Tetrahedron Letters, Vol. 34, No. 38, pp. 5987-5990, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

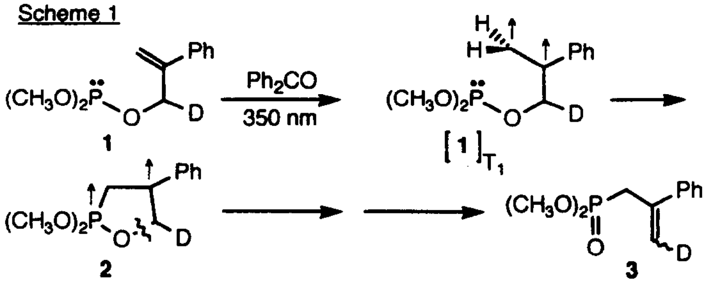
Effect of Placement of Phosphorus in a Ring on the Triplet-Sensitized Photorearrangements of 2-Phenylallyl Phosphites

Srinivasan Ganapathy, R. Thomas Cambron, Kevin P. Dockery, Yuh-Wern Wu,
Joel M. Harris,* and Wesley G. Bentrude*
Department of Chemistry, University of Utah, Salt Lake City, UT 84112

Abstract: The triplet-sensitized photorearrangement of 2-phenylallyl phosphite **4** is of the order 50-100 times less efficient than that for its acyclic counterpart, **1**. This surprising effect can be understood in terms of the influence of the spiro ring system of **10** on the rate of its conversion to thermodynamically more stable **11** from which phosphonate **12** is formed.

An earlier report[1] from this laboratory showed that dimethyl 2-phenylallyl phosphite, $(MeO)_2POCH_2C(Ph){=}CH_2$ (**1**), undergoes benzophenone-sensitized photorearrangement to the phosphonate, $(MeO)_2P(O)CH_2C(Ph)C{=}CH_2$ (**3**), totally regioselectively, and near-quantitatively, even at complete conversion of **1**. The measured quantum yield for formation of **3**, $\Phi_p(3)$, in *benzene* is 0.22.[2a] It was proposed that triplet phosphoranyl 1,3-biradical **2** is the key intermediate in this process. We report here an *unexpected reduction* in the efficiency of this photorearrangement on placing phosphorus in a six-membered ring. This finding is seen to be best understood in terms of the influence of the spiro ring system (structure **5**, represented by **10** in Scheme 2) that leads to a decrease in the rate of permutational isomerization of the initially formed phosphoranyl 1,3-biradical, **5**, a step we propose to be essential to the formation of phosphonates **3** and **6** via **2** and **5**.

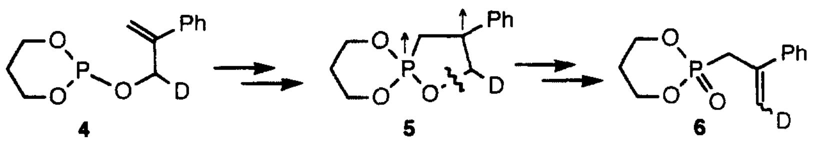
Scheme 1



Thus, we were surprised to observe that phosphite **4** reacted only very sluggishly under conditions[3] of benzophenone photosensitization ($\Phi_p(6) = 0.003$ in C_6H_6).[2a] The regiochemistry of benzophenone-sensitized conversion of **4** to **6**, equation 1, was the same as that for the benzophenone-sensitized conversion of **1** → **3** as required if the photorearrangements of **1** and **4** have common mechanisms. (From ^2H NMR measurements on **1**, **3**, and isolated **4**, and **6**.) Clearly, based on the mechanism of Scheme 1 and equation 1, the low efficiency of the reaction of **4** may arise from either poor triplet energy transfer or decreased subsequent reactivity of its triplet excited state.

However, an alternative mechanism for the photorearrangements of **1** and **4** needs to be considered.

