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Photoinduced Single-Electron-Transfer-Initiated Rearrangements of 2-Phenylallyl Phosphites

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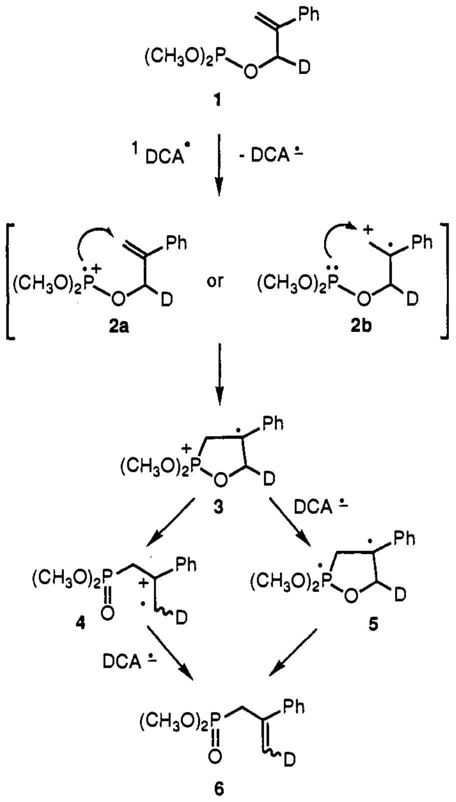
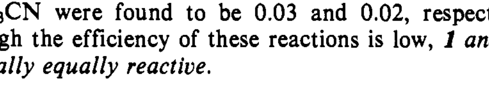
Recently, several accounts have appeared[1] of reactions of cation radicals derived from three-coordinate phosphorus[2] [$(RO)_3P^{\bullet+}$, $Ph_2(RO)P^{\bullet+}$, $Ph_3P^{\bullet+}$] with nucleophiles, including *inter*molecular attacks on π bonds of alkenes. (Such cation radicals from phosphites otherwise undergo unimolecular cleavage processes.[3b]) It seemed possible to us that rearrangement of the 2-phenylallyl phosphite **1** to the corresponding 2-phenylallylphosphonate **6** might be accomplished by an intramolecular, photoinduced, single-electron-transfer process (PSET),[4] Scheme I. Step **2** → **3** is the *intra*molecular equivalent of the postulated first step in the reaction of such cation radicals with alkenes.[1] Since $(EtO)_3P$ and α-methylstyrene have comparable oxidation potentials in acetonitrile (1.57[3] and 1.76 eV,[5] respectively, vs SCE), the site of removal of the electron in not precisely defined in Scheme I. The cyclization of cation radical **2b** finds analogy in the recently reported *intra*molecular reactions of stilbene cation radicals with tethered amine functionalities.[6] Notably, the cyclized cation radical intermediate **3** is the same in either case. Electron recapture would then occur via **3** → **5** or **4** → **6**.

The first excited singlet state of 9,10-dicyanoanthracene, $^1DCA^*$, is an ideal single-electron-transfer agent for the formation of **2a** or **2b**, Scheme I. The free energy change for removal of an electron from $(EtO)_3P$ by $^1DCA^*$ in CH_3CN is approximately −11 kcal/mol, and from α-methylstyrene, −7 kcal/mol (Rehm–Weller equation).[7] DCA absorbs light strongly at relatively long wavelengths, 340–440 nm, well beyond the absorption of the 2-phenylallyl chromophore of **1**. In addition, the energy of $^1DCA^*$ (66.4 kcal/mol)[8] is much less than that of the first singlet of α-methylstyrene (99.6 kcal/mol)[9a] and, presumably, that of **1**. Also, the possibility of triplet energy transfer by DCA to **1** is excluded, as its first triplet, $^3DCA^*$, is only 41.8 kcal/mol[10] above the ground state, while that of α-methylstyrene is about 62 kcal/mol.[9]

Scheme I



Indeed, when an approximately 0.02 M solution of **1** in CH_3CN, saturated with DCA (approximately 0.002 M), was irradiated through Pyrex with light from a medium-pressure 450-W Hg lamp, filtered through a $CuSO_4$–$NaNO_2$–NH_4OH solution[11] to isolate the bands at 406 and 436 nm, clean formation of **6** was observed. The rearrangement displayed the *complete regioselectivity* depicted in Scheme I, as demonstrated by the ^2H NMR spectra of starting **1** and isolated **6**. Likewise, the six-membered-ring phosphite **8** (2-(2-phenylallyl)-1,3,2-dioxaphosphorinane) was converted to its phosphonate **9**, againly cleanly and with complete regioselectivity.



