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PHOTOREARRANGEMENTS OF BENZYL PHOSPHITES. STEREOCHEMISTRY AT PHOSPHORUS

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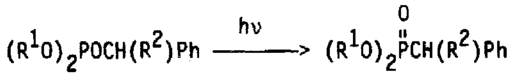
Summary: The photo-Arbuzov rearrangement of a cyclic benzyl phosphite is shown to proceed with retention of configuration at phosphorus. The mechanistic and potential synthetic implications of this result are discussed.

Recently we reported[1] the facile photorearrangement of benzyl phosphites to the corresponding benzylphosphonates, reaction 1. The process was shown to be near-quantitative, applicable over a number of structural variations (R^1 = alkyl, $CH_2CH_2CH_2$; R^2 = H, CH_3,

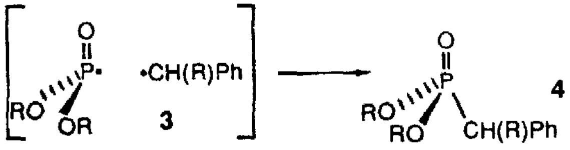


$$(R^1O)_2POCH(R^2)Ph \xrightarrow{h\nu} (R^1O)_2\overset{O}{\overset{\|}{P}}CH(R^2)Ph \qquad (1)$$

cyclopropyl), and totally *regioselective* for the rearrangement of the $PhCH(R^2)O$ moiety. Mechanistically, the reactions were found to be primarily *intramolecular*. The photorearrangement of **1** to **2** was seen to be >90% stereoselective with *retention* of

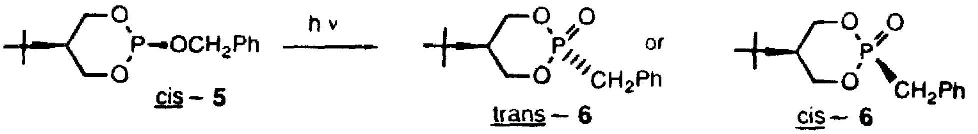
(2)

configuration at carbon. Only minimal (<1%) amounts of the dimer of radical $Ph(CH_3)CH\cdot$ were detected. It was concluded that if radical pair **3** is on the major reaction pathway, it must be very short-lived.[1]



(3)

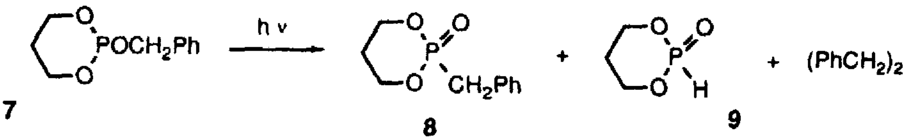
We report here the study of the stereochemistry at phosphorus of the photorearrangements of the diastereomeric benzyl phosphites *cis*- and *trans*-**5**. As depicted in equation 4, the question asked is whether phosphorus retains its stereochemical integrity (*cis*-**5** → *trans*-**6**), undergoes inversion (*cis*-**5** → *cis*-**6**), or suffers partial or total loss of stereochemistry (*cis*-**5** → *cis*- and *trans*-**6**). The conclusion from the present studies, *cis*-**5** → *trans*-**6** and



cis-5 trans-6 cis-6 (4)

trans-5 → cis-6, is important to the mechanistic understanding of this photoreaction and also has synthetic implications.

Preparatory to the stereochemical work, the photorearrangement of **7** was examined by GLC (equation 5). In C_6H_6 and cyclohexane at >90% conversion of **7**, the yield of **8** was 95%. (Hanovia 450 W medium pressure lamp, quartz tubes, argon-flushed). Phosphite **9** (3-4%) along with 2-4% of **10** also resulted. (Based on **7** consumed, corrected for 2 $PhCH_2\cdot \rightarrow PhCH_2CH_2Ph$.) Addition of MeOH (1-2 mole equivalents) to the reaction mixture failed to result in the GLC detection of $MeOCH_2Ph$[2] (< 0.5%) or toluene (< 0.5%) which rules out formation of trappable $PhCH_2^+$ or $PhCH_2^-$. $PhCH_2Ph$ could not be detected as a product in benzene.



