Reactivity of Phosphorus-Centered Radicals Generated during the Photoreaction of Diphenylphosphinous Acid with 10-Methylacridinium Salt

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Diphenylphosphinous acid (**1**) reacts with 10-methylacridinium iodide (**2a**) in aqueous acetonitrile during irradiation by visible light under an argon atmosphere at 20 °C to afford diphenylphosphinic acid (**3**) and 10-methylacridan (**4**). The effects of the solvent and atmosphere and the effect of added iodide ion (I^-) or iodine (I_2) on the product distribution show that the mechanism involves initial single-electron transfer (SET) from **1** to **2a** in the photoexcited state, by which cation radical $\mathbf{1}^{+\bullet}$ and dihydroacridinyl radical $\mathbf{2}^\bullet$ are generated. Cation radical $\mathbf{1}^{+\bullet}$ undergoes electrophilic reaction with water in the solvent, and the resulting phosphoranyl radical decomposes through SET to iodine atom ($I^\bullet$) rather than undergoing β-scission, eventually giving **3**. Protonation to $\mathbf{2}^\bullet$ followed by reduction by I^- affords **4**. These reaction sequences make up the catalytic $I^\bullet/I^-$ couple. The results are interpreted on the basis of reported redox potentials.

Trivalent phosphorus compounds act as electron donors.[1-3] For example, phosphines,[4] phosphonites,[5] phosphinites,[5] and phosphites[4,5] readily donate an electron to diazonium salts, by which the corresponding cation radicals are generated from the trivalent phosphorus compounds. Such cation radicals have electrophilic reactivity when a nucleophile is present, affording the corresponding phosphoranyl radicals. Thus, reaction of a trivalent phosphorus compound with an electron acceptor in the presence of a nucleophile would be useful in studies of both cationic and neutral phosphorus-centered radicals. Meanwhile, trivalent phosphorus cation radicals may be of use in organic syntheses.[6] The elucidation of the reactivity of the cation radicals from trivalent phosphorus compounds is of great importance for these reasons.

10-Methylacridinium salt (**2**) is a good electron acceptor when photoexcited,[7,8] and we have found that photoredox between triphenylphosphine,[9] alkyl diphenylphosphinite,[10] or diphenylphosphinous acid (**1**)[11] and 10-methylacridinium iodide (**2a**) takes place in aqueous acetonitrile through initial single-electron transfer (SET) from the trivalent phosphorus compound to **2a** in the photoexcited state. It has also been found that iodide ion (I^-) or iodine (I_2) is crucial in the photoredox, which may be a clue to the elucidation of the reactivity of the trivalent phosphorus cation radical initially generated by SET. In a preliminary report, we have suggested that the photoreaction of **1** with **2a** is catalyzed by an iodine atom ($I^\bullet$)/I^- couple.[11] Reactions of several kinds of electron donors with **2** have been investigated in connection with the chemistry of naturally occurring nicotinamide adenine dinucleotide (NAD^+), providing many electrochemical data for **2** and related compounds.[12,13] These data are useful to find if the mechanism including the catalysis by an $I^\bullet/I^-$ couple is reasonable in terms of redox potentials of the participating species.

In this article, we present the results of further investigation on the photoreaction of **1** with **2** in aqueous acetonitrile and analyze these results on the basis of an electrochemical data available, showing that an $I^\bullet/I^-$ couple does act as a catalyst in the reaction. Thus, the cation radical generated from **1** by the initial SET undergoes electrophilic reaction with water in the solvent to give the phosphoranyl radical, which is then oxidized by $I^\bullet$ that is generated either from I^- during the reduction of **2a** to **4** or from I_2 through its photodissociation. The reactions of trivalent phosphorus cation radicals and phosphoranyl radicals that have been revealed in the present study may provide useful information as to the reactivity of such phosphorus-centered radicals.

Results and Discussion

Photoreaction of Diphenylphosphine Oxide (1′) with 2a. Phosphine oxide **1′**, the more stable pentavalent tautomer of **1**, was reacted with an equimolar

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(1) Powell, R. L.; Hall, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 5403.

(2) Pandey, G.; Pooranchand, D.; Bhalerao, U. T. *Tetrahedron* **1991**, *47*, 1745.

(3) (a) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1987**, 1708. (b) Okamoto, T.; Takagi, S.; Shiragami, T.; Inoue, H. *Chem. Lett.* **1993**, 687.

(4) (a) Yasui, S.; Fujii, M.; Kawano, C.; Nishimura, Y.; Ohno, A. *Tetrahedron Lett.* **1991**, *32*, 5601. (b) Yasui, S.; Fujii, M.; Kawano, C.; Nishimura, Y.; Shioji, K.; Ohno, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 177.

(5) Yasui, S.; Shioji, K.; Ohno, A. *Tetrahedron Lett.* **1994**, *35*, 2695.

(6) Ganapathy, S.; Dockery, K. P.; Sopchik, A. E.; Bentrude, W. G. *J. Am. Chem. Soc.* **1993**, *115*, 8863.

(7) Fukuzumi, S.; Kitano, T.; Mochida, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1236.

(8) (a) Fukuzumi, S.; Kitano, T.; Tanaka, T. *Chem. Lett.* **1989**, 1231. (b) Fukuzumi, S.; Kitano, T.; Mochida, K. *Chem. Lett.* **1989**, 2177.

(9) Yasui, S.; Ohno, A. *Tetrahedron Lett.* **1991**, *32*, 1047.

(10) Yasui, S.; Shioji, K.; Yoshihara, M.; Maeshima, T.; Ohno, A. *Tetrahedron Lett.* **1992**, *33*, 7189.

(11) Yasui, S.; Shioji, K.; Ohno, A.; Yoshihara, M. *Chem. Lett.* **1993**, 1393.

(12) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(13) (a) Shinkai, S.; Tsuno, T.; Manabe, O. *J. Chem. Soc., Perkin Trans. 2* **1984**, 661. (b) Kreevoy, M. M.; Kotchevar, A. T. *J. Am. Chem. Soc.* **1990**, *112*, 3579. (c) Anne, A.; Moiroux, J. *J. Org. Chem.* **1990**, *55*, 4608. (d) Anne, A.; Hapiot, P.; Moiroux, J.; Neta, P.; Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 4694. (e) Coleman, C. A.; Rose, J. G.; Murray, C. J. *J. Am. Chem. Soc.* **1992**, *114*, 9755.

