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PHOSPHINIDENE OXIDE. PHOTOLYSIS OF 1-PHENYL-3-PHOSPHOLENE OXIDES

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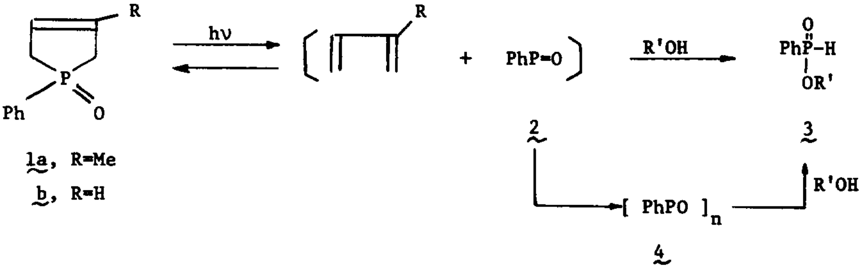
Much attention has been given to the generation of phosphinidenes[1-4] and their oxides[5-7] because of their synthetic value in the formation of phosphorous heterocycles and as a phosphorylating agents. Previous examples of generating these species from cyclic phosphorous compounds have been restricted to the thermal decomposition of bicyclic compounds containing a phosphorous bridge.[5-7]

In our investigation on the photochemical reactions of monocyclic phosphorous compounds,[8] we found a novel and simple route to the efficient generation of phenylphosphinidene oxide.

Irradiation of 1-phenyl-3-methyl-3-phospholene oxide (1a, 2.0g) in methanol (250ml) for 3 hrs. gave a 70% yield of methyl phenylphosphinate (3, R'=Me) as a sole isolable product, which was easily separated from the reaction mixture by silica gel chromatography and/or simple distillation (b.p. 92°/0.7mm). The formation of the phosphinate, which showed identical n.m.r. spectrum with that reported,[7] is easily explained by the insertion of phosphinidene oxide (2) into O-H bond of methanol. The presence of isoprene, which was evident from g.c. and n.m.r. spectrum of the reaction mixture, supported the transient existence of 2. The phosphinate (3) was isolated upon photolysis of 1b in methanol, however, in lower yield.



R in **1**	R'OH	Conversion, %*	**3**, %*
Me	MeOH	66	80
H	MeOH	30	21
Me	EtOH	53	80
Me	^{i}PrOH	41	76
Me	^{t}BuOH	36	(49)

* Determined by g.c. after irradiation for 3 hrs. Value in parentheses shows isolated yield because of decomposition of **3** (R'=^{t}Bu) in g.c.

Similar reaction took place in other alcohols. The decrease in the rate of disappearance of **1** as well as that of formation of **3** in going from methanol to t-butyl alcohol suggested that **2**, once formed, reacts with diene to regenerate the starting cyclic olefin **1** in less reactive alcohols. Further, when **1a** was irradiated in benzene, consumption of **1a** was very slow and no other products but isoprene were detected by g.c. After irradiation, addition of methanol to the benzene solution in dark gave 10% of **3** (R'=Me), suggesting the formation[7] of poly(phosphinidene oxide)(**4**) from **2** in inert solvent.

Other trapping agents of phosphinidene oxide are under investigation.

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