J. Org. Chem. **2000,** *65,* 6167−6172

Laser Flash Photolysis Evidence for Styryl Radical Cation Cyclization in the SET-Induced Photorearrangement of a *p*-Methoxy-Substituted 2-Phenylallyl Phosphite

Deepak Shukla,[‡] Cuong Lu,[†] Norman P. Schepp,[‡] Wesley G. Bentrude,*[,†] and
Linda J. Johnston*[,‡]

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and
National Research Council Canada, Ottawa, Canada K1A 0R6

bentrude@chemistry.utah.edu

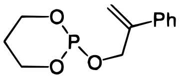
Received May 2, 2000

The SET-induced photorearrangement of dimethyl 2-(4-methoxyphenyl)allyl phosphite, **9** (UV light, uranium glass filter, 9,10-dicyanoanthracene (DCA), biphenyl), gives phosphonate **12** in 83% isolated yield. Laser flash irradiation at 355 nm of oxygen saturated solutions of phosphite **9** containing DCA and biphenyl generates the transient UV spectrum of the biphenyl radical cation that is quenched by electron transfer from phosphite **9** ($k_q = 8.9 \times 10^9$ M^{-1} s^{-1} at 20 °C) to form the 4-methoxystyryl cation **10**. The UV spectrum of **10** decays by a measured first-order rate constant of 8.0×10^6 s^{-1}, presumably to generate the cyclic distonic radical cation **11**. Intermediate **10** was further characterized by measurement of the second-order rate constants for its reaction with azide, chloride, and bromide ions and with the neutral nucleophile trimethyl phosphite. This study provides the first spectroscopic evidence regarding the proposed mechanism (Schemes 1 and 2) for the SET-induced photorearrangements of dimethyl 2-arylallyl phosphites to the corresponding 2-arylallylphosphonates. Moreover, absolute rate constants for the intramolecular trapping of alkene radical cations have seldom been measured. The removal of the electron from the styryl moiety of phosphite **9**, rather than from phosphorus, and the detectability of **10** arise from the stabilizing effect of the 4-methoxy substituent. These results, however, do not allow conclusions to be made concerning the site of removal of an electron in the SET-induced photorearrangement of dimethyl 2-phenylallyl phosphite **1** to phosphonate **6**.

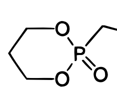
Introduction

The rearrangement of dimethyl 2-phenylallyl phosphite **1** to the corresponding 2-phenylallyphosphonate, **6**, can be photoinduced via an SET process with the singlet excited state of 9,10-dicyanoanthracene (^{1}DCA*) as the electron acceptor (Scheme 1).[1] The regiochemistry of the process, determined previously by deuterium NMR spectroscopy, is shown in Scheme 1. The initial site of oxidation of **1** is unknown, because the oxidation half-wave potentials for the model systems trimethyl phosphite, $(MeO)_3P$ ($E_{ox} = 1.64$ eV[2]), and α-methylstyrene, $MeCPh{=}CH_2$ ($E_{ox} = 1.76$ eV[3]), are quite similar. Nevertheless, cyclization of the initial radical cation (**2a** or **2b**) is proposed to generate the distonic 1,3-radical cation **3**.[1] Two potential routes for formation of **6** are given in Scheme 1: (1) β scission of **3** followed by reduction of the resulting 2-phenylallylphosphonate radical cation, **5**, and (2) reduction of radical cation **3** to the phosphoranyl 1,3-diradical, **4**, followed by β scission to introduce the two π bonds in **6**. Although intermolecular trapping of radical cations has been extensively studied, there are still relatively few examples of intramolecular cyclizations. Reported examples include trapping of alkene radical cations by alcohols,[4] carboxylic acids,[5] and remote alkenes.[6,7]

The quantum yield for formation of phosphonate **6** (ϕ_P) on SET-induced photorearrangement of **1** with DCA, 0.03, has been shown to be identical with that for generation of phosphonate **8** from phosphite **7**.[1] This is



7



8

in contrast to the very different quantum yields noted[8]

---

* Linda.Johnston@nrc.ca.

[†] University of Utah.

[‡] National Research Council, Canada.

(2) Ganapathy, S.; Dockery, K. P.; Sopchik, A. E.; Bentrude, W. G. *J. Am. Chem. Soc.* **1993**, *115*, 8863. The stereochemistry at phosphorus for this rearrangement has recently been reported: Hager, D. C.; Sopchik, A. E.; Bentrude, W. G. *J. Org. Chem.* **2000**, *65*, 2778.

(3) Oxidation potential vs SCE for $(MeO)_3P$, 1.64 eV (Ohmori, H.; Nakai, S.; Masui, M. *J. Chem. Soc., Perkin Trans.* **1979**, 2023).

(4) Oxidation potential for α-methylstryene vs SCE, 1.76 eV (Katz, M.; Riemenschneider, P.; Wendt, H. *Electrochim. Acta* **1972**, *17*, 1595).

(5) (a) McManus, K. A.; Arnold, D. R. *Can. J. Chem.* **1995**, *73*, 2158. (b) Herbetz, T.; Roth, H. D. *J. Am. Chem. Soc.* **1996**, *118*, 10954. (c) Dai, S.; Wang, J. T.; Williams, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1063. (d) Jiang, Z. Q.; Foote, C. S. *Tetrahedron Lett.* **1983**, *24*, 461.