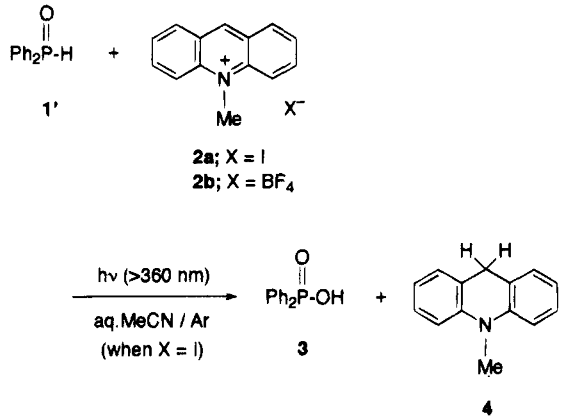
0022-3263/95/1960-2099$09.00/0

Table 1. Photoreaction of 1′ with 2a[a]

entry	atmosphere	time (min)	yield[b] (%) 3	4	5[c]	other (%)
1	Ar	60	100	59	0	
2	Ar	(55) + 60[d]	100	63	0	
3	air	60	57	0	14	**8** (29)
4	air	(55) + 60[d]	52	0	18	**8** (30)
5[e]	Ar	110	94	46	<1	
6[f]	Ar	60	11	0	37	**1′** (52)[g]
7[h]	air	130	0			**1′** (97)[g]

[a] Xe lamp, >360 nm with Toshiba glass filter L-39. $[1']_0 = [2]_0 = 1.25 \times 10^{-2}$ M. In aqueous MeCN at 20 °C. [b] Based on $[1']_0$ used; determined by HPLC. [c] Detected as **6** by HPLC; for details, see ref 22. [d] The reaction was carried out in the dark for 55 min before 60 min of irradiation. [e] >390 nm with Toshiba glass filter L-42. [f] >480 nm with Toshiba glass filter Y-51. [g] Recovered. [h] In the absence of **2a**.

Scheme 1



amount of **2a** in aqueous acetonitrile[14] during irradiation by visible light from a xenon lamp (>360 nm with a glass filter) under an argon atmosphere at 20 °C for 60 min. The reaction mixture was analyzed by HPLC, GC, GCMS, LCMS, and ^{1}H and ^{31}P NMR spectroscopy, and the results confirmed formation of diphenylphosphinic acid (**3**) in a quantitative yield and of 10-methylacridan (**4**) in a moderate yield (Table 1, entry 1; Scheme 1). In the absence of **2a**, **1′** was stable during prolonged irradiation even under aerobic conditions (entry 7).

The time course of the reaction was examined by HPLC (Figure 1a), which showed that a cationic adduct (**5**) is formed initially from **1′** and **2a** and then disappears gradually as **1′** disappears and **3** and **4** appear. Since **5** is formed reversibly in the dark,[15] it is likely that it is an abortive adduct not responsible for the photoreaction rather than an intermediate in the photoprocess (Scheme 2). In fact, the second-order rate constant observed for the thermal formation of **5** (9.0×10^{-2} mol^{-1} dm^3 s^{-1})[15] accounts well for the increase in the amount of **5** at an early stage of the reaction (initial part of the curve for **5** in Figure 1a). As shown in Figure 1b, the reaction in the dark has no effect on the subsequent photoprocess (see also Table 1, entries 2 and 4).

The mechanism for the thermal formation of **5** involves initial nucleophilic attack of the phosphorus atom in diphenylphosphinous acid (**1**), the trivalent tautomer of **1′**,[16] upon the 9-carbon in **2**, giving a phosphonium salt (**5′**) as an intermediate (Scheme 2).[15] The hydrolysis of **5′** to afford **3** and **4** is not likely to occur. Phosphonium ions are hydrolyzed under basic conditions,[1,17] whereas

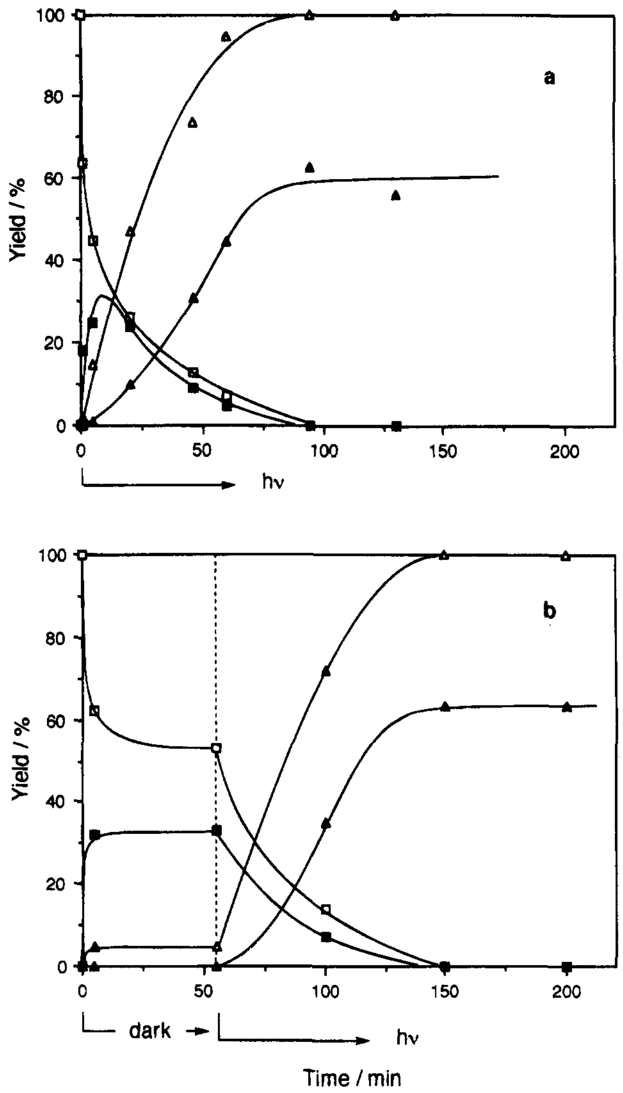
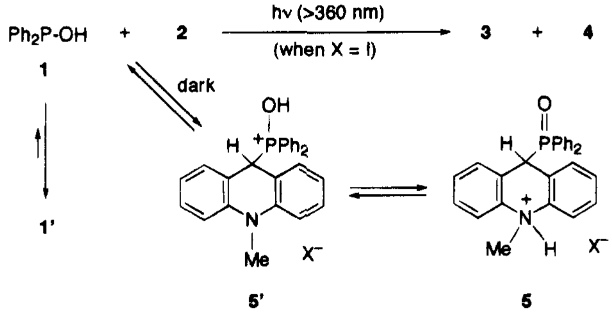


Figure 1. Time course of photoreaction of **1′** with **2a** in aqueous acetonitrile under an argon atmosphere at 20 °C. Solutions of **1′** and **2a** were mixed during irradiation (a), or irradiation was started 55 min after the mixing (b). □, △, ▲, and ■ denote the yields of **1′**, **3**, **4**, and **5**, respectively.