8 **9**

Consistent with a PSET process (Scheme I) involving initial electron transfer to $^1DCA^*$, DCA singlets were found to be quenched very efficiently by **1** and **8** in CH_3CN at 26 °C with k_q = 7.26 × 10^9 and 7.34 × 10^9 M^{-1} s^{-1}, respectively.[12] The quantum yields for formation of phosphonate, ϕ_p, from **1** and **8** in CH_3CN were found to be 0.03 and 0.02, respectively.[14] Although the efficiency of these reactions is low, ***1** and **8** are essentially equally reactive.*

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[2] The name "phosphoniumyl radical" has been suggested for these cation radical intermediates since they conceptually would result from hydrogen atom abstraction from the phosphonium species Z_3PH^+: Tordo, P. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley and Sons: Chichester, 1990; Chapter 6.

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[6] Lewis, F. D.; Reddy, G. D. *Tetrahedron Lett.* **1992**, *33*, 4249.

[7] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. Calculated using −0.89 eV vs SCE as the reduction potential of DCA,[10] 1.57 eV vs SCE as the oxidation potential of triethyl phosphite,[3a] 1.76 eV for the oxidation potential of α-methylstyrene,[4] 0.06 as the Coulombic term in acetonitrile, and 2.88 eV for the energy of $^1DCA^*$.[10]

[8] Lewis, F. D. In Ref 4, Chapter 4.1.

[9] (a) Determined from the O–O band of the $S_0 \rightarrow S_1$ absorption given in Crosby, P. M.; Dyke, J. M.; Metcalfe, J.; Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 183. (b) Tuqlang, N. I.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 457.

[10] Darmanyan, A. P. *Chem. Phys. Lett.* **1984**, *110*, 89.

[11] Schapp, A. P.; Lopez, L.; Gahon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663.

[12] Calculated form Stern–Volmer constants obtained from the steady-state fluorescence quenching of 10^{-5} M DCA in acetonitrile at 355 nm, assuming a DCA singlet lifetime of 15.3 ns.[13]

[13] Erikson, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659.

[14] A Quantacount electronic actinometer from Photon Technology International, Inc., calibrated with the potassium ferrioxalate actinometer, was used with 0.2 M solutions of **1** and **8** at 405 nm.

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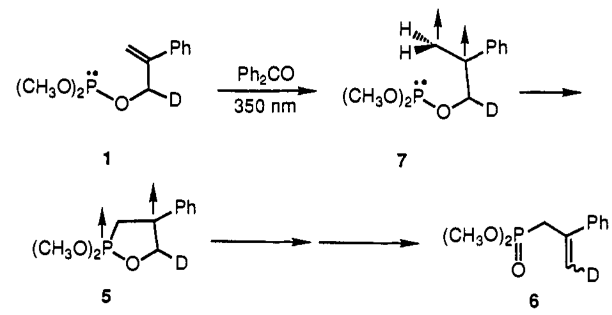
Scheme II



We previously reported the virtually quantitative, totally regioselective, benzophenone-sensitized photorearrangement of **1** to **6**.[15] It was proposed that the process involves intramolecular reaction of a 1,2-biradical-like, triplet styryl functionality (**7**) with three-coordinate phosphorus to yield triplet biradical **5** (Scheme II).[16] This intermediate then gives product via an energetically favorable and kinetically rapid β scission step (**5** → **6**). Biradical **5**, it should be noted, is a possible intermediate common to both Schemes I and II. The near-equal photoefficiencies of formation of **6** and **9** in the processes initiated by SET to DCA is in direct contrast to the quantum yields, ϕ_p, for the reported benzophenone-sensitized rearrangement of **1** and the more recently studied **8** in C_6H_6 of 0.22[15] and 0.003,[17] respectively. *The mechanistic distinction between the DCA and benzophenone-sensitized processes is, thereby, clearly delineated.*

