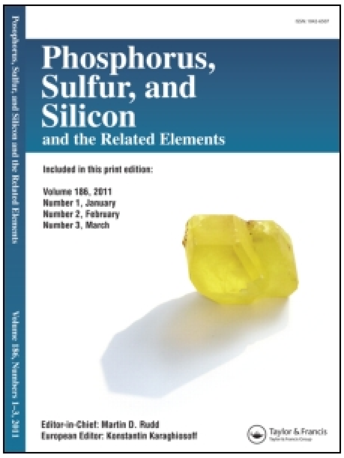

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Photo-Induced Rearrangements of Allyl and Benzyl Phosphites. Potential Phosphoranyl 1,3-Biradical Intermediates

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PHOTO-INDUCED REARRANGEMENTS OF ALLYL AND BENZYL PHOSPHITES. POTENTIAL PHOSPHORANYL 1,3-BIRADICAL INTERMEDIATES

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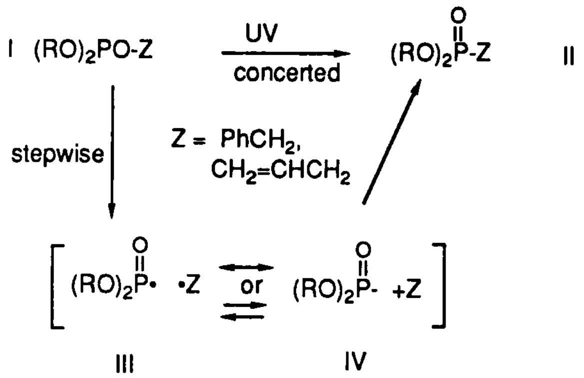
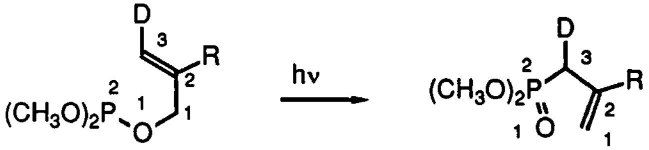
Abstract Allyl and benzyl phosphites undergo photoisomerization to the corresponding allyl- and benzylphosphonates. The triplet-sensitized photorearrangements of the allyl systems are regiospecific. A triplet 5-membered ring 1,3-phosphoranyl biradical intermediate is proposed. Optically active phosphites, chiral at the benzyl carbon, undergo intramolecular photo-Arbuzov rearrangement with very predominant retention of configuration at carbon.

Our longstanding interest in free-radical processes involving organophosphorus derivatives, particularly routes featuring phosphoranyl radicals,[1] has led us to investigate what are in essence photo-Arbuzov reactions of phosphites, I, into which UV light can be readily introduced by way of a chromophore, Z. Indeed, irradiation through quartz using a medium pressure 450 W Hg lamp with either benzene or cyclohexane as solvent resulted in



the facile rearrangement of benzyl and allyl phosphites to the corresponding phosphonates, II.

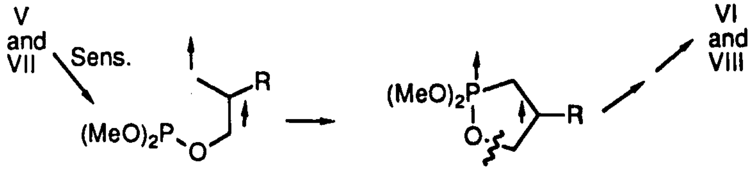
The photorearrangement of allyl phosphite V (0.1 M) could be sensitized by p-xylene (0.6 M) in cyclopentane (Corex filter, 254 nm) which resulted in an increase in yield at 40% conversion from 25 to 70% and a 4-fold increase in rate of consumption of V. The sensitized reaction is regiospecific as shown below (^{2}H NMR, deuterium at C-3). More strikingly, photorearrangement VII → VIII was photosensitized by benzophenone (1:1 VII:Ph_2CO in benzene, Pyrex) with a 10-fold increase in rate of VII consumption and an increase in yield of VIII from 54% (59% conversion) to >95% (100% conversion). This process also is regiospecific (deuterium at C-1).