Scheme 2



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(14) The Karl–Fisher measurement showed the water content of this solvent to be 0.1%. The addition of 0.5% water to the solvent caused little, if any, difference in the results.

(15) On the basis of UV–vis and ^{1}H and ^{31}P NMR spectroscopy as well as HPLC analysis, we have found that the thermal reaction of **1′** with **2** in aqueous acetonitrile results in reversible formation of cationic adduct **5**. In the presence of a base, **5** is readily deprotonated to afford phosphine oxide **6**. The reaction has also been analyzed kinetically. Yasui, S.; Shioji, K.; Ohno, A.; Yoshihara, M. *Heteroatom. Chem.* **1995**, in press.

(16) Tautomerization of **1′** to **1** upon the reaction has been reported. (a) Hunt, B. B.; Saunders, B. C. *J. Chem. Soc.* **1957**, 2413. (b) Campbell, I. G. M.; Stevens, I. D. R. *Chem. Commun.* **1966**, 505. (c) Warren, S. G. *Angew. Chem., Int. Ed. Engl.* **1968**, 7, 606.

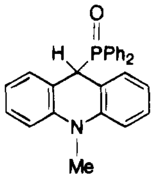
Table 2. Effects of I^- and I_2 on Photoreaction of 1′ with 2 under an Argon Atmosphere[a]

entry	X in **2**	additive (equiv)[b]	yield[c] (%) **1′**[d]	**3**	**4**	**5**[e]
1[f]	I		0	100	59	0
8	BF_4		67	0	0	33
9	BF_4	I^- (1.0)[g]	16	75	46	3
10	I	I^- (1.0)[g]	0	90	98	0
11	I	I^- (3.0)[g]	0	82	100	0
12	BF_4	Br^- (1.0)[h]	36	0	0	57
13	BF_4	I_2 (1.0)[i]	7	93	52	0
14	I	I_2 (1.0)[i]	<1	99	41	0
15	BF_4	I_2 (2.0)[i]	11	88	44	0
16	I	I_2 (2.0)[i]	7	91	23	0
17	I	I_2 (3.0)[i]	0	100	5	0
18[j]	I		21	77	50 (100)[k]	0
19[l]		I_2 (1.0)[i]	39	61		
20[l,m]		I_2 (1.0)[i]	75	21		

[a] Xe lamp, >360 nm. $[\mathbf{1'}]_0 = [\mathbf{2}]_0 = 1.25 \times 10^{-2}$ M. In aqueous MeCN for 60 min at 20 °C unless otherwise noted. [b] Equivalence to the initial amount of **1′**. [c] Based on $[\mathbf{1'}]_0$ used; determined by HPLC. [d] Recovered. [e] Detected as **6** on HPLC; for details, see ref 22. [f] Taken from Table 1 for comparison. [g] Tetrabutylammonium iodide. [h] Tetrabutylammonium bromide. [i] Equivalence as iodine atom. [j] $[\mathbf{1'}]_0 = 2.50 \times 10^{-2}$ M, for 150 min. [k] Based on $[\mathbf{2}]_0$ used. [l] In the absence of **2**. [m] In the dark.

the reaction conditions we used are acidic because decreasing positive charge accompanied by the conversion of the acridinium cation is compensated for by an increased number of protons. In addition, the photoreaction under aerobic conditions gives little, if any, of the reduction product **4** (entry 3), suggesting that radicals are involved in the photoreaction.

Compound **5** (or **5′**) is readily deprotonated in the presence of a base, resulting in precipitation of a material insoluble in acetonitrile, (9,10-dihydro-10-methyl-9-acridinyl)diphenylphosphine oxide (**6**).[15] The possibility that **6** formed by an unknown process is an intermediate has been ruled out; neither **3** nor **4** was produced when a suspension of **6** in aqueous acetonitrile was irradiated in the presence of **2a** under acidic or neutral conditions.



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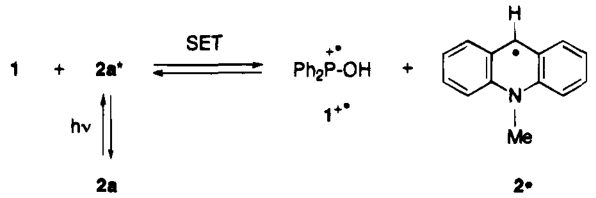
Effects of I^- and I_2 on the Photoreaction. When **1′** was photolyzed with 10-methylacridinium tetrafluoroborate (**2b**) in place of the iodide salt **2a** under otherwise identical conditions, redox did not take place and only **5** was formed through a thermal process (Table 2, entry 8). The photoreaction of **1′** with **2b** in the presence of tetrabutylammonium iodide afforded **3** and **4** (entry 9), whereas added bromide ion (Br^-) had no effect on the reaction (entry 12). These results show that I^- is crucial in this photoreaction. To explain such a role of I^-, several mechanisms are possible.