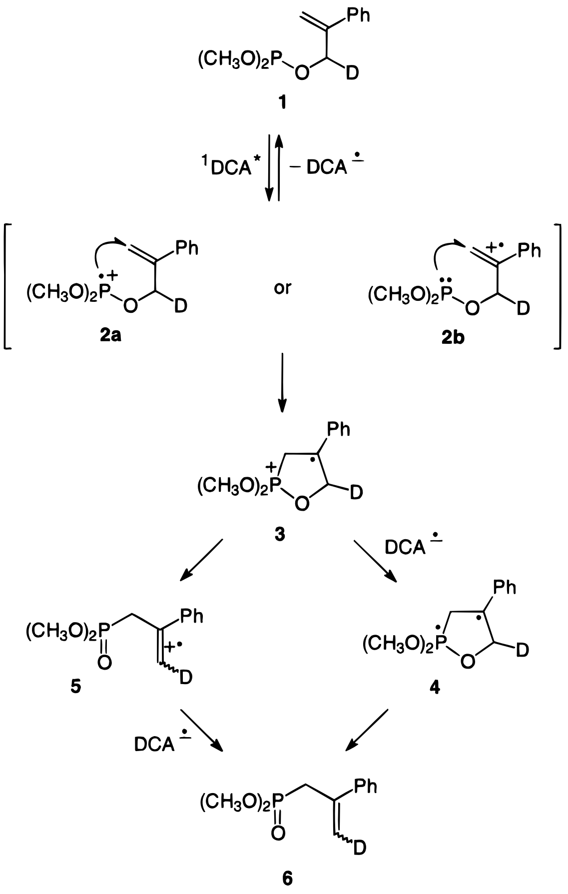
(6) (a) Gassman, P. G.; Bottoroff, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 7547. (b) Gassman, P. G.; DeSilva, S. A. *J. Am. Chem. Soc.* **1991**, *113*, 9870.

(7) (a) Arnold, D. R.; McManus, K. A. *Can. J. Chem.* **1998**, *76*, 1238. (b) Arnold, D. R.; Connor, D. A.; McManus, K. A.; Bakshi, P. K.; Cameron, T. S. *Can. J. Chem.* **1996**, *74*, 602. (c) Weng, H.; Scarlata, C.; Roth, H. D. *J. Am. Chem. Soc.* **1996**, *118*, 10947. (d) Kim, T.; Mirafzal, G. A.; Liu, J.; Bauld, N. L. *J. Am. Chem. Soc.* **1993**, *115*, 7653.

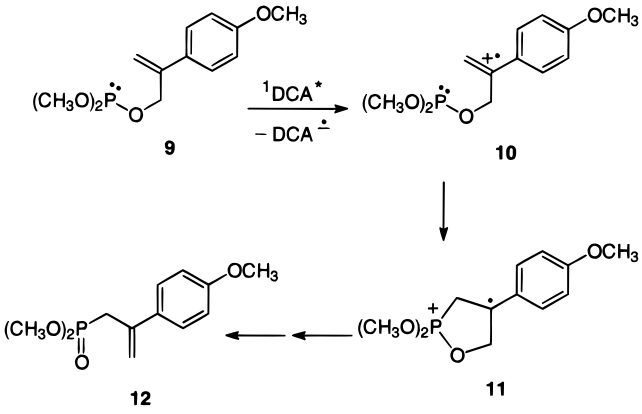
(8) (a) Tamai, T.; Mizuno, K.; Hashida, I.; Otsuji, Y.; Ishida, A.; Takamuku, S. *Chem Lett.* **1994**, 149. (b) Mizuno, K.; Tamai, T.; Hashida, I.; Otsuji, Y.; Kuriyama, Y.; Tokumaru, K. *J. Org. Chem.* **1994**, *59*, 7329. (c) Gollnick, K.; Schnatterer, S.; Utschick, G. *J. Org. Chem.* **1993**, *58*, 6049.

10.1021/jo0006775 CCC: $19.00

Scheme 1



Scheme 2



for the regiospecific, *triplet-sensitized* photorearrangements of **1** ($\phi_P = 0.2-0.3$) and **7** ($\phi_P = 0.003$) to **6** and **8**, respectively.

In the present paper we report the successful detection of the 4-methoxystyryl radical cation **10** (Scheme 2), generated from dimethyl 2-(4-methoxyphenyl)allyl phosphite **9** by laser flash photolysis (LFP) techniques and the observation of the first-order decay of **10**, *presumably to give the cyclic distonic 1,3-radical cation* ***11***. These results provide strong corroborative evidence for the presumed mechanism of the photorearrangement of **9**. The readily oxidized 4-methoxystyryl group ensures donation of the electron from the styryl moiety of phosphite **9** to the excited singlet of DCA. The measured rate constant for cyclization of the initial radical cation also provides one of the first examples of absolute kinetic data for intramolecular nucleophilic trapping of an alkene radical cation.[9]

Results and Discussion

Direct experimental evidence concerning the proposed mechanism of Scheme 1 has not been presented up to now. The Weller equation[11] estimates oxidation of $(MeO)_3P$ by ^{1}DCA* to be energetically favorable by 10 kcal/mol[12] while electron removal from α-methylstyrene should be accompanied by an energy release of 7 kcal/mol.[12] As noted earlier[1] these values are too similar to predict with assurance that the site of removal of the electron by the excited singlet DCA from **1** should be the phosphorus atom rather than the styryl π bond.

