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Structure-Reactivity Studies of the Triplet-Sensitized Photorearrangements of Allyl Phosphites

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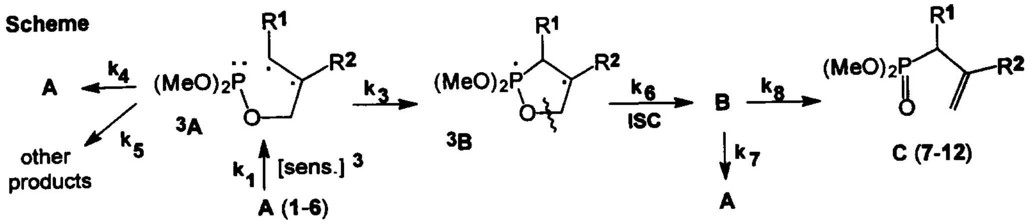
Abstract: The relative quantum efficiencies of allylphosphonate (**7-12**) formation, from the triplet-sensitized photorearrangement of allyl phosphites (**1-6**), can be qualitatively correlated using the 1,2-biradical model for π-π* excited states and considering the effect on excited state energies and lifetimes of placing the π bond in a small ring. © 1997 Elsevier Science Ltd.

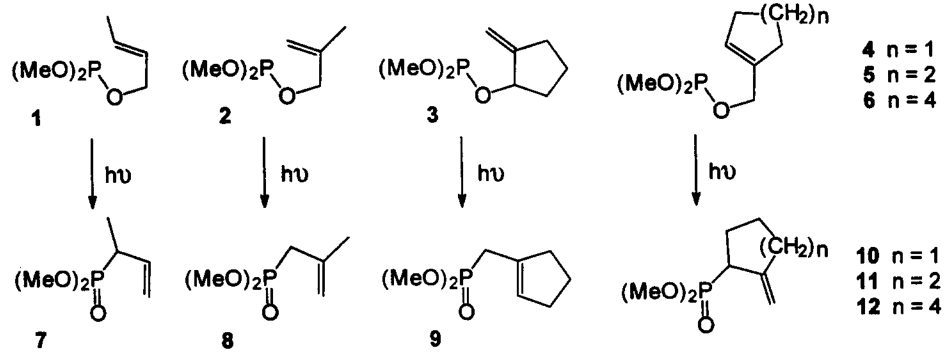
Recent physical measurements on the π-π* triplet excited states of alkenes, especially aryl-substituted ones, show them to be essentially 1,2-biradicals[1] with the spin-unpaired electrons in individual, *perpendicular p* orbitals. Nonetheless, few studies have been published that correlate the structures and reactivities of the triplet excited states of alkenes with the 1,2-biradical model. An example of such a correlation is the addition of triplet 1-phenylcyclohexene to its ground state.[2] Another is a recent study of effects of structure on the rates of ring-openings of cyclopropylcarbinyl, π-π* "1,2-biradical" excited states that were seen to parallel nicely those of cyclopropylcarbinyl monoradicals.[3] Furthermore, the increased energy of the *planar* π-π* triplet of β-cyclopropyl-(3*H*)-indene resulted in an accelerated rate of cyclopropylcarbinyl ring opening compared to the monoradical model.[3] Doubtless, it is the high energies of planar 1-phenylcyclopropenyl π-π* triplet excited states that leads to their rapid intramolecular hydrogen abstraction reactions.[4]

The regiospecific, triplet sensitized photorearrangements of allyl phosphites (A) to the corresponding allylphosphonates (C), discovered by this research group,[5] have been interpreted according to the Scheme shown:



The triplet 1,2-biradical-like π-π* alkene moiety of ^{3}A undergoes intramolecular oxidative addition of its *monoradical-like* carbon terminus to phosphorus (k_3) to give the assumed 1,3-phosphoranyl biradical ^{3}**B**. β scission of ground state 1,3-biradical **B** affords allylphosphonate C.[5]

We report here a study of the relative quantum yields, Φ_P(rel), for the triplet, *o*-xylene-sensitized[6] formation of dimethyl allylphosphonates **7-12** from the series of allyl phosphites **1-6** (see Table). The propensities of various ground-state, carbon *monoradicals* to react with three-coordinated phosphorus compounds, e.g. phosphites ($(RO)_3P$), have recently been correlated with radical structure (radicals, reactivity order = Ph, bicyclo[1.1.1]pent-1-yl>primary>secondary>tertiary, benzylic).[7] In the present work we conclude that application of the *"1,2-biradical analogy"* to the alkene terminus of the π-π* triplets (^{3}A) of **1-6**, along with consideration of the expected effect on π-π* triplet energies and lifetimes of inclusion of the double bond in a ring, can *qualitatively explain the primary trends in quantum yields found for formation of allylphosphonates* ***7-12***. Effects of R^2 on ^{3}**B** stability and of phosphite structure on the rate of β scission (k_8) also appear to play a role.