Scheme 3



First, SET from I^- to the acridinium cation **2** in the photoexcited state **2***, which produces dihydroacridinyl radical **2•**, may trigger the photoreaction. Indeed, this SET is exothermic; $E^0_{red}(\mathbf{2}^*/\mathbf{2}^\bullet) = 2.3$ V vs SCE[7,18] is higher than $E^0_{ox}(I_2/2I^-) = 0.290$ V vs SCE.[19] However, this possibility can be discounted because the reaction in the presence of Br^- in place of I^- does not afford the photoredox products **3** and **4**. If I^- undergoes photoredox through SET to **2***, Br^- would likewise donate an electron to **2*** to cause the reaction, since the oxidation potential of a $Br_2/2Br^-$ couple (0.819 V vs SCE)[19] also is lower than the reduction potential for a **2***/**2•** couple. Acridinyl radical **2•**, when produced by SET, would dimerize,[7,9] but there is no evidence for the formation of the dimer from **2•**. In addition, ^{1}H NMR resonances from acridinium iodide (**2a**) in CD_3CN were identical to those from the tetrafluoroborate salt **2b** even at concentrations higher than that used for the photolysis, and the spectra did not change on replacement of the solvent by CD_3OD. These observations preclude the occurrence of a tight ion pair between the acridinium cation and I^- under conditions which make SET from I^- to **2*** improbable. Spectrophotometrical and ^{1}H NMR spectroscopic assays confirmed that the photolysis of **2a** in the absence of **1′** results in its quantitative recovery.

Second, it is possible that I^- donates an electron to thermally formed phosphonium ion **5′** under these photochemical conditions. This possibility is based on the premise that SET from a halide to an onium salt occurs readily during irradiation,[20] but it is unlikely because neither **5′** nor I^- absorbs light of the wavelengths used. In fact, **1′** did not behave catalytically in this photoreaction; according to this mechanism, the radical intermediate generated from **5′** through SET from I^- would undergo fragmentation to yield **4** as well as **1** (and subsequently **1′**), providing catalysis by **1′**.

Finally, it is most likely that redox catalysis by an $I^\bullet/I^-$ couple is involved in this photoreaction (Schemes 3–6). Results in Table 1 (entries 5 and 6) indicate that light with wavelengths between 390 and 480 nm is responsible for the photolysis. The species that can undergo photoexcitation is **2a**.[21] Meanwhile, **1′** is in thermal equilibrium with its trivalent tautomer **1**.[15,16] These observations taken together allow us to predict that the reaction is initiated by SET from **1** to **2a** in the photoexcited state, **2a***, by which cation radical $\mathbf{1}^{+\bullet}$ and dihydroacridinyl radical **2•**, respectively, are generated (Scheme 3). There have been several precedents that trivalent phosphorus compounds donate an electron to **2a***.[9-11,22] Judging from

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[17] Zanger, M.; Vander Werf, C. A.; McEwen, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3806.

[18] This value has been reported without a mention of what the counteranion of the acridinium cation is. However, it is unlikely that a counteranion much affects the reduction potential of this cationic substrate.

[19] deBethune, A. J.; Licht, T. S.; Swendeman, N. *J. Electrochem. Soc.* **1959**, *106*, 616.

[20] (a) Nagao, Y.; Shima, K.: Sakurai, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3122. (b) Hacker, N. P.; Leff, D. V.; Dektar, J. L. *J. Org. Chem.* **1991**, *56*, 2280. (c) Imrie, C.; Modro, T. A.; Rohwer, E. R.; Wagener, C. C. P. *J. Org. Chem.* **1993**, *58*, 5643.

[21] There have been numerous works by Fukuzumi and his co-workers to show that **2** is excited to its singlet state by absorbing the light of these wavelengths. For example, see: Fukuzumi, S.; Tanaka, T. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Chapter 10.

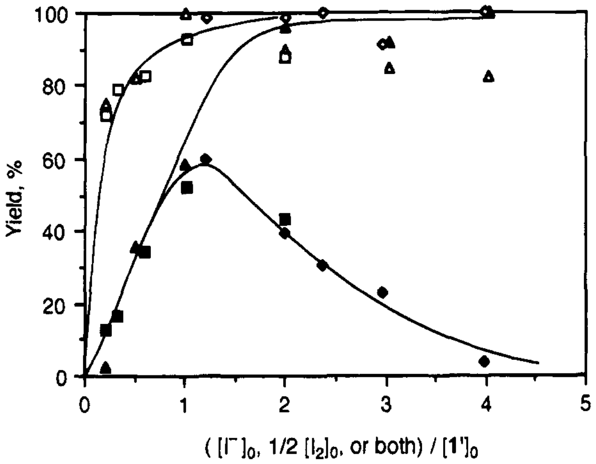
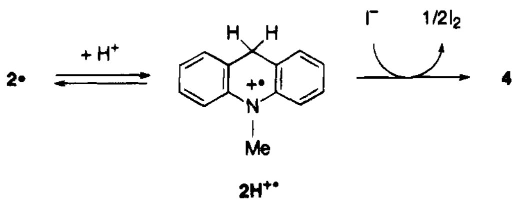


Figure 2. Dependence of the yields of **3** and **4** on the ratio of the total amount of I^-, $I^•$ equivalent, or both to the initial amount of **1′**; for the reactions of **1′** with **2a** (X = I) in the presence of tetrabutylammonium iodide (△ and ▲), with **2b** (X = BF_4) in the presence of iodine (☐ and ■), and with **2a** (X = I) in the presence of iodine (◇ and ◆). Open and closed symbols denote the yields of **3** and **4**, respectively.

Scheme 4

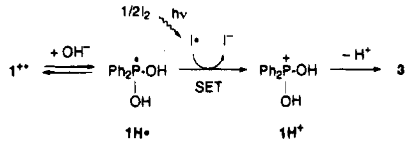


the oxidation potential reported for triphenylphosphine, E^0_{ox} = 1.0[23] or 1.40 V[24] vs SCE, the oxidation potential for **1** might be lower than the reduction potential for **2a***, E^0_{red} = 2.3 V vs SCE.[7,18]

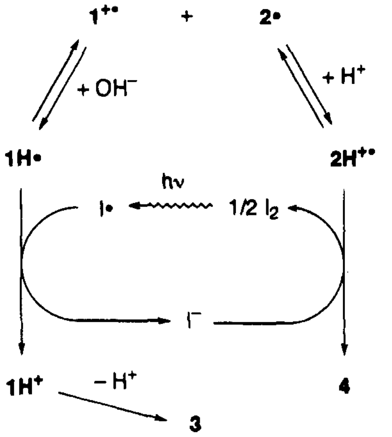
The dihydroacridinyl radical **2**• generated is protonated to some extent to produce cation radical **2H**$^{+•}$,[25] and **2H**$^{+•}$ once formed would be reduced readily by I^- since the reduction potential $E^0_{red}(\mathbf{2H}^{+•}/\mathbf{4})$ = 0.80 V vs SCE[12] is much higher than the oxidation potential $E^0_{ox}(I_2/2I^-)$ = 0.290 V vs SCE[19,26] (Scheme 4). Protonation to **2**• is suggested by the observation that **4** is formed sluggishly at the early stage of the reaction and that its formation is accelerated as the reaction proceeds (Figure 1a); as mentioned above, the acidity of the reaction mixture increases as the reaction continues. ^1H NMR and GCMS analyses of the reaction in acetonitrile containing D_2O confirm the incorporation of a proton from water into the 9-position in **4**. Evidence of this mechanism is that an increase in the amount of I^- added causes an increased yield of **4** to become a quantitative yield when a 4-equiv amount of I^- is present (Table 2, entries 10 and 11; Figure 2).