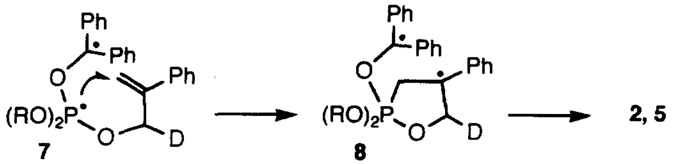
This route involves initial photoinduced single-electron transfer from phosphorus to triplet benzophenone followed by electrophilic addition of the phosphorus cation radical to the styryl moiety to give a five-membered ring cation radical intermediate otherwise similar to 1,3-biradicals **2** and **5**. Although this SET process in *CH_3CN* is estimated (Rhem-Weller equation[4]) to be only *marginally unfavorable* energetically,[5,7] we found the phosphorescence of triplet benzophenone to be rapidly quenched by $(EtO)_3P$ in CH_3CN, $k_Q = (1.3 \pm 0.1) \times 10^9\ M^{-1}s^{-1}$. It was for this reason that the above Φ_P were measured[2a] in benzene in which ΔG for the same electron transfer should be *greatly* disfavored, i.e. by 30 kcal/mol.[4,5] Unfortunately, determination of k_Q for the benzophenone phosphorescence quenching by **1** and **4** in *benzene*, as a measure of the relative efficiencies of triplet energy transfer, was unsuccessful.



1)

Indisputable evidence *against* an electron-transfer mechanism for the benzophenone triplet induced photorearrangements of **1** and **4** comes from our recent study of the rearrangements of **1** to **3** and **4** to **6** induced by the first singlet excited state of 9,10-dicyanoanthracene in CH_3CN.[8] In these processes, *which do involve photo-induced electron transfer*, the photorearrangements of **1** and **4** occur with reduced but *essentially identical* quantum yields: $\Phi_P = 0.03$ or **1**; $\Phi_P = 0.02$ for **4**.[2b] Measured values of Φ_P for benzophenone-sensitized photorearrangement of **1** and **4** in *CH_3CN* (0.32 and 0.004, respectively) were determined[2b] to be very close to those in *benzene*, consistent with a common mechanism in the two solvents, presumably the triplet process of Scheme 1 and equation 1. Rate constants, k_Q, for quenching of the phosphorescence of triplet Ph_2CO by **1** and **4** in *CH_3CN* were determined to be essentially the same, $(4.0 \pm 0.1) \times 10^9\ M^{-1}s^{-1}$ and $(4.5 \pm 0.1) \times 10^9\ M^{-1}s^{-1}$, respectively. Thus, from relative Φ_P values, $(\Phi_P(1)/\Phi_P(4)$, for photorearrangement of **1** and **4** in benzene and CH_3CN, *the presumed triplet excited state of **4** is 50-100 times less reactive than that of **1**.*

One also must consider the possibility that phosphites **1** and **4** quench the phosphorescence of triplet Ph_2CO *chemically* by the reactions of equation 2 that lead ultimately to product phosphonate. Indeed, Ph_2CO is known to mimic the reactions of an alkoxy radical to give photoreaction products with Ph_3P that most probably arise from an adduct like **7**.[9]



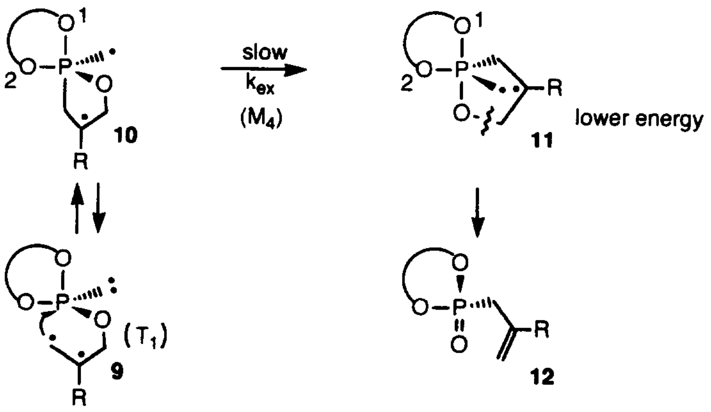
2)