The photolyses of **1-6** were carried out in matched, septum-fitted, quartz test tubes, each of which contained 2.5 mL of a solution of phosphite (0.005 M) and tri-*n*-propyl phosphate (internal standard, about 0.005 M) in 10% *o*-xylene/cyclohexane (v/v). The solutions were purged with argon for 10 min, placed in a merry-go-round apparatus, and irradiated with 254 nm light from a Rayonet reactor. The photorearrangements were monitored by GLC. Relative quantum efficiencies for phosphonate formation, Φ_P(rel), were determined from the times required to reach 20% consumption of each phosphite multiplied by the accountability of phosphite consumed in terms of phosphonate formed. These results appear in the Table. (Reactions of phosphites **1**, and **3-6** occurred with nearly complete regiospecificities,[5] which *excludes*

Table. *o*-Xylene-Sensitized Photorearrangements of Allyl Phosphites

Phosphite	Time, min[a]	Φ_C(rel)[b]	% Acc.[c]	Φ_P(rel)[d]
1	90	1.0	50	1.0
2	15	6.0	75	9.0
3	5	18.0	76	27
4	9	10	76	15
5	35	2.6	65	3.4
6	60	1.5	60	1.8

[a] Time required for 20% consumption of phosphite under constant 254 nm light flux. [b] Relative quantum yields for consumption of phosphites **1-6**. [c] Accountability of phosphite consumption in terms of phosphonate formation: [(moles phosphite consumed)/(moles phosphonate formed)] X 100. [d] Relative quantum yields for formation of phosphonates **7-12**.

the formation of more than minor amounts of phosphonyl [$(MeO)_2P(O)\bullet$]/substituted-allyl radical pairs.)

The value of Φ_P for a given phosphite (eqs 4 and 5) is equal to the product of the quantum yields for sensitization of **A** (Φ_S, eqs 2 and 3), cyclization to ^{3}**B** (Φ_{CY}), and β scission to product **C** (Φ_β) (see Scheme).

$$S \xrightarrow{h\nu} {}^1S \xrightarrow{ISC} {}^3S \qquad 1)$$

$$^3S + A \xrightarrow{k_1} S + {}^3A \qquad 2)$$

$$^3S \xrightarrow{k_2} \text{ground state} \qquad 3)$$

$$\Phi_P = \Phi_S \Phi_{CY} \Phi_\beta \qquad 4)$$

$$= [k_1/(k_1 + k_2)][k_3/(k_3 + k_4 + k_5)][k_8/(k_7 + k_8)] \qquad 5)$$

To interpret the changes in Φ_P in terms of the influence of variations in phosphite structure on Φ_S and Φ_{CY} alone, the efficiency of sensitization of **1-6** must be relatively constant. In this regard, the range of Φ_P(rel) values was nearly the same (25-30) for *o*-xylene and its isomer *m*-xylene which might be expected to have different steric requirements for energy transfer to phosphites **1-6**. The efficiency of sensitization by *m*-xylene, as measured by the time required to reach 20% conversion of a given phosphite, was consistently lower than that for *o*-xylene, but only by 10-20%. Thus, energy transfer is only slightly less efficient from *m*-xylene, consistent with a lack of severe structural constraints on the efficiency of triplet energy transfer.

Indeed, the relative overall quantum yields, Φ_P(rel), can be interpreted in terms of Φ_{CY} and Φ_β (eqs 4 and 5) and reasonable expectations of the effects of phosphite structure change on these two quantum yields. For example, the observed 9-fold reduction in Φ_P(rel) for **1** compared to **2** (see Table) is reasonable if the *secondary carbon radical center* of ^{3}**A** from **1** leads to a reduced value of k_3 (and thus Φ_{CY}), and an increase in k_7 (reformation of allyl phosphite **A**(**1**)) with concomitant reduction in Φ_β.[7] Previously, it has been seen that *primary but not secondary alkyl monoradicals* add reversibly to trialkyl phosphites and yield product alkylphosphonates when a sufficiently rapid β scission process is available:[8]

$$Et\bullet + (MeO)_2POCH_2Ph \rightleftarrows (MeO)_2\dot{P}(Et)OCH_2Ph \rightarrow (MeO)_2P(O)Et + PhCH_2\bullet$$

