (**3**) which should cyclise to give carbazoles. Thus 2,2-dimethoxy-3-(4-methoxyphenyl)-2-phenyl-2,3-dihydrobenz-1,3,2-oxazaphosph(v)oline (**1**; X=MeO; Y=H), on irradiation in benzene with a medium pressure mercury lamp and pyrex filter, gave 3-methoxy carbazole (**4**; X=MeO; Y = H; 34%) and dimethyl phenylphosphonate. The unsubstituted phospholine (**1**; X=Y=H) behaved similarly. The isolation of isomerically pure 3-methoxy-7-methylcarbazole (**4**; X=MeO; Y=Me) from photolysis of the phospholine (**1**; X=MeO; Y=Me) can be satisfactorily accounted for by participation of a species such as (**3**). The reaction is therefore a phosphorus analogue of the Graebe-Ullmann conversion of arylbenzotriazoles into carbazoles[2] and represents a two-step complete deoxygenation of the readily available ethers (**2**) to give the carbazoles (**4**).



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