In an initial laser flash photolytic approach to study of the mechanism of Scheme 1, using dimethyl 2-phenylallyl phosphite **1** and several photosensitizers, none of the potential intermediates, **2**–**5**, could be detected in either acetonitrile or 2,2,2-trifluoroethanol. Failure to detect the initial radical cation may indicate that its lifetime is too short for detection due to rapid cyclization. Alternately, the radical cation may not have a sufficiently strong UV–visible absorption for detection under our conditions, particularly if it is localized on phosphorus (**2a**). Although styrene radical cations have been characterized by LFP, it is worth noting that the α-methylstyrene radical cation is too short-lived for nanosecond measurements in acetonitrile but can be observed in TFE.[15] Thus, observation of a radical cation localized on the styryl moiety of **1** can be difficult, even in the absence of rapid intramolecular cyclization.

The stabilizing effect on styryl radical cations of a 4-methoxy substituent has been well documented.[15,16] The removal of an electron from *p*-methoxystyrene ($E_{ox} = 1.49$ eV[16]) by ^{1}DCA* is 13 kcal/mol exergonic, i.e., 6 kcal/mol more favorable than the −7 kcal/mol value estimated earlier for α-methylstyrene as a model for **1**. Furthermore, electron transfer from the styryl group of **9** (Scheme 2) is likely to be 2–3 kcal/mol more exergonic than that from *p*-methoxystyrene by analogy with the effects of α-methyl substitution (actually CH_2O in **9**) on the oxidation potentials of related styrenes.[16] Thus, the

---

[8] (a) Bentrude, W. G.; Dockery, K. P.; Ganapathy, S.; Lee, S.-G.; Tabet, M.; Wu, Y. W.; Cambron, R. T.; Harris, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 6192. (b) Ganapathy, S.; Cambron, R. T.; Dockery, K. P.; Wu, Y. W. *Tetrahedron. Lett.* **1993**, *34*, 5987. (c) Bentrude, W. G.; Lee, S.-G. *J. Am. Chem. Soc.* **1987**, *109*, 1577. (d) Bentrude, W. G.; Lee, S.-G.; Akutagawa, K.; Ye, W.; Charbonnel, Y.; Omelanczuk, J. *Phosphorus Sulfur* **1987**, *30*, 105. The stereochemistry at phosphorus of this rearrangement has recently been reported: Hager, D. C.; Bentrude, W. G. *J. Org. Chem.* **2000**, *65*, 2786.

[9] Several rate constants for intramolecular dimerization[6d,7,10] and Diels–Alder cyclizations[6d,10] of alkene radical cations have been reported.

[10] Schepp, N. P.; Shukla, D.; Sarker, H.; Bauld, N. L. Johnston, L. J. *J. Am. Chem. Soc.* **1997**, *119*, 10325.

[11] Rehm, D.; Weller, A. *Isr. J. Chem.* **1979**, *8*, 4269.

[12] Calculated using −0.89 eV vs SCE as the reduction potential for DCA,[13] 1.64 eV for the oxidation potential of $(MeO)_3P$,[2] 1.76 eV for the oxidation potential of α-methylstyrene,[3] 0.06 eV as the Coulombic term in acetonitrile,[14] and 2.88 eV for the energy of the first singlet of DCA (^{1}DCA*).[13]

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

[14] Table 2 of *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; Part C, Chapter 4.1.

[15] Johnston, L. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1993**, *115*, 6564.

[16] Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872.

4-methoxy-substituted analogue of **1** should provide a better substrate for obtaining spectroscopic and kinetic information on the initial radical cation and its further rearrangements. Therefore, dimethyl 2-(4-methoxyphenyl)allyl phosphite **9** was prepared by standard techniques from reaction of dimethyl *N,N*-dimethylphosphoramidite with the requisite alcohol, 2-(4-methoxyphenyl)-2-propen-1-ol. Purified phosphite was characterized spectroscopically and by conversion to the phosphate, **9-O**, easily identified by NMR, elemental analysis, and HRMS (Experimental Section).

Product Study. Authentic phosphonate **12** was prepared near-quantitatively (93% isolated yield) by the sensitization of the photorearrangement of **9** by benzophenone triplet, populated by Pyrex-filtered light from a 450 W medium-pressure mercury UV lamp (see Experimental Section). The near-quantitative triplet-sensitized conversion of dimethyl 2-phenylallyl phosphite (**1**) to the corresponding 2-phenylallylphosphonate (**6**) was reported earlier.[8] The structure of **12** was readily verified by mass spectrometry (LRMS and HRMS) along with ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

The excited singlet DCA-induced photorearrangement of a deoxygenated 0.14 M acetonitrile solution of **9** that was also 0.02 M in DCA and contained a large excess of biphenyl (4 M) as cosensitizer was carried out by irradiation through Pyrex with 350 nm light from a Rayonet reactor. The reaction was monitored by GC which showed the consumption of phosphite **9** to be complete in 72 h. Phosphonate **12** was obtained by radial chromatography in 83% *isolated* yield.

Laser Flash Photolysis (LFP). An important aspect of the mechanism of the DCA/biphenyl cosensitized rearrangement of **9** was revealed in a LFP study. In particular the removal of an electron from **9** gives the detectable radical cation **10** *with the radical cation localized in the 2-(4-methoxyphenyl)allyl functionality*. This means that, as anticipated, the methoxy substitution has rendered the alkene site the one of definitively lower oxidation potential and also has sufficiently stabilized the radical cation to make it observable.