The reduced Φ_P(rel) value for 1 is highly consistent with the 1,2-biradical model for alkene π-π triplet excited states in which the terminus of ^{3}A from 1 behaves like a secondary monoradical center.* The value of Φ_P(rel) for **2** also may contain a contribution from an increase in k_3,[7] and thus Φ_{CY}, resulting from the stabilizing influence of the methyl substitution in the biradical ^{3}**B** formed from **2** (R^1 = H; R^2 = Me). Moreover, formation from **2** of a disubstituted olefin in **C**(**8**) may further *increase* Φ_P(rel) via an increase in k_8 and thus Φ_β. The alkene moiety in **7** (from **1**) is monosubstituted.

Allyl phosphite **3**, which photorearranges with greatest efficiency (Φ_P(rel) = 27) in the series **1-6**, appears to benefit from three favorable rate constants: large k_3, small k_7 (*primary alkyl radical-equivalent* (^{3}**A**) attack on phosphorus, tertiary radical center in ^{3}**B**), and large k_8. The latter is associated with the formation of allylphosphonate **9** containing a stable *trisubstituted* double bond. Furthermore, the bicyclic biradical ^{3}**B** from **3** appears from Dreiding models to be pyramidal at the carbon radical center and, therefore, a high-energy species that is prone to very rapid β scission (k_8). All favor increased Φ_{CY} and Φ_β.

At first glance the high quantum yield for **4** (Φ_P(rel) =15) might appear anomalous. As with **1** (Φ_P(rel) = 1), a *secondary-like* carbon radical center of triplet **4** (^{3}A) attacks phosphorus (k_3 disfavored, k_7 favored).[7] As with **2**, k_3 is favored by the tertiary carbon center in diradical ^{3}**B**, and a disubstituted alkene system (phosphonate **10**) is formed on β scission (increased k_8). Therefore, a value of Φ_P(rel) between those for **1** and **2** might have been expected. We interpret the unexpectedly large relative phosphonate quantum yield for **4** (Φ_P(rel)=15) to result primarily from the anticipated[1] *extended lifetime* of the *planar* π-π* triplet state for **4** (k_4 very much reduced) and *several kcal/mol higher* π-π* *triplet energy* (k_3 increased). Both effects increase Φ_{CY}. The lifetime and triplet energy phenomena stem from the placement of the C=C bond in the five-membered ring.[1] Thus, the π-π* triplet of **4** is constrained to retain the higher energy, parallel alignment of its adjacent *p* orbitals rather than relax its geometry to one with the *p* orbitals orthogonal; and rapid energy loss from ^{3}**A** to give ground state A(**4**) by the free-rotor mechanism is unavailable. *These factors should lead to a much increased value of* Φ_{CY}, likely the largest for any phosphite in the series. Furthermore, for **4** the strain engendered by the five/five ring structure of ^{3}**B** may well enhance the values of k_8 (β scission) and Φ_P(rel), as was proposed above for **3**.

For phosphites **5** and **6**, bond rotation is much freer, leading to reduced π-π* triplet lifetimes and energies. Their Φ_P(rel) values are small, as expected for the 1,2-biradical model in which the carbon center becoming bonded to phosphorus in ^{3}**B** is secondary (k_3 reduced), as it is for **1**.[7] For **5** and **6**, the tertiary carbon center in ^{3}**B** and disubstituted alkene moiety in **11** and **12** should enhance Φ_{CY} and Φ_β. These factors, also present in the photorearrangement of **2**, may lead to the observed slightly larger Φ_P(rel) values for **5** (2.6) and **6** (1.5) compared to that for **1**(1.0).

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6. Xylenes are typically the sensitizers of choice for the high energy π-π* triplets of non-aryl-substituted alkenes. See Kropp, P.J. *J. Org. Photochem.* **1979**, *4*, 1.
7. In fact ^{3}A → ^{3}B may be reversible ($k_3 \approx k_{-3}$). However, the interpretations made in the text are unaffected. Thus, when the attacking "radical center" in ^{3}A is secondary (phosphites **1** and **4-6**), the expected increase in k_{-3} and decrease in Φ_C would simply accentuate the influence on Φ_P of the anticipated parallel increase in k_7 (see text); i.e. both Φ_β *and* Φ_C (and consequently Φ_P) would be reduced.
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