

Reactivity of a Phosphoranyl Radical Generated by Photoreaction of Phenyl Diphenylphosphinite with 10-Methylacridinium Iodide. α -Scission vs. Single Electron Transfer

Shinro Yasui*

Tezukayama College, Gakuen-Minami, Nara 631, Japan