Thus, laser excitation (355 nm) of an oxygen-saturated acetonitrile solution of DCA (5.0×10^{-4} M, $OD_{355nm} = 0.52$) containing biphenyl (0.2 M) at 20 °C gave the characteristic transient spectrum[17]of biphenyl radical cation ($\lambda_{max} = 390$ and 680 nm, $\tau \approx 1.7\ \mu$s). The decay of the biphenyl radical cation was enhanced in the presence of **9**. The slope of a linear plot of the observed rate constant for decay of the biphenyl radical cation, k_{obs}, vs [**9**] ([**9**] = 0.0002−0.0009 M, seven points, correlation coefficient = 0.99734) yielded a second-order rate constant, $k_q = 8.9 \times 10^9$ M^{-1} s^{-1}. At [**9**] = 0.002 M, the biphenyl radical cation spectrum was completely quenched with the concomitant formation of a new transient with two absorption bands (Figure 1, $\lambda = 610$ and 380 nm). The identical decay kinetics for the two bands ($k_0 = 8.0 \times 10^6$ s^{-1}) showed that they belong to a single species. The close similarity of this spectrum to that of the 4-methoxystyrene radical cation in CH_3CN[15] assigns it to the radical cation of **9** with the ion radical localized on the *p*-methoxystyrene moiety (**10**). An experiment in the absence of biphenyl cosensitizer failed to give detectable concentrations of transient **10**. The use of biphenyl to increase the efficiency of production of free radical ions in other photoinduced SET reactions is well-documented.[18]

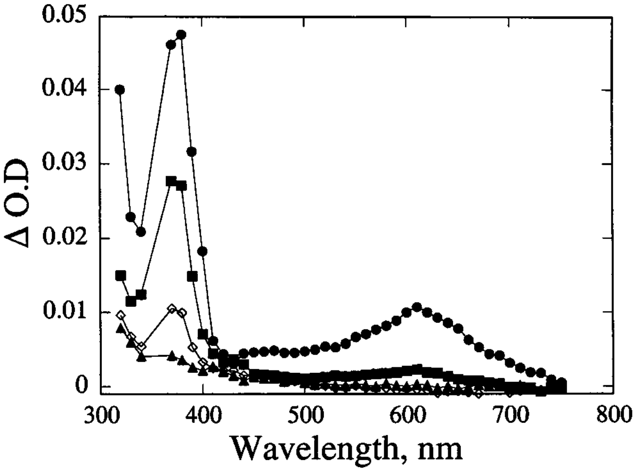


Figure 1. Transient absorption spectra of **10** obtained by 355 nm excitation of 9,10-dicyanoanthracene (3×10^{-4} M) in the presence of 0.15 M biphenyl and 1.5 mM dimethyl 2-(4-methoxyphenyl)allyl phosphite **9** in oxygen-purged acetonitrile. Spectra were recorded 0.24 (●), 1.04 (■), 3.0 (◇), and 6.4 (▲) μs after the laser pulse.

Intermediate **10** decayed in the presence of added nucleophiles, Nu, in CH_3CN with an observed rate constant, k_{obs}, correlated with nucleophile concentration by the rate equation:

$$k_{obs} = k_0 + k_{Nu}[Nu]$$

Nicely linear plots (correlation coefficients greater than 0.99) of [Nu] vs k_{obs} for azide, chloride, and bromide ion, that included the experimentally determined origin value of k_0 ([Nu] = 0) mentioned earlier, yielded second-order rate constants for nucleophilic attack: $k_{azide} = 1.9 \times 10^{10}$ M^{-1} s^{-1}; $k_{Cl} = 2.2 \times 10^{10}$ M^{-1} s^{-1}; $k_{Br} = 1.8 \times 10^{10}$ M^{-1} s^{-1}. The similarity of these rate constants to those previously determined for attack of this series of nucleophiles on 4-methoxystyrene radical cation itself is consistent with assignment of the observed transient to radical cation **10**. To further confirm that the rate constant for decay of **10** is limited by intramolecular cyclization, we examined the reaction of the radical cation from *p*-methoxystyrene itself with trimethyl phosphite in oxygen-saturated acetonitrile. The measured second-order rate constant of 4.4×10^8 M^{-1} s^{-1} is consistent with previous measurements of the reactivity of other uncharged nucleophiles such as alcohols with styrene radical cations[15] and clearly indicates that phosphites are efficient radical cation traps.

The observed first-order decay of **10** in the absence of added nucleophiles, k_0, presumably is for the cyclization step **10** → **11**. By comparison, the radical cation from *p*-methoxystyrene is approximately 2 orders of magnitude longer lived in the same solvent in the absence of

---

(17) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(18) The use of ^{1}DCA* to generate biphenyl radical cation leads to a quantum yield of cage escape to give free radical ions of 0.83. The high yield is due to the fact that back electron transfer between biphenyl radical cation and cyanoaromatic sensitizer radical anions is sufficiently exergonic to fall in the Marcus inverted region and is thus much slower than is typical for more easily oxidized donors. Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

nucleophiles.[15] The additional substituent in **10**, the β-CH_2OP, would be expected to further lengthen the lifetime of the radical cation.