Scheme 5 shows the transformation of **1**$^{+•}$ to **3**. Since trivalent phosphorus cation radicals usually behave as electrophiles,[2,4,5,9-11,22,27] there is little doubt that **1**$^{+•}$ reacts with water in the solvent to produce phosphoranyl radical **1H**• under the reaction conditions used. β-Scission of the resulting radical **1H**•, which produces **3** by liberating a hydrogen atom (H•), would occur only with difficulty, since there is no species available to accept H•. Meanwhile, iodine (I_2) that has been generated through the oxidation of I^- by **2H**$^{+•}$ dissociates into two iodine atoms (2I•) under these photochemical conditions.[28] It is therefore probable that **1H**• undergoes one-electron oxidation by I• to give phosphonium ion **1H**$^+$. The half-wave reduction potential for tetraphenylphosphonium ion, $E_{1/2}$ = −1.68 V vs SCE,[29] predicts that the oxidation potential for a **1H**$^+$/**1H**• couple is much lower than $E^0_{red}(I^•/I^-)$ = 0.95 V vs SCE.[30] Similar processes in which I• oxidizes a phosphoranyl radical have been reported.[10,22,31] Subsequently, **1H**$^+$ is deprotonated to **3** in the usual way.[32]

Scheme 5



Scheme 6



Thus, photoredox between **1** and **2** proceeds with the aid of catalysis by an I•/I^- couple, as summarized in Scheme 6.

As predicted, I_2 has the same effect on the yields of **3** and **4** as I^- when there is less I_2 (as I•) than **1′** (Figure 2; Table 2, entries 13 and 14).

Stoichiometry of the Reactions under an Argon Atmosphere. Figure 2 shows that more than an equivalent amount of I_2 (as I•) suppresses the formation of reduction product **4**. This finding suggests that I_2 causes thermal oxidation of **4** to the starting material **2**, making the apparent yield of **4** lower (see also Table 2, entries 15–17).[33] Meanwhile, I_2 by itself oxidizes some portion

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[22] Yasui, S.; Shioji, K.; Ohno, A. *Heteroatom Chem.* **1994**, *5*, 85.

[23] Ohmori, H.; Nakai, S.; Masui, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1333.

[24] Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537.

[25] Fukuzumi, S.; Tokuda, Y. *Chem. Lett.* **1992**, 1721.

[26] The reduction potential $E^0_{red}(\mathbf{2H}^{+•}/\mathbf{4})$ = 0.80 V vs SCE is lower than $E^0_{red}(I^•/I^-)$ = 0.95 V vs SCE, which suggests that the reduction of **2H**$^{+•}$ to **4** is coupled to the oxidation of I^- to $^1/_2I_2$ rather than to the oxidation of I^- to I•. See ref 30.

[27] Ohmori, H.; Sakai, K.; Nagai, N.; Mizuki, Y.; Masui, M. *Chem. Pharm. Bull.* **1985**, *33*, 373.

[28] (a) Lampe, F. W.; Noyes, R. M. *J. Am. Chem. Soc.* **1954**, *76*, 2140. (b) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1980**, *45*, 2654.

[29] Morris, M. D.; Kok, G. L. *Encycl. Electrochem. Elem.* **1979**, *13*, 1.

[30] This value was estimated from $E^0_{ox}(I_2/2I^-)$ with thermochemical corrections for the formation of I_2. Tokumaru, K. *Chem. Lett.* **1992**, 523.

[31] (a) Davidson, R. S. *Tetrahedron* **1969**, *25*, 3383. (b) Plumb, J. B.; Obrycki, R.; Griffin, C. E. *J. Org. Chem.* **1966**, *31*, 2455. (c) Fu, J.-J. L.; Bentrude, W. G. *J. Am. Chem. Soc.* **1972**, *94*, 7710.

[32] For example, see: Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415.

[33] Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *Inorg. Chem.* **1990**, *29*, 653.

Table 3. Photoreaction of 1′ with 2 in a Solvent Containing Methanol under an Argon Atmosphere[a]

entry	X in **2**	solvent[b]	time (min)	yield[c] (%) **3**	**4**	**7**	**5**[d]
21	I	AM	90	71	56	25	0
22	BF_4	AM	120	0	0	0[e]	35
23	I	M	100	6	0	26	(57)[f]

[a] Xe lamp, >360 nm. $[\mathbf{1'}]_0 = [\mathbf{2}]_0 = 1.25 \times 10^{-2}$ M. At 20 °C. [b] M = MeOH; AM = aqueous MeCN containing 0.5% MeOH. [c] Based on $[\mathbf{1'}]_0$ used; determined by HPLC. [d] Detected as **6** on HPLC; for details, see ref 22. [e] 60% of **1′** was recovered. [f] Total yield of **5** and **6**, **6** being the major product.

of the starting material **1′** to **3** within the period tested under an argon atmosphere during irradiation (entry 19),[34] boosting the yield of **3**.[35] These I_2-mediated oxidations of **1** and **4** to **3** and **2**, respectively, may take place when the initial iodine species added is I^-, since I^- is eventually oxidized to I_2 in this photoreaction. In other words, the presence of any amount of I_2 or I^- results in a lower yield of **4** than that of **3**, which explains the discrepancy observed between the yields of **3** and **4**. Control experiments suggested that there is a contribution from another reaction of I_2 with **4** during photolysis in which an adduct of unknown structure is formed. Consumption of **4** and I_2 in such a reaction lowers the yield of **4** and interrupts catalysis by an $I^{\bullet}/I^-$ couple. These phenomena may account, at least in part, for the low efficiency of the catalysis. Accordingly, the stoichiometry of this photoreaction under an argon atmosphere is probably the simple one shown in Scheme 1. When an excess of **1′** was reacted with **2a** during irradiation for a prolonged period, the yield of **4** improved (entry 18).

