Photolysis of Benzoylmethylene(triphenyl)phosphorane

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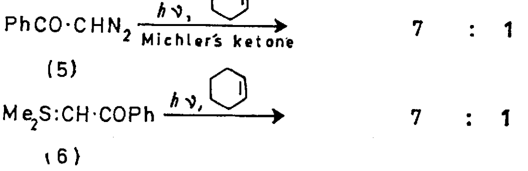
Summary Direct (>3000 Å) and sensitized photolyses of benzoylmethylene(triphenyl)phosphorane in cyclohexene yielded 1 : 1·2 and 6·5 : 1 ratios of acetophenone and 7-norcaryl phenyl ketone, respectively, demonstrating that benzoylcarbene is a primary photoproduct.

As part of our studies on the photochemistry of organophosphorus compounds we have examined the photolysis of benzoylmethylenetriphenylphosphorane (**1**).[1]† The principal mode of decomposition upon irradiation (<3000 Å) of analogous methylenephosphoranes is reported to be cleavage of a Ph–P bond.[2] Although a carbene intermediate was postulated for irradiations performed with light of wavelength >3000 Å,[2] the formation of cyclopropane products was not observed when photoreactions were performed in cyclohexene, and all products reported can be rationalized in terms of a free-radical mechanism. Here, we demonstrate that a carbene, resulting from rupture of the P=C bond, is formed during irradiation of methylenephosphoranes.

Direct irradiation of (**1**)‡ gave, among other products, triphenylphosphine (**2**), acetophenone (**3**), and 7-norcaryl phenyl ketone (**4**). The relative yields of (**3**) and (**4**), determined by g.l.c., were 1 : 1·2; sensitized irradiation of (**1**) with Michler's ketone at 3660 Å† [<10% absorption by (**1**)] led to a 6·5 : 1 ratio of (**3**) and (**4**).



Hammond and his co-workers[3] found the major product from triplet benzoylcarbene [generated from diazoacetophenone (**5**)] and cyclohexene to be a 7 : 1 mixture of (**3**) and (**4**). An identical distribution was found by Trost[4] from the photochemical decomposition of dimethylsulphonium phenacylide (**6**) in cyclohexene. Since the ratios of

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† Analytical and physical data agreed with those reported.

‡ Nitrogen was bubbled through < 1% solutions of (**1**) for at least 15 min. Direct irradiations were performed at ambient temperature with a 450 W high-pressure mercury vapour lamp (Pyrex filters). Sensitized irradiations were performed with four 125 W UV Products phosphor-coated low pressure lamps.

(**3**) to (**4**) from sensitized photolysis of (**1**) and from decompositions of (**5**) and (**6**) are nearly identical, the same intermediate triplet benzoylcarbene is most likely involved.[3,4] *A much larger* relative yield of (**4**) during the direct photodecomposition of (**1**) indicates that a singlet carbene is the principal reactive intermediate.[5] That decomposition of (**1**) occurs in an excited state manifold and not in a hot ground state is indicated by the lack ($<1\%$) of phenylacetylene, the product of thermal decomposition of (**1**).[6]

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