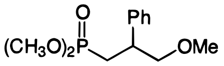
The rate constant for cyclization of radical cation **10** can be compared to literature data for related radical cation cyclizations of alkenes. For example, rate constants that vary from 3×10^6 to 1.2×10^9 s^{-1} have been reported for intramolecular dimerization and cycloaddition of *p*-methoxy-β-alkylstyrene radical cations.[6d,10] Similar data are available for radical cation-initiated dimerization of several 1,ω-bis(diarylethenyl)alkanes.[7] Although absolute kinetic data are not available for the intramolecular nucleophilic trapping of alkene radical cations, the competition between inter- and intramolecular alcohol trapping has given rise to an estimate of $\sim 2 \times 10^6$ s^{-1} for the rate of intramolecular trapping of a vinylcyclopropane radical cation.[4b] The relatively slow reaction has been suggested to reflect steric hindrance to intramolecular capture.

In contrast to the results described for phosphite **9**, use of biphenyl cosensitizer with DCA under conditions similar to those employed for **9** failed to cleanly effect the rearrangement of **1** (unpublished results[19]), although in the absence of biphenyl reasonably high yields of **6** were obtained. A second product, $(MeO)_2P(O)C_6H_4$-C_6H_5 (two isomers), from competing phosphorylation of biphenyl was observed along with **6**. This product most likely arises from nucleophilic attack by **1** on the biphenyl radical cation. (The same phosphorylation product is formed exclusively when $(MeO)_3P$ instead of **1** is used.[19]) This indicates that electron transfer from **1** to the biphenyl radical cation is energetically relatively unfavorable, and reaction with phosphorus, acting as a nucleophile, competes with electron transfer. (Literature data on reactions of nucleophiles with styrene and anthracene radical cations indicate that electron transfer is favored over nucleophilic addition when the former is exergonic by 0.1−0.2 eV.[20]) Clearly, the energetics of electron transfer to biphenyl radical cation from the 4-methoxystyryl moiety of **9** is greatly favored over donation of an electron from either the styryl functionality or phosphorus atom of **1** or **9** and is also more rapid than nucleophilic attack by phosphorus. However, these results do not allow the site of removal of the electron from **1** by $^1DCA^*$ to be assigned.

Unfortunately, the cyclic distonic radical cation **11**, which should display UV absorption characteristic of a benzylic radical, is not detected by the LFP experiments, perhaps because it undergoes very rapid reaction. The detection of a benzylic radical is also complicated by the fact that there is significant ground-state absorption at 320 nm under the conditions required for the photosensitized electron-transfer experiments using DCA/biphenyl. Furthermore, the present study gives no definitive information for phosphite **1** concerning the two pathways for conversion of **3** to **6** in Scheme 1. However, if **3** → **5** were the operative mechanism for this photorearrangement (Scheme 1), evidence for formation of the 4-methoxy analogue of **5** might have been encountered in the LFP kinetic study of **9**. The kinetic measurements then should have been poorly behaved because of the expected similarities of the UV spectra of **10** and the 4-methoxy analogue of **5**. However, the latter radical cation may be rapidly reduced by $DCA^{-\bullet}$. This process should be ~2.3 eV exergonic, based on an estimated oxidation potential of 1.4 eV for *p*-methoxy-α-methylstyrene[16] and the known reduction potential of DCA (−0.89 eV[13]).

A model for the reduction of **3** to 1,3-biradical **4** by $DCA^{-\bullet}$ might be the reduction of $[RPPh_3]^+$ for which reduction potentials have been published.[21] Conversion of **3** to **4** by $DCA^{-\bullet}$ is thereby estimated to be *endergonic* by 11 kcal/mol. It is likely that the reduction potential for **3** is in fact more favorable since $[(RO)_3PR']^+$, a closer model for **3**, should have a less negative one-electron reduction potential as a result of the electronegative alkoxy substitutents on phosphorus. Furthermore, the formation of 1,3-biradical **4** may be energetically more favorable than the above model estimates since certain cyclic five-membered ring 1,3-diradicals in all-carbon ring systems are known to be stabilized relative to their monoradical counterparts.[22] Moreover, energetically unfavorable reductions can occur as essential steps in electron-transfer chemistry. The energetics of the potential alternative competing step **3** → **5** of Scheme 1 is not readily approximated, although the introduction of two π bonds should be energetically favorable.

Evidence *against* the process **3** → **5** comes from unsuccessful attempts to trap **5** with MeOH (unpublished[19]) in studies of the SET-induced rearrangement of **1** with DCA as electron acceptor. Although an approximate 8% yield of methanol adduct **13** results when **1** is rearranged under SET conditions in the presence of MeOH, its generation lags considerably behind formation of **6**. We assign the origin of **13** to the DCA-sensitized addition of MeOH to **6**, a reaction which we found to be readily induced in an independent experiment.[19] The lack of formation of trimethyl phosphate in the reactions with methanol as a trap argues for the initial formation of **2b** rather than **2a**.



13

Conclusions

A laser flash photolysis study of the $^1DCA^*$-induced photorearrangement of the allyl phosphite **9** to phosphonate **12** gives UV absorption spectroscopic evidence for the formation of the transient radical cation **10**. Intermediate **10** is further characterized by reasonable values of second-order rate constants for its reaction with a series of added nucleophiles. The lifetime of **10** is approximately 100 times shorter than that of its simpler counterpart, *p*-methoxystyrene itself. The measured first-order rate constant for its disappearance (8.0×10^6 M^{-1} s^{-1}) presumably corresponds to the cyclization step **10** → **11** and provides one of the first calibrations of an intramolecular trapping rate for an alkene radical cation. Such data are of key importance in development of a firm mechanistic basis for the use of radical ion chemistry in

---

[19] Dockery, K. P. Ph.D. Dissertation, University of Utah, 1995.