7 **8** **9** **10** (5)

The previously known phosphite **5**[3] was prepared as a series of configurationally stable cis/trans mixtures and photorearranged under the same conditions in benzene or cyclohexane to >95% conversion. The stereochemical results appear in **Table 1**. The ratios of diastereomers of **5** were determined by ^{31}P NMR or, following stereospecific oxidation with S_8, by GLC. GLC analysis gave the product phosphonate ratios. Analyses of reactions carried to lower conversions of **5** demonstrated that the thermodynamically less stable trans-**5** was consumed more rapidly than cis-**5**. Products and yields were very similar to those generated on irradiation of **7**. Evident from the **Table 1** is the highly stereospecific nature of the photorearrangement of **5**, which proceeds with retention of configuration at phosphorus. That is, the $P-O-CH_2Ph$ oxygen which is converted to the P=O remains on the same side of the ring with respect to the t-butyl group.

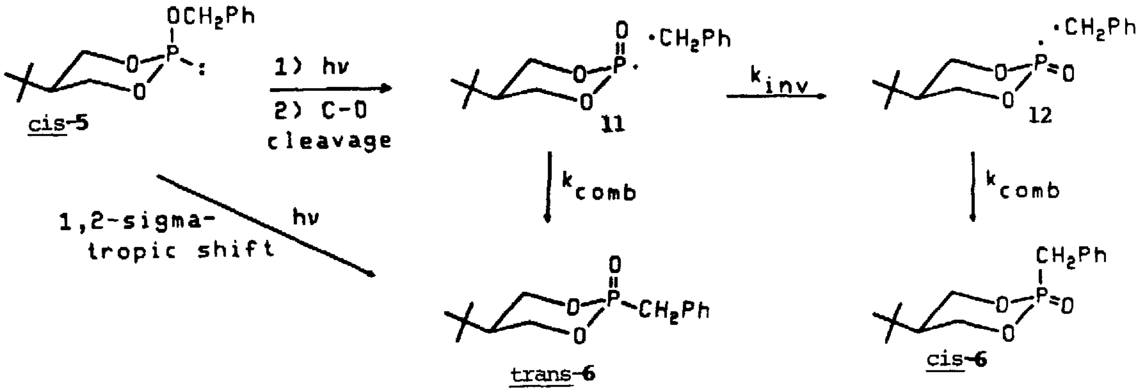
Table 1. Photorearrangement of Several cis/trans Isomeric Ratios of Phosphite **5**.

Solvent	cis-5/trans-5[a]	trans-6/cis-6[b]
C_6H_6	95/5	96/4
C_6H_{12}	95/5	90/10
C_6H_6	11/89	11/89
C_6H_{12}	11/89	19/81
C_6H_6	44/56[c]	48/52
C_6H_{12}	43/57[c]	45/55

[a] ^{31}P NMR. [b] GLC. [c] S_8 addition followed by GLC.

The observed retention of stereochemistry at phosphorus, along with the previously reported retention at the migrating carbon,[1] is completely consistent with Woodward-Hoffman predictions[4] for a concerted, singlet, photochemical, four-electron, suprafacial 1,2-sigmatropic shift. However, the bibenzyl and phosphite **9** formed requires that at least a component of the rearrangement involves radical pairs. Ultimate resolution of the question of what fraction of the reaction preceeds via radical pairs may be possible via quantitative CIDNP studies.