To avoid totally the possibility of either electron-transfer or chemical initiation of these photorearrangements, triphenylene[10] was used as a triplet sensitizer;[3] and Φ_P[2b] and k_Q values for **1** and **4** in *benzene* were determined. Since triphenylene triplet does not phosphoresce, the quenching rate constants, k_Q, were determined by photothermal lens spectroscopy.[11] Rate constants for quenching by **1**, $(4.4 \pm 0.6) \times 10^9\ M^{-1}s^{-1}$, and **4**, $(3.7 \pm 0.3) \times 10^9\ M^{-1}s^{-1}$, are closely similar to one another and, incidentally, to those noted above for quenching of Ph_2CO phosphorescence by **1** and **4** in *CH_3CN*. Significantly, Φ_P for **1** (0.25) and **4**

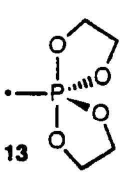
(0.003) in *benzene* were determined[2b] to be very close to those measured with benzophenone as sensitizer (see above); and the total regioselectivity corresponding to that depicted in Scheme 1 and equation 1 also was found with triphenylene sensitization of the photorearrangements of both **1** and **4**.

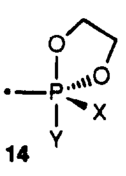
The most reasonable conclusion to be drawn from these results is that the triplet excited states of both benzophenone and triphenylene *transfer triplet energy* to **1** and **4** in an efficient manner at the 0.01-0.07 M concentrations of phosphites and 0.05 M concentrations of sensitizer used in these experiments. One is forced, therefore, to try to understand the relatively low reactivity of the triplet excited state of **4** towards formation of **6**. Scheme 2 depicts the *apical* introduction of the attacking primary alkyl radical-like terminus of the triplet styryl moiety (**9**) in formation of the *initial* trigonal bipyramidal, phosphoranyl 1,3-biradical intermediate, **10**. Kinetic ESR, and product evidence for the *reversible apical entrance* and departure of alkyl substituents in σ-type phosphoranyl radicals is strong;[12] and monoradicals related to **9** are clearly near-trigonal bipyramidal in structure.[13] Adduct **10**, however is thermodynamically less stable than is **11** which has the ring substituents in energetically more-favored positions. We suggest that for **10** to be successfully trapped, *the thermodynamically favorable and presumably irreversible permutation 10 → 11 must be rapid.* Once-formed, **11** then leads to phosphonate **12**.

Scheme 2



Permutation **10** → **11** (mode 4, M_4[14]) involves two ring atoms and the odd electron on phosphorus. Kinetic ESR investigations have established[15] that this permutation (or any other) for spiro radical **13** cannot be detected even at 120 °C, the upper temperature limit at which this radical could be observed. By contrast, the same permutation process involving the five-membered ring and the odd electron for radicals like **14**[16] proceeds rapidly with observed k_{ex} of 10^6 - 10^8 s^{-1} at a relatively low temperature, 0 °C.[16] Therefore, the rearrangement


13


14

equivalent to **10** → **11** (Scheme 2), but with oxygen atoms 1 and 2 not in a ring (biradical **2**, from phosphite **1**), will be relatively rapid, while for spiro radicals (biradical **5** from phosphite **4**), **10** → **11** will be too slow to compete efficiently with reconversion of **10** to **9** most likely as its ground state. It also appears that direct formation of **12** from **10** is not fast enough to compete with **10**→**9**.

The above treatment combines in novel fashion knowledge of the reversible, apical addition of primary alkyl radicals to three-coordinate phosphorus with the established effect of spiro structures on the permutational isomerization rates of phosphoranyl radicals. Provided, thereby, is an understanding of the factors that determine the efficiencies of the above photorearrangements which involve somewhat unusual 1,3-biradicals. This approach also incorporates and substantiates the view that styryl triplets are essentially 1,2-biradicals[17] that add to three-coordinate phosphorus in much the same way as do primary alkyl radicals.

Acknowledgment. Support of this research by National Science Foundation grants to W.G.B. and J.M.H. is gratefully acknowledged.