V R = H
VII R = Ph

VI R = H
VIII R = Ph

Both singlet and triplet excited states of alkenes are known to abstract hydrogen readily[2] and undergo addition to carbon-carbon double bonds,[3] reactions typical of alkyl radicals. A mechanism consistent with the findings for the photosensitized reactions is a stepwise one in which the triplet alkene, IX, adds oxidatively like a carbon radical to phosphorus[4] to yield a phosphoranyl 1,3 biradical, X, which after spin inversion undergoes β scission to give the product allylphosphonates, VI and VIII. An intermolecular precedent for reaction of a triplet alkene with tricovalent phosphorus is the photosensitized

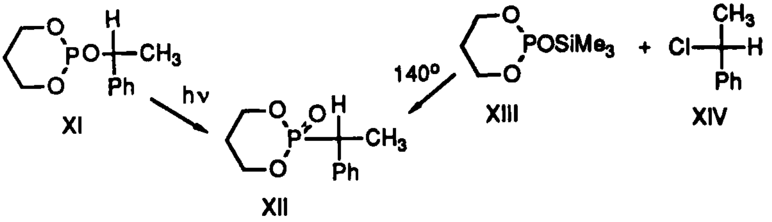


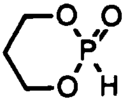
IX X

displacement of $Ph_2P\cdot$ from Ph_2PPPh_2 by triplet $Ph_2C{=}CH_2$.[5]

Direct irradiation (S_1 chemistry) of V and VII led to loss of regiospecificity. Little evidence for the diffusion of radicals (III) or ions (IV) outside the solvent cage could be found for either the T_1 or S_1 photorearrangements. Crossover experiments excluded intermolecular reactions, including chain processes. Loss of regiospecificity in the S_1 reactions may reflect the operation of competing concerted 1,2- and 2,3-sigmatropic rearrangements.

Only formal 1,2-rearrangements are available to benzyl phosphites.[6] These photo-Arbuzov processes were investigated with respect to the stereochemistry at carbon in the system XI → XII. Irradiation of XI through quartz (benzene solvent) gave XII with >95% retention of configuration at carbon. The overall stereochemistry was demonstrated by reference to that of the thermal Arbuzov process, XIII + XIV → XII (inversion at carbon), and the Michaelis-Becker reaction of XIV with the sodium salt of XV (inversion at carbon). The enantiomeric purity of XII was determined by ^1H NMR at 300 or 500 MHz following addition of optically active t-Bu(Ph)P(S)OH. The methyl groups of the enantiomers of XII became diastereotopic with well-separated chemical shifts. XVI and XVII represent other examples of benzyl phosphites which undergo this reaction.

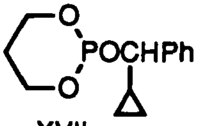




XV

$(MeO)_2POCH_2Ph$

XVI



XVII

The multiplicity of the excited states of the photo-Arbuzov rearrangements is not known. $(MeO)_2P(O)H$, XV, and $PhCH_2CH_2Ph$ are formed as products but in no more than 1-2% relative to product benzylphosphonate. This, together with the high degree of retentive stereochemistry, and results of crossover experiments with a pair of $(RO)_2POCH_2Ar$, suggests that radical pairs (III), if present in major amounts, are very short-lived since they do not compete well with diffusion ($k_{diff} = 10^9$-10^{10}s) or undergo rotation within the solvent cage. Indeed, the major portion of the reaction may proceed in concerted fashion.

Acknowledgment. Support of this research by grants from the National Science Foundation and the National Cancer Institute is gratefully acknowledged.

REFERENCES

1. For recent reviews see: W. G. Bentrude in Reactive Intermediates, Vol. 3., R. A. Abramovitch, Ed., London, 1983, pp. 199-298. W. G. Bentrude, Acc. Chem. Res., **15**, 117 (1982). B. P Roberts in Advances in Free Radical Chemistry, Vol. 6, G. H. Williams, Ed., Heyden and Sons, London, 1979, pp. 225-289.
2. See the reviews by P. J. Kropp, Org. Photochem., **4**, 1 (1979); Molec. Photochem., **9**, 39 (1978/79).
3. N. J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, CA, 1978, Ch. 10.
4. W. G. Bentrude, J. J. L. Fu, and P. E. Rogers, J. Am. Chem. Soc., **95**, 3625 (1973) and refs. therein. A. G. Davies, D. Griller, and B. P. Roberts, J. Chem. Soc. Perkin Trans 2, 2224 (1972).
5. R. Okazaki, Y. Hirabayaski, K. Tamura and N. Inamoto, J. Chem. Soc. Perkin Trans 1, 1034 (1976).
6. Trialkyl phosphites undergo photo-Arbuzov reactions only extremely slowly if at all in our hands. (See, however, R. B. LaCount and C. E. Griffin, Tetrahedron Lett., 3071 (1965).) Intermolecular free-radical Arbuzov rearrangements of trialkyl phosphites occur with reactive radicals such as Ph•, Me•, Et• and Me_2N•. The latter three require that a stable benzyl radical be generated in the subsequent β scission. (Ref. 4 and W. G. Bentrude, W. D. Alley, N. A. Johnson, M. Murakami, K. Nishikida, and H. W. Tan, J. Am. Chem. Soc., **99**, 4383 (1977).)