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Mechanistic Studies of the Photolysis of Phosphonium Salts

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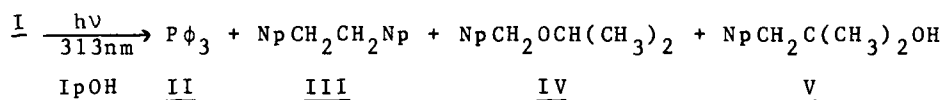
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Mechanistic Studies of the Photolysis of Phosphonium Salts

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As part of our continuing interest in the mechanistic photochemistry of phosphonium salts (Toscano *et al.*, *Chem. Commun.*, 567 (1973); *J. Phys. Chem.*, 83(9), 1213 (1979)) we have investigated the photodecomposition (313 nm irradiation) of (1-naphthylmethyl)triphenylphosphonium (I) chloride and tetrafluoroborate in deaerated isopropanol:



The observed photoproducts ($\phi_{\text{II}} = \phi_{\text{IV}} + \phi_{\text{V}} + 2\phi_{\text{III}} = 0.08$), which presumably arise from the excited singlet state (I is non-fluorescent), are consistent with either competitive homolytic cleavage or initial homolytic cleavage and subsequent rapid electron transfer, with little or no direct participation of the counterion in the primary photoprocess(es).

Comparative studies of the photolysis of the homologous salts $[\text{Np}(\text{CH}_2)_n \text{P}\phi_3^+ \text{X}^-]$ are currently in progress.