[20] Johnston, L. J.; Schepp, N. P. *Adv. Electron-Transfer Chem.* **1996**, *5*, 41.

[21] On the basis of the average of one-electron reduction potentials vs SCE of $[PhCMe_2PPh_3]^+$ (−1.5 eV) and $[MeCPh_2PPh_3]$ (−1.24 eV) (Saveant, J. M.; Binh, S. K. *J. Org. Chem.* **1977**, *42*, 1242) and the reduction potential of DCA (−0.89 eV[13]).

[22] Adam. W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929.

synthesis and in probing biological reaction mechanisms. The results also provide supporting evidence for the reaction mechanism proposed in Scheme 1 with initial formation of radical cation **10**, analogous to **2b**, at least when a stabilizing 4-methoxy substituent is attached to the phenyl ring. Unfortunately, no spectroscopic evidence for the intermediates analogous to **3**−**5** was encountered.[23]

Experimental Section

General Methods. Starting materials were obtained from Aldrich or Acros and, unless otherwise indicated, were used without further purification. Anhydrous solvents were obtained as follows: diethyl ether (Et$_2$O), tetrahydrofuran (THF), and benzene were distilled over sodium/benzophenone under nitrogen; methylene chloride and acetonitrile were distilled over calcium hydride under argon. Triethylamine and diisopropylamine were distilled over calcium hydride prior to use. Benzophenone was recrystallized from ethanol. All atmosphere-sensitive reaction solutions were prepared under argon using glovebag techniques and then run under argon. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F$_{254}$ precoated silica gel plates. Column chromatography was carried out with silica gel 60 (230−400 mesh) from Mallinckrodt. Chromatography performed on a Chromatotron[7] 7924T apparatus utilized silica gel 60 PF$_{254}$ containing gypsum purchased from EM Science. Distillations were performed on a short-path distillation apparatus. Melting points are uncorrected. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross, GA, and by Midwest Microlab, LLC, Indianapolis, IN.

NMR and GC Measurements. Proton (^{1}H), carbon (^{13}C), and phosphorus (^{31}P) NMR spectra were recorded routinely and referenced to the usual standards. NMR splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sept (septet), and m (multiplet). Coupling constants (J) are in hertz. J values refer to proton−proton coupling unless otherwise stated. ^{13}C NMR J values designate carbon−phosphorus couplings. Gas chromatography (GC) was performed in the FID mode on 20 m × 0.25 mm × 0.25 μm fused silica DB-1 phase capillary column. GC-MS (EI) measurements (70 eV) utilized a 30 m × 0.25 mm × 0.25 μm fused silica HP-1 phase capillary column. High-resolution EIMS measurements also were at 70 eV. The molecular ion is indicated by [M$^+$].

Laser Flash Photolysis. The flash photolysis system has been described in detail elsewhere.[24] For these experiments a Lumonics HY750 Nd:YAG laser (355 nm, 10 ns/pulse, <50 mJ/pulse) was used for sample excitation. Samples were contained in 7 × 7 mm^2 quartz cells and were deaerated by purging with oxygen prior to laser irradiation.

Dimethyl *N,N*-diisopropylphosphoramidite was routinely prepared by coaddition under argon of a solution of (isoPr$_2$N)$_2$PCl (94 g, 0.46 mol) in diethyl ether (100 mL) and triethylamine (94 g, 0.93 mol) in methanol (30 g, 0.93 mol) to 650 mL of stirred diethyl ether at room temperature, followed by stirring overnight, then filtration and distillation. ^{31}P NMR (121.4 MHz, CDCl$_3$): δ 150.21 [lit.[25] δ 151.0].

Preparation of 2-(4-Methoxyphenyl)-2-propene. A procedure adapted from Maryanoff and Reitz[26] was used. To a stirred solution of methyl triphenylphosphonium bromide (48 g, 0.13 mol) in dry tetrahydrofuran (500 mL), cooled to −20 °C, was added 2.5 M of n-BuLi in hexane (53 mL, 0.13 mol) via syringe. After 30 min of stirring at −20 °C, 4-methoxyacetophenone (10 g, 67 mmol) was added in one portion. The reaction was quenched with water (100 mL) and extracted with tetrahydrofuran (3 × 50 mL) which was washed with aqueous sodium chloride (3 × 50 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo to give a brown oil. Distillation in vacuo (bp 51 °C at 0.35 Torr) yielded white crystals (8.1 g, 82% yield); mp 33.5−34.5 °C (lit.[27] 32.0−32.5 °C). ^{1}H NMR (299.7 MHz, CDCl$_3$): δ 2.13 (dd, ^4J = 1.5 Hz, ^4J = 0.7 Hz, 3H), 3.81 (s, 3H), 4.99 (dq, ^4J = 1.5 Hz, ^2J = 2.4 Hz, 1H), 5.28 (dq, ^2J = 2.4 Hz, ^4J = 0.7 Hz, 1H), 6.85−7.43 (m, 4H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 21.91 (CH$_3$), 55.25, 110.64, 113.51, 126.58, 133.70, 159.04, 142.52; LRMS (EI) m/z 148 (M$^+$, 53), 135 (78), 105 (44), 89 (65), 77 (87), 61 (20), 51 (20), 43 (47), 28 (100). HRMS (EI): calcd for C$_{10}$H$_{12}$O [M$^+$] 148.0888. Found: 148.0909. Anal. Calcd for C$_{10}$H$_{12}$O: C, 81.04; H, 8.16. Found: C, 81.22; H, 8.29.