The major emphasis of the present communication is the PSET mechanism for the electrocyclic rearrangements observed. However, the potential preparative advantage of the DCA-induced rearrangements when phosphorus is in a six-membered ring is worth noting. Thus, benzophenone-sensitized rearrangement of cyclic phosphite **8** is so inefficient ($\phi_p = 0.003$ for **8**[17]) as to be impractical from a preparative standpoint. By contrast, the *DCA-initiated PSET process* of the present manuscript, carried out on a 75–100-mg scale, led to 90% consumption of **8** in 20 h to give **9** in 60–70% yields (GLC, based on total starting **8**). At similar conversions (12 h), **1** was transformed to phosphonate **6** in 70–75% yields. *Clearly, the PSET rearrangement of six-membered-ring phosphite **8** to **9*** proceeds in useful fashion.

The process of Scheme I has a further potential synthetic advantage over the triplet-sensitized reaction of Scheme II, where either cyclic or acyclic phosphites are concerned. Thus, the presence of a chromophore that absorbs at relatively long wavelengths may limit the choice of triplet sensitizers. However, the electron-accepting singlet excited states of several molecules commonly used in PSET processes, including DCA, are formed by absorption of light at wavelengths well beyond the absorbance of many chromophores. An example of the synthetic potential of the PSET process is a preliminary study of the rearrangement of the mixture of diastereomers (60/40, trans/cis; ^{31}P NMR) of a thymidine-based cyclic 3′,5′-phosphite (**10**, T = thymin-1-yl) to the diastereomers of the corresponding phosphonate, **11** (cis/trans ≅ 40/60). (Cis or trans refers to relation of thymin-1-yl and 2-phenylallyl.) This process proceeds without interference by the strongly absorbing nucleobase, thymin-1-yl ($\lambda_{max} \sim 265$ nm; essentially no UV absorption above 300 nm). Irradiation of a 0.01 M solution of 40 mg of **10** in acetonitrile, saturated with DCA, led to 70–75% consumption of **10** in 9 h to yield 60–65% of **11**, based on consumed **10** (quantitative ^{31}P NMR measurements with $(CH_3O)_3PS$ as internal standard, 50-s repetition rate). The individual diastereomers of **11** were isolated from a 200-mg scale reaction by HPLC on silica gel (98/2 $CHCl_3/CH_3OH$) and fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and by FAB HRMS. The conversion of **10** to **11** fails in the absence of DCA. Furthermore, although an allylphosphonate such as **11** might be formed by the Michaelis–Arbuzov reaction[18] of a trialkyl phosphite with an allyl halide or tosylate, the possibility of multiple-site alkylation is a distinct drawback. This would be especially true in applications to purine nucleosides which are subject to alkylation at the nucleobase.

In summary, we view the PSET rearrangements of **1** and **8** to be mechanistically novel processes with a potential for synthetic applications that is yet to be fully investigated. The possibility of increasing the efficiency of these PSET processes, e.g., through addition of cosensitizers such as biphenyl[11,19] or metal salts[19b,20] to reduce back electron transfer (**2** → **1**),[21] will be explored. The scope of these processes with allyl phosphites with other substituents in place of the 2-phenyl also is being studied.

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Supplementary Material Available: ^{1}H, ^{13}C, and ^{31}P NMR spectral and HRMS data for the individual diastereomers of **11** as well as ^{1}H and ^{31}P NMR data for **10**; preparative details for **10** (11 pages). Ordering information is given on any current masthead page.

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(15) The value 0.22 was obtained under refined conditions of measurement[14,17] and replaces the 0.8 value reported earlier (Bentrude, W. G.; Lee, S.-G.; Akutagawa, K.; Ye, W.; Charbonnel, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1577).

(16) The photorearrangements of **1** and **8** also can be sensitized by triphenylene with regiochemistries and similar quantum yields identical to those determined with benzophenone.[15,17] Since the energetics of singlet energy transfer and/or SET to **1** or **8** by triphenylene are very unfavorable, the triplet nature of the triphenylene-sensitized processes is clear. By inference the interpretation of the benzophenone-sensitized photorearrangements of **1** and **8** as triplet processes is supported by the triphenylene experiments.

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