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PHOTOREARRANGEMENT OF ALLYL DIPHENYL PHOSPHATE VIA POSSIBLE TYPE-II REACTION AND PHOSPHORANYL 1,3-BIRADICALS

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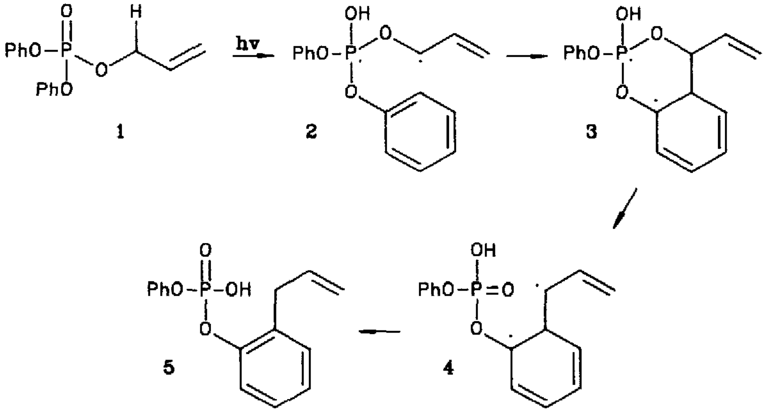
Summary: A Norrish type-II reaction is proposed for the photorearrangement of allyl diphenyl phosphate to *ortho*-allylphenyl phenyl phosphate. In contrast to the type-II mechanism in carbonyl compounds, the reaction is postulated to proceed through a five-membered transition state to produce a phosphoranyl 1,3-biradical which subsequently rearranges to the observed product.

We report here the first proposed Norrish type-II hydrogen atom abstraction in the photolysis of phosphate esters. Irradiation[1] of allyl diphenyl phosphate (**1**) in deoxygenated methanol solution at 254 nm produces the rearranged product **5** as the major product. In contrast to the usual type-II mechanism[2], the reaction is postulated to proceed through a five-membered transition state and the phosphoranyl 1,3-biradical **2**. Subsequent radical substitution on a phenyl ring and further rearrangement affords the observed product.



The quantum yield for destruction of starting material was found to be 0.025 ± 0.005 using ferrioxalate actinometry[3] and HPLC analysis.[4] At low conversions (≤10%) product yields are 95-100%. The structure of **5** was established both by spectroscopic and chromatographic comparison to the authentic compound and by chemical analysis (alkaline hydrolysis of **5** yielded equimolar amounts of phenol and *ortho*-allylphenol). Minor amounts of other photoproducts appear from available chromatographic and spectroscopic data to be isomers of **5**.

Arguments can be made in favor of this rearrangement proceeding through a type-II reaction. First, the intramolecular hydrogen atom abstraction step is favorable due to the lability of the allylic hydrogens. Indeed, allyl diphenyl phosphate undergoes this rearrangement much more efficiently than other alkyl diphenyl phosphates we have examined.[5] Second, the preference for five-membered cyclic intermediates in the chemistry of tetravalent phosphorus compounds[6] supports a five-center transition state. We have found that *tert*-butyl diphenyl phosphate, which could undergo type-II reaction only through a six-center abstraction, is not nearly as photoreactive under the conditions of the experiment. On the other hand, the normal type-II reaction has been evidenced in trichloromethylphosphonate esters, but not phosphate esters, and only with the strongly electron-withdrawing trichloromethyl group.[7] Third, phosphoranyl 1,3-biradicals similar to **2** and **3** have been proposed recently by Bentrude as likely intermediates in the photolysis of allyl phosphites[8] and β-ketoethyl phosphites.[9] In these cases, however, the five-membered cyclic biradicals, formed via intermolecular reaction of phosphites with excited alkenes and ketones, respectively, are also 1,4-biradicals and undergo the normal type-II cleavage reaction. Finally, the high yields at low conversions are consistent with the reaction being intramolecular, or at least one which occurs within the solvent cage.

Biradical **2** can then attack a phenyl ring through a favorable geometry, leading to another conjugated phosphoranyl biradical **3**. Cleavage to the 1,3-biradical **4**, followed by hydrogen atom migration, yields the observed product.

Excitation of the phosphate moiety must come about by energy transfer from an excited state of the phenyl ring. At 254 nm the extinction coefficient for light absorption by the phenyl chromophore ($\approx 550\ M^{-1}cm^{-1}$) is nearly four thousand times greater than that for the phosphate chromophore.

Other mechanistic pathways can be suggested, but none appear to lead easily to **5**: First, Givens[10] has observed products from heterolytic C-O bond cleavage in benzyl phosphates. Simple homolytic or heterolytic cleavage of the allyl C-O bond followed by radical or electrophilic substitution on the phenyl ring could give **5**, but we detect no other products from side reactions of these intermediates, such as 1,5-hexadiene, 3-methoxypropene, or diphenyl phosphate. The reaction must be either intramolecular or a radical-pair mechanism in which recombination is much faster than diffusive separation of the radicals. Second, Finnegan[11] has shown that alkyl diaryl phosphates undergo coupling of the aryl rings, producing biphenyl derivatives, via electron transfer from the aryl group to the phosphate. However, this occurs efficiently only with strongly electron-donating aryl groups: in the case of triphenyl phosphate the quantum yield for biphenyl formation was only 0.0006.[11] We do observe a small amount of biphenyl as a side product in our photolysis. A charge-transfer intermediate in allyl diphenyl phosphate could lead to coupling between a phenyl ring and the allyl group, but this would not be expected to give the observed isomer. Lastly, although various cycloaddition reactions between benzene and olefins are known, such reactions likely would not yield the observed product.[12]

We are currently examining the photochemistry of various alkyl diphenyl phosphates with the goal of establishing the generality of this reaction. Additional studies in progress are aimed at understanding the photophysical processes involved.

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References and Notes

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4. 25-cm x 4.6-mm i.d. 10-μm C_8 column; gradient: 20% CH_3OH, 0.05 M H_3PO_4 to 100% CH_3OH.
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