Preparation of 4-Methoxyacetophenone Tosylhydrazone. A solution of 4-methoxyacetophenone (60 g, 0.40 mol) in methanol (500 mL) was magnetically stirred at room temperature for 5 min. Tosylhydrazide (93 g, 0.50 mol) was added in one portion followed by 2 drops of concentrated hydrochloric acid. The reaction solution was stirred for another 3 h at room temperature, monitored by TLC, and then placed in a freezer overnight. The hydrazone precipitated from solution as a white solid that was washed with 250 mL of cold methanol and then dried in vacuo overnight to give 125 g (98% yield): mp 164.5−165.5 °C (dec) [lit.[28] mp 166−168 °C (dec)]. HRMS (EI): calcd for C$_{16}$H$_{18}$N$_2$O$_3$S [M$^+$] 318.1038. Found 318.1037. Anal. Calcd for C$_{16}$H$_{18}$N$_2$O$_3$S: C, 60.36; H, 5.70. Found: C, 60.44; H, 5.75.

Preparation of 2-(4-Methoxyphenyl)-2-propen-1-ol. The method was adapted from that of Chamberlin and co-workers.[29] To a stirred solution of 4-methoxyacetophenone tosylhydrazone (10 g, 31 mmol) and tetrahydrofuran (300 mL) at 0 °C under argon was added, dropwise, 2.5 M n-BuLi in hexane (42 mL, 0.10 mol) via syringe. The resulting red solution was stirred at 0 °C until the evolution of N$_2$ gas was complete. Paraformaldehyde (1.9 g, 63 mmol), dried overnight over phosphorus pentoxide in a desiccator, was added in one portion. The reaction mixture changed color from dark red to creamy yellow. The stirred solution was warmed to room temperature and held overnight or until completion of the reaction (monitored by TLC). The reaction was quenched with aqueous ammonium chloride (100 mL) and extracted with ethyl acetate (3 × 50 mL) which was dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo to give a dark brown oil that was purified by column chromatography on silica gel (eluted with 10% triethylamine, 30% ethyl acetate−hexanes) to give a solid, recrystallized from ethyl acetate/hexanes to yield white crystals (2.9 g, 55% yield): mp 78−79 °C [lit.[29] mp 71−73 °C]. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 1.80 (s, 1H), 3.81 (s, 3H), 4.50 (s, 2H), 5.25 (dt, ^4J = 1.5 Hz, ^2J = 1.2 Hz, 1H), 5.38 (dt, ^2J = 1.2 Hz, ^4J = 0.7 Hz, 1H), 6.85−7.42 (m, 4H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 55.27, 65.10, 111.05, 113.85, 127.18, 130.83, 159.37, 146.50. Anal. Calcd for C$_{10}$H$_{12}$O$_2$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.37.

Preparation of Dimethyl 2-(4-Methoxyphenyl)-2-propen-1-yl Phosphite (9). A solution of 2-(4-methoxyphenyl)-

---

[23] A reviewer has suggested that these SET processes involve back electron transfer from the DCA anion radical to **2b** or **10** to generate the triplet excited state of **1** and **9**, respectively, that then leads to phosphonate via mechanisms previously proposed by the Bentrude group[8] for triplet excited states of allyl phosphites formed by triplet sensitization. This is highly unlikely, however, because of (1) the predicted low efficiency of initial triplet ion pair generation, (2) the likely inability of the bimolecular electron transfer to **2b** or **10** to compete with cyclization to **3** or **11**, and (3) the likelihood that electron transfer from DCA anion radical to phosphite radical cation would not be exoergic enough to generate triplet phosphite efficiently. Furthermore, the close similarity in values (ca. 0.025) for the quantum efficiency of phosphonate formation from **1** and from its counterpart with phosphorus in a six-membered ring when excited singlet DCA is the SET agent[1] is contrary to the known at least 100-fold greater efficiency of triplet sensitized reaction of **1**.[8]

[24] Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430.

[25] Mag, M.; Engels, J. W. *Nucleosides Nucleotides* **1988**, *7*, 725.

[26] Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

[27] Deno, N. C.; Frederick, A. K.; Peterson, H. J. *J. Am. Chem. Soc.* **1965**, *87*, 2157.

[28] McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.

[29] Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *Tetrahedron Lett.* **1986**, *27*, 5579.

2-propen-1-ol (1.0 g, 6.1 mmol), dimethyl *N*,*N*-diisopropylphosphoramidite (1.4 g, 7.3 mmol), dry acetonitrile (15 mL), and 1*H*-tetrazole (61 mg, 0.87 mmol) was stirred under argon at ambient temperature overnight and filtered using Schlenck techniques to remove the amine salts which were washed with cold diethyl ether (3 × 10 mL). Solvent was removed using a vacuum pump and a coldfinger solvent trap to yield an oily residue. Distillation (bp 105 °C/1.4 Torr) produced a clear oil (1.3 g, 83% yield, 99% GC purity). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.50 (d, $^3J_{HP} = 10.5$ Hz, 6H), 3.82 (s, 3H), 4.69 (ddd, $^3J_{HP} = 7.8$ Hz, $^4J = 1.2$ Hz, $^4J = 0.7$ Hz, 2H), 5.32 (dt, $^4J = 1.2$ Hz, $^2J = 1.2$ Hz, 1H), 5.43 (d, $^4J = 0.7$ Hz, 1H), 6.86−7.42 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 49.28 (d, $^2J = 10.3$ Hz), 55.27, 63.91 (d, $^2J = 12.3$ Hz), 112.41, 113.73, 127.21, 130.76, 159.37, 143.80 (d, $^3J = 4.8$ Hz). NMR (121.5 MHz, $CDCl_3$): δ 141.25. Elemental analysis was obtained on the phosphate, **9-O**.