Photoreaction in a Solvent Containing Methanol. When photolysis of **1′** with **2a** was carried out in aqueous acetonitrile containing a small amount of methanol (0.5% v/v) under otherwise identical conditions,[36] both phosphinic acid **3** and its methyl ester, methyl diphenylphosphinate (**7**), were obtained as oxidation products from **1** together with **4** (Table 3, entry 21). The yield of the oxidation products **3** and **7** taken together and the yield of the reduction product **4** were comparable with those obtained in the reaction in methanol-free acetonitrile. These results are evidence for the existence of cation radical $\mathbf{1}^{+\bullet}$ as an intermediate. Thus, $\mathbf{1}^{+\bullet}$ reacts competitively with water and methanol in the solvent to give phosphoranyl radicals **1H•** and **1M•**, respectively, which are then oxidized to **3** and **7**, respectively, through SET to I•, followed by deprotonation (Scheme 7). The phosphonium ion $\mathbf{1H}^+$ produces **3**, and another phosphonium ion ($\mathbf{1M}^+$) eliminates exclusively a proton, affording **7**.

No photoredox products were obtained when the photolysis of **1′** was carried out with **2b** (X = BF_4) in this solvent system (entry 22). This result shows that phosphoranyl radical **1M•**, like **1H•**, decomposes by SET to I•, with little β-scission of **1M•** taking place, if any (Scheme 7). The related phosphoranyl radical $Ph_2\dot{P}(OH)OPr^i$, which is generated in the photoreaction of isopropyl diphenylphosphinite with **2a**, likewise undergoes SET to I• in preference to β-scission, even though this radical could even liberate isopropyl radical that is more stable than methyl radical.[10]

Scheme 7

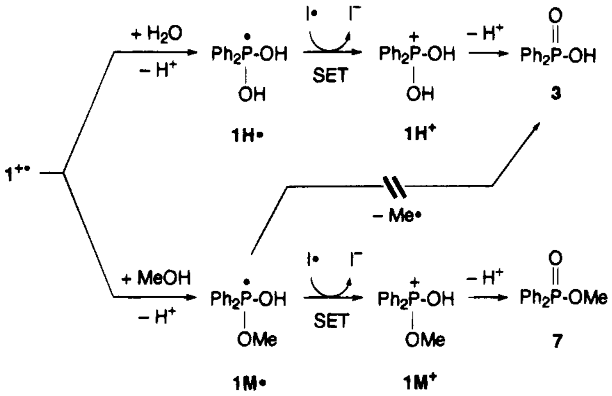

Table 4. Photoreaction of 1′ with 2 under Aerobic Conditions[a]

entry	**2**, equiv[b]	X in **2**	additive (equiv)[b]	solvent[c]	time (min)	yield[d] (%) **1′**[e]	**3**	**7**	**8**	**9**	**5**[f]
3[g]	1.0	I		A	60	0	57		29	2	14
24	1.0	BF_4	I^- (0.1)[h]	A	60	0	40		43	1	16
25	1.0	BF_4	I_2 (0.1)[i]	A	60	0	45		39	0	2
26	1.0	BF_4	Br^- (1.0)[j]	A	240	12	45		5	0	38
27	0.5	I		A	60	0	53		25	2	9
28	0.1	I		A	60	0	46		53	2	0
29	0.1	BF_4	I_2 (1.0)[i]	A	30	0	81		11	0	0
30	1.0	BF_4		A	60	47	18		0	<1	30
31	1.0	BF_4		A	240	29	43		0	<1	19
32	0.1	BF_4		A	60	67	25		0	<1	4
33[k]	0.1	BF_4		A	180	0	90		0	<2	0
34	1.0	I		AM	20	0	25	32	20	0	22
35	1.0	BF_4		AM	120	46	30	<1	0	0	23
36[l]	1.0		I_2 (1.0)[i]	A	60	11	80		<3		

[a] Xe lamp, >360 nm. $[\mathbf{1'}]_0 = 1.25 \times 10^{-2}$ M. Under aerobic conditions at 20 °C. [b] Equivalence to the initial amount of **1′**. [c] A = aqueous MeCN; AM = aqueous MeCN containing 0.5% MeOH. [d] Based on $[\mathbf{1'}]_0$ used; determined by HPLC. **4** was not detected. [e] Recovered. [f] Detected as **6** on HPLC; for details, see ref 22. [g] Data taken from Table 1 for comparison. [h] Tetrabutylammonium iodide. [i] Equivalence as iodine radical. [j] Tetrabutylammonium bromide. [k] Under an oxygen atmosphere. [l] In the absence of **2**.

Photoreaction under Aerobic Conditions. During photolysis with **2a** under aerobic conditions, **1′** was consumed within 60 min to give **3** (Table 4, entry 3). The reaction also afforded another product **8**, whose structure will be given later; because of this product, less **3** was produced. On the other hand, ^1H NMR spectroscopy showed that **2a** is recovered almost quantitatively in this reaction.[37] As discussed above, under an argon atmosphere, trivalent phosphorus compound **1** is converted to **3** by the reaction sequence shown in Schemes 3 and 5. The sequence operates under aerobic conditions as well, since there is no step for the direct participation of dioxygen in this sequence. Dioxygen may participate in the reaction by oxidizing I^- to I• (Scheme 8, process A). In this way, an $I^{\bullet}/I^-$ couple works catalytically without being coupled to the reduction of **2** to **4**. The catalytic behavior of I^- predicted in this way has been found experimentally (entry 24). Under these photochemical conditions, if I_2 was introduced, it could dissociate into I• and enter the catalytic cycle. Indeed, the reactions in

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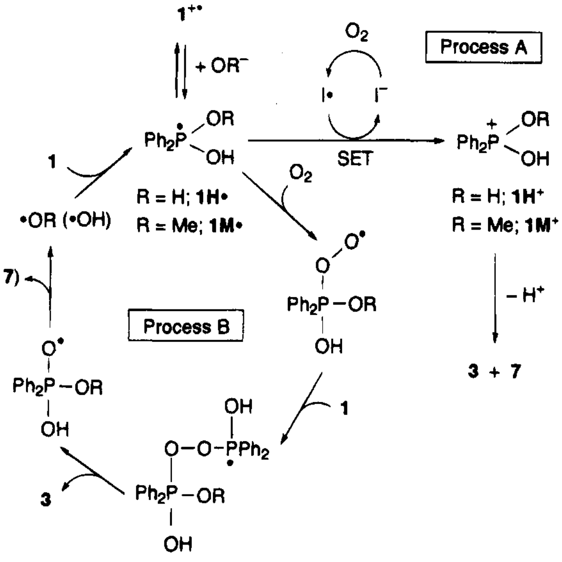
(34) Probably the oxidation product **3** results partly from the thermal oxidation of **1** by I_2 with the aid of water in the solvent (see Table 2, entry 20). Bentrude, W. G.; Sopchik, A. E.; Gajda, T. *J. Am. Chem. Soc.* **1989**, *111*, 3981. See also ref 39.