Shown below is a radical-pair mechanism for photorearrangement of cis-**5**. Clearly, if an appreciable proportion of the reaction proceeds via pair **11**, they must be formed in close proximity with enough attraction between them that only a small fraction undergo diffusive separation. *Further, **11** ⟶ **12** is not nearly so rapid as **11** ⟶ trans-**6**. That is, pyramidal* inversion at phosphorus is slower than radical combination. The configurational integrity of pyramidal[5] phosphonyl radicals during reaction has been observed previously.[6] The preservation of stereochemistry at both carbon and phosphorus along with the very small amount of diffusion of benzylic radicals means that $k_{comb} >> k_{diff}, k_{inv}, k_{rot}$.[7] *Evidence has recently been* presented[8] for the unusually rapid combination ($k_{comb} > 10^9\ s^{-1}$) of caged alkyl and iron-complexed hydroxyl radicals formed in close proximity during P-450 catalyzed hydrocarbon oxidation.



The photo-Arbuzov rearrangement is similar to the thermal Stevens rearrangement which has been studied stereochemically[9] and by quantitative CIDNP.[10] It was ascertained that in $CHCl_3$ either a major portion of that reaction proceeds by a concerted pathway or that radical pairs combine on a time scale too short for rotation or diffusion to compete. As was noted,[10] the distinction between those alternative mechanisms is not easily made.

Preparatively, this new photorearrangement holds potential as a superior method for the introduction of chiral carbon of known configuration directly bonded to phosphorus. Its use may lead ultimately to new chiral phosphines of interest as ligands in organometal-catalyzed asymmetric induction.[11]

Acknowledgment

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References

1. Omelanzcuk, J.; Sopchik, A. E.; Lee, S. G.; Akutagawa, K., Cairns, S. M.; Bentrude, W. G. J. Am. Chem. Soc. **1988**, 110, 6908.
2. The photocleavage of benzylic phosphates gives benzyl cations trapped by alcohols as the ether. (Givens, R.S.; Matuszewski, B. J. Am. Chem. Soc. **1984**, 106, 6860).
3. Bentrude, W. G.; Alley, W. D.; Johnson, N. A.; Murakami, M.; Nishikida, K.; Tan, H. W. J. Am. Chem. Soc. **1977**, 99, 4383. Assignment of structures to the individual diastereomers of **6** was parallel to that for the corresponding methylphosphonates, Bajwa, G.S.; Bentrude, W.G. Tetrahedron Lett. **1980**, 21, 4683.
4. Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry; Verlag Chemie: Weinheim, 1970.
5. Davies, A. G.; Griller, D.; Roberts, B. P. J. Am. Chem. Soc. **1972**, 94, 1782.
6. Reiff, L. P.; Aaron, H. S. J. Am. Chem. Soc. **1970**, 92, 5275. Szafraniec, L. J.; Reiff, L. P.; Aaron, H. S. ibid. **1970**, 92, 6391. Farnham, W. B.; Murray, R. K., Jr.; Mislow, K. J. Chem. Soc. (D) **1971**, 146.
7. Relative rate constants for caged singlet $PhCH_3CH\cdot$ pairs, initially separated by N_2, and formed from the precursor azo compound were determined to be $k_{rot}:k_{diff}:k_{comb}$ = 15:2.4:1.0. Greene, F. D.; Berwick, M. A.; Stowell, J. C. J. Am. Chem. Soc. **1970**, 92, 867. Kopecky, K. R.; Gillan, T. Can. J. Chem. **1969**, 47, 2371.
8. Ortiz de Montellano, P. R.; Stearns, R. A. J. Am. Chem. Soc. **1987**, 109, 3415.
9. Ollis, W. D.; Rey, M.; Sutherland, I. O. J. Chem. Soc., Chem. Commun. **1975**, 543.
10. Dolling, U. H.; Closs, G. L.; Cohen, A. H. J. Chem. Soc., Chem. Commun. **1975**, 545.
11. Kagan, H. B. In Asymmetric Synth.; Vol. 5; Morrison, J. D., Ed.; Academic Press: Orlando, Florida, 1985.

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