Photorearrangement of Phosphite 9 to Dimethyl 2-(4-Methoxyphenyl)-2-propen-1-ylphosphonate 12. Method A. Triplet Sensitization. Using glovebag techniques under an argon atmosphere, a 5 mL solution in benzene of dimethyl 2-(4-methoxyphenyl)-2-propen-1-yl phosphite, **9** (0.58 g, 2.3 mmol), and benzophenone (35 mg, 0.19 mmol) was prepared in a Pyrex test tube that was capped with a rubber septum which was tied with a copper wire and was further sealed with five layers of Parafilm. The solution was purged with argon for 15 min and irradiated with Pyrex-filtered light from a medium pressure 450 W Hg lamp. The reaction was followed by GC and also by ^{31}P NMR measurements on aliquots withdrawn from the reaction solution. On total consumption of phosphite (7 h), the solvent was removed in vacuo to give **9** as an oil that was purified by radial chromatography (Chromatotron,[7] eluted with 30% ethyl acetate−hexanes) to give a colorless oil (0.54 g, 93% yield, 99% GC purity). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.06 (dd, $^2J_{HP} = 22.1$ Hz, $^4J = 0.7$ Hz), 3.65 (d, $^3J_{HP} = 10.7$ Hz, 6H), 3.82, 5.26 (dd, $^2J = 5.6$ Hz, $^4J = 1.0$ Hz, 1H), 5.47 (dd, $^2J = 5.6$ Hz, $^4J = 0.7$ Hz, 1H), 6.86−7.15 (m, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 32.35 (d, $^1J = 138.7$ Hz), 52.78 (d, $^2J = 6.6$ Hz), 55.28, 113.69, 127.37 (d, $^4J = 1.0$ Hz), 132.89 (d, $^3J = 4.0$ Hz), 159.36, 115.68 (d, $^3J = 11.1$ Hz), 137.64 (d, $^2J = 10.3$ Hz). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 29.95. LRMS (EI): *m*/*z* 256 (M^+, 100), 160 (49), 148 (83), 133 (21), 115 (24), 109 (28), 103 (22), 94 (23), 91 (20). HRMS (EI): calcd for $C_{12}H_{17}O_4P$ [M^+] 256.0864. Found: 256.0856.

Method B. SET Induced. Similarly, a 5.0 mL acetonitrile solution of dimethyl 2-(4-methoxyphenyl)-2-propen-1-yl phosphite, **9** (0.17 g, 0.76 mmol), 9,10-dicyanoanthracene (11 mg, 0.05 mmol), and biphenyl (3.1 g, 0.02 mol) was prepared under argon. The solution was added to an argon-flushed Pyrex test tube, capped as in Method A, and irradiated with light from a Rayonet photoreactor (six 350 nm lamps). Upon total consumption of phosphite (73 h), the solvent was removed in vacuo to give a yellow oil. Purification by radial chromatography on silica gel (Chromatotron,[7] eluted with 30% ethyl acetate−hexanes) gave a colorless oil (0.14 g, 83% yield, 99% GC purity) that was spectroscopically identical to the material prepared by Method A.

Preparation of Dimethyl 2-(4-Methoxyphenyl)-2-propen-1-yl Phosphate (9-O). To a stirred solution of phosphite **9** (0.14 g, 0.55 mmol) in pentane (10 mL) were added two drops of 3.0 M anhydrous *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane. Total consumption of **9** was confirmed by TLC. The solution was dried with anhydrous magnesium sulfate and filtered. Solvent removal in vacuo and purification by radial chromatography on silica gel (Chromatotron,[7] eluted with 30% ethyl acetate−hexanes) gave a colorless oil (0.14 g, 95% yield). ^{1}H NMR (299.7 MHz, $CDCl_3$): δ 3.72 (d, $^3J_{HP} = 11.0$ Hz, 6H), 3.82 (s, 3H), 4.92 (dd, $^3J_{HP} = 7.6$ Hz, $^4J = 0.7$ Hz), 5.35 (dt, $^2J = 1.2$ Hz, $^4J = 0.7$ Hz, 1H), 5.50 (d, $^4J = 0.7$ Hz, 1H), 6.87−7.42 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 54.31 (d, $^2J = 6.1$ Hz), 55.29, 69.02 (d, $^2J = 5.5$ Hz), 113.87, 127.21, 129.88, 159.59 (aromatic), 113.97, 141.95 (d, $^3J = 7.3$ Hz). ^{31} P NMR (121.3 MHz, $CDCl_3$): δ 1.83. LRMS (EI): *m*/*z* 272 (M^+, 100), 146 (20), 131 (14), 103 (12). HRMS (EI): calcd for $C_{12}H_{17}O_5P$ [M^+] 272.0814. Found: 272.0798. Anal. Calcd for $C_{12}H_{17}O_5P$: C, 52.94; H, 6.29. Found: C, 52.28; H, 6.41.

Acknowledgment. We gratefully acknowledge support of this research by grants from the National Science Foundation (W.G.B.) and the Public Health Service (W.G.B).

JO0006775