(35) The yield of **4** obtained in the presence of an equivalent amount of I_2 (as I•) was 52% (entry 13), which may show that the formation of **3** is mainly coupled to the reduction of **2** to **4** when the reaction is carried out with **2** during irradiation.

(36) In neat methanol, only the thermally formed adduct **5** underwent rapid deprotonation to give **6** even with irradiation. No reduction product **4** was obtained in this reaction (see Table 3, entry 23).

(37) Adduct **5** also was formed in this reaction through a thermal process.

Scheme 8

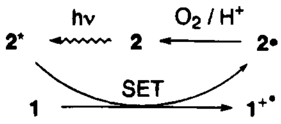


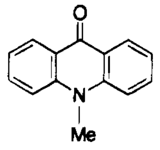
the presence of I_2 gave the results similar to those obtained in the presence of I^- (entry 25).

The oxidation product **3** also was formed when neither I^- nor I_2 was present, even though one-electron oxidation of phosphoranyl radical **1H**$^\bullet$ is impossible under these conditions (entries 30–33). This finding strongly suggests the appearance of a phosphoranyl radical intermediate during the reaction. Phosphoranyl radical **1H**$^\bullet$, once formed, is oxidized under aerobic conditions through a chain reaction (Scheme 8, process B); such chain reactions, in which trivalent phosphorus compounds are oxidized by dioxygen to the corresponding pentavalent oxo compounds via the corresponding phosphoranyl radicals, are well known.[38] The results given in Table 4 show that the reaction proceeds much faster via process A than via process B, suggesting that process B takes place only when an iodine species is not available. Bromide ion (Br^-) added instead of I^- has little effect on the oxidation of **1′** to **3** under the conditions used (entry 26). Although the oxidation potential of a $Br^\bullet/Br^-$ couple is not known, the redox potentials for $I^\bullet/I^-$, $I_2/2I^-$, and $Br_2/2Br^-$ couples (0.95 V,[30] 0.290 V,[19] and 0.819 V[19] vs SCE, respectively) suggest that $E^0_{ox}(Br^\bullet/Br^-)$ might be higher than or at least close to the reduction potential of dioxygen under acidic conditions (1.0 V vs SCE).[19] That is, bromine atom ($Br^\bullet$) would not be produced from Br^- under the conditions used, so there is no oxidant available to oxidize **1H**$^\bullet$ to **1H**$^+$. In the presence of Br^- instead of I^-, only process B would operate.

The photolysis of **1′** by itself gave no oxidation product **3** even under aerobic conditions (see Table 1, entry 7). The addition of I_2 brought about the oxidation of **1′** to **3** (entry 36),[39] but the reaction was not completed unless acridinium salt **2** was present. These findings imply that **2** initiates the reaction. That is, **2** in the photoexcited state, **2***, accepts an electron from **1** generating cation radical $\mathbf{1}^{+\bullet}$, the incipient intermediate for the oxidation of **1′**. The resulting acridinyl radical **2**$^\bullet$ is easily reoxidized by dioxygen to **2** with the formation of a trace amount of 10-methylacridone (**9**) under the presently occurring acidic conditions (Scheme 9); the oxidation of **2**$^\bullet$ by dioxygen gives **2** or **9** under acidic or neutral conditions, respectively.[40] Catalysis by a **2**/**2**$^\bullet$ couple thus predicted is seen in the results from reactions with I^- (entries 27 and 28) or with I_2 (entry 29) and in the results from reactions without iodine species (entries 32 and 33).

Scheme 9





9

As mentioned above, the photoreaction of **1′** with **2** under aerobic conditions proceeds predominantly via process A when an iodine species is present. So, if the photoreaction is carried out in aqueous acetonitrile containing a small amount of methanol (0.5% v/v) in the presence of I^- or I_2, both phosphinic acid (**3**) and its methyl ester **7** would be given, and the product ratio **3**/**7** would not differ much from the ratio observed under an argon atmosphere, although the unexpected formation of **8** may interfere with quantitative prediction of the ratio under aerobic conditions. On the other hand, photoreaction in the same solvent system in the absence of an iodine species proceeds via the chain reaction of process B only. A main species acting as a chain carrier in this chain is **1H**$^\bullet$, not **1M**$^\bullet$, since this chain might be efficient enough as reported.[38] As a result, **3** would be formed in larger amounts than **7**. The results show that this is the case. Thus, the yields of **3** and **7** obtained from the reaction in the presence of I^- are comparable with each other (entry 34), whereas the reaction with neither I^- nor I_2 affords **3** in a moderate yield along with only a trace amount of **7** (entry 35).

The unexpected product **8** was formed during the photolysis of **1′** with **2** in the presence of I^- or I_2 under aerobic conditions. This product **8** was detected by HPLC but not by GC, and repeated HPLC of the reaction mixture showed the gradual conversion of **8** to **3** in the dark. An attempt to isolate **8** by preparative TLC with silica gel resulted in isolation of **3** in a theoretical amount. These findings indicate that **8** is easily converted to **3** under acidic conditions. Spectroscopic analyses of the mixture suggested that **8** has a moiety of $Ph_2P(=O)$. Thus, LCMS showed only one fragment at *m/z* = 199; this fragment is a major one from diphenylphosphinic acid ($Ph_2P(=O)OH$, **3**). A UV spectrum obtained from an HPLC apparatus equipped with a photodiode array detector gave the pattern for compounds $Ph_2P(=O)X$. In addition, a ^{31}P NMR spectrum of the reaction mixture had a signal at 29.2 ppm (δ from H_3PO_4) and a signal from **3** at 29.8 ppm, with similar intensities. The formation of **8** requires an iodine species (I^- or I_2), but

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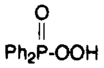
[38] (a) Walling, C.; Rabinowitz, R. *J. Am. Chem. Soc.* **1959**, *81*, 1243. (b) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 2528.

[39] Probably $I^\bullet$ that is generated from I_2 under these photochemical conditions attacks the phosphorus in **1** to afford phosphoranyl radical $Ph_2\dot{P}(OH)I$, which, like **1H**$^\bullet$, may be converted to **3** via the processes similar to those in Scheme 8 under the aerobic conditions. Under an argon atmosphere, on the other hand, it decomposes to **3** only via SET to $I^\bullet$, the yield of **3** being lower (see Table 2, entry 19).

[40] Fukuzumi, S.; Ishikawa, M.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1037.

when the reaction was carried out in the presence of a 0.1-equiv amount of I^- or I_2, the yield of **8** considerably exceeded 10% (entries 24 and 25, respectively), indicating that **8** does not contain an iodine atom. On the basis of these observations, we tentatively identify **8** to be diphenylphosphinic hydrogen peroxide.



$Ph_2P(=O)\text{-}OOH$

8

It still remains uncertain why I^- or I_2 causes the formation of **8** under these photochemical conditions. Methylene blue (MB), which sensitizes dioxygen in the ground state to the singlet-excited state, seems to take on the role of I^- or I_2. Thus, when an acetonitrile solution containing **1′**, **2b** ($X = BF_4$), and MB (molar ratio = 10:5:1) was photolyzed under an oxygen atmosphere for 2.5 h, **8** was obtained in 14% yield together with the starting material **1′** (10%) and phosphinic acid (**3**) (76%). Photolysis without **2** under otherwise identical conditions gave only 4% of **8** and 7% of **3**, resulting in 89% recovery of **1′**. These results suggest that singlet oxygen and **2** are responsible for the formation of **8**. Iodide ion or more likely I_2 may help in the generation of singlet oxygen in this photoreaction. Details of the mechanism of the formation of **8** and the structure of **8** will be published elsewhere.

Energetics That Discriminate between Thermal and Photochemical Processes. Trivalent phosphorus compound **1** reacts with acridinium salt **2** either in the ground state or the photoexcited state via an ionic or radical mechanism, respectively. The reason why the mechanism depends on the reaction conditions may be in line with the concept of the "curve-crossing model" developed by Pross.[41] This model predicts that the position of a transition state of a given reaction is governed by the position of the intersection of the potential energy curves for the reactant and the product. Photochemical conditions bring about excitation of **2**; in other words, the curve for the reactant is raised by photoexcitation, which makes the position of the intersection of the two curves for this configuration earlier than that for the ground-state configuration. As a result, a reaction under photochemical conditions would have an earlier transition state that has less bonding character between the donor (**1**) and the acceptor (**2**) than a thermal reaction. Thus, the process during irradiation is preferred by SET (Figure 3).

Concluding Remarks. Catalysis by an $I^{\bullet}/I^-$ couple occurs in the photoredox between diphenylphosphinous acid (**1**) and 10-methylacridinium salt **2**. Unit reactions of the phosphorus-centered radicals generated during this photoreaction were demonstrated. Thus, (1) cation radical $\mathbf{1}^{+\bullet}$, which is initially generated through SET from **1** to **2***, undergoes an ionic reaction with water or methanol to give phosphoranyl radical $\mathbf{1H}^{\bullet}$ or $\mathbf{1M}^{\bullet}$, respectively, and (2) the resulting phosphoranyl radical $\mathbf{1H}^{\bullet}$ or $\mathbf{1M}^{\bullet}$ decomposes through SET to $I^{\bullet}$ rather than β-scission.

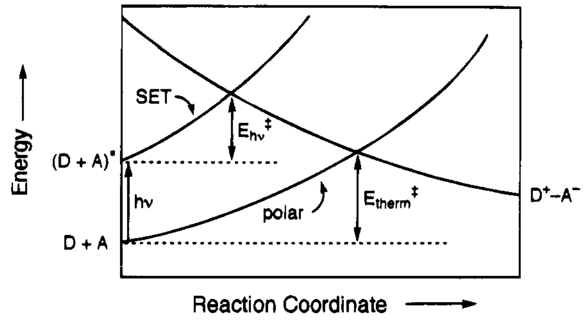


Figure 3. Energy diagram for a reaction between an electron donor (D) and an electron acceptor (A) in the ground and photoexcited states.

Experimental Section

Instruments. HPLC was performed with a Tosoh CCPD dual pump equipped with a photodiode array UV–visible detector (Shimadzu SPD M6A) on a Cosmosil 5-Ph column (4.6 × 150 mm) with water/methanol (20/80, v/v) as eluent. GC was performed with a Shimadzu GC-12A gas chromatograph. Mass spectra were obtained on a Shimadzu GCMS-QP2000A gas chromatograph–mass spectrometer equipped with a Shimadzu GC-MSPAC 200S data processor. ^{1}H and ^{31}P NMR spectra were recorded on a Varian XL 200 NMR spectrometer.

Materials. Diphenylphosphine oxide (**1′**)[31a] and 10-methylacridinium salts **2a** and **2b**[42,43] were prepared by the procedures reported previously.

General Procedure. The general procedure for the photoreactions was as described previously.[22] Identification of the products was based on comparisons of their retention times on GC and HPLC with those of authentic samples. The UV–visible spectra obtained on an HPLC apparatus equipped with a photodiode array detector were compared with those from authentic samples for identification of the products. GCMS and LCMS were performed when necessary. Adduct **5** was detected on HPLC as phosphine oxide **6**.[22] The yield of **8** was calculated by comparison of the peak area on HPLC arising from absorption at 210 nm with that of diphenylphosphine oxide (**1′**), with the assumptions that the chromophore in **8** is a $Ph_2P(=O)$ moiety, as in **1′**, and that its extinction coefficient is identical to that of **1′** at this wavelength. The assumption was verified by the observation that diphenylphosphinic acid (**3**), which also has the same chromophore as **1′**, has a nearly identical extinction coefficient at any given wavelength as that of **1′**.

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(41) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

(42) Yasui, S.; Shioji, K.; Yoshihara, M.; Maeshima, T.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2077.

(43) Roberts, R. M. G.; Ostovic, D.; Kreevoy, M. M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 257.