References

1. Bentrude, W.G.; Lee, S.-G.; Akutagawa, K.; Ye, W.; Charbonnel, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1577.
2. (a) The present value, 0.22, was obtained by use of a Quantacount electronic actinometer, Photon Technology International, calibrated with potassium ferrioxalate, and replaces the earlier number of 0.8[1] obtained on a merry-go-round apparatus. (b) All Φ_P reported herein are from the Quantacount instrument.
3. Solutions 0.05 M in sensitizer, 0.01-0.07 M in **1** or **4**, 5X freeze-pump-thaw degassed, were flame sealed and irradiated at 335 nm to less than 7% conversion of phosphite. Analysis by GC with added internal standard.
4. Rhem, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
5. Parameters used in Rhem-Weller calculations. Benzophenone: E_T, 69.2 kcal/mol;[6a] E_{red}, -1.68 eV[6b] vs SCE, CH_3CN. Triphenylene: E_S, 83.4 kcal/mol;[6a] E_T, 66.5 kcal/mol,[6a] E_{red}, -2.22 eV vs SCE, CH_3CN.[4] $(EtO)_3P$: E_{ox}, 1.57 eV vs SCE, CH_3CN.[6c] α-Methylstyrene: E_S, 99.6 kcal/mol;[6d] E_T, 62 kcal/mol;[6d,17] E_{ox}, 1.76 eV,[6e] SCE, CH_3CN.
6. (a) Murov, S.L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. (b) Roth, H.D.; Lamola, A.A. *J. Am. Chem Soc.* **1974**, *96*, 6270. (c) Ohmori, H.; Nakai, S.; Masui, J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2023. (d) Crosby, P.M.; Dyke, J.M.; Metcalfe, J.; Rest, A.J.; Salisbury, K.; Sodeu, J.R.; *J. Chem. Soc., Perkin Trans. 2* **1977**, 183. (e) Katz, M.: Riemenschneider, P.; Wendt., H. *Electrochem. Acta* **1972**, *17*, 1595.
7. ΔG for SET from phosphorus of $(EtO)_3P$ or π bond of α-methylstyrene to triplet benzophenone, +4 kcal/mol and +9 kcal/mol, respectively (CH_3CN).[4]
8. Ganapathy, S.; Dockery, K.P.; Sopchik, A.E.; Bentrude, W.G. *J. Am. Chem. Soc.* in press.
9. Fox, M.A. *J. Am. Chem. Soc.* **1979**, *101*, 5339. Chow, Y.L.; Marciniak, B. *J. Org. Chem.*, **1983**, *48*, 2910.
10. ΔG for SET from phosphorus of $(EtO)_3P$ to triphenylene triplet, +44 kcal/mol (benzene).[4] Singlet sensitization by triphenylene also is highly endothermic.[5]
11. Braslavsky, S.; Hiebel, A.E. *Chem. Rev.* **1992**, *92*, 1381. Cambron, R.T.; Harris, J.M. *J. Phys. Chem.* submitted.
12. Cooper, J.W.; Roberts, B.P. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 808.
13. For reviews of phosphoranyl radical chemistry see Bentrude, W.G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F.R., Ed.; John Wiley and Sons: Chichester, 1990, Vol. 1; Ch.14. Bentrude, W.G. In *Reactive Intermediates*; Abramovitch, R.A., Ed.; Plenum Press: New York; 1983, Vol. 3; Ch. 4. Bentrude, W.G. *Acc. Chem. Res.*, **1982**, *15*, 117. Roberts, B.P. In *Advances in Free Radical Chemistry*; Williams, G.H., Ed.; Heyden: London, 1979, Vol. 6; pp. 225-284.
14. Musher, J.I. *J. Chem. Ed.* **1974**, *51*, 94; *J. Am. Chem. Soc.* **1972**, *94*, 5662.
15. Griller, D; Roberts, B.P. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1416.
16. Cooper, J.W.; Parrot, M.J.; Roberts, B.P. *J. Chem. Soc., Perkin Trans 2* **1977**, 730.
17. Spectroscopic evidence for the 1,2-biradical nature of alkene triplets have been presented. Ni., T.; Caldwell R.A.; Melton, L.A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

(Received in USA 7 June 1993; accepted 22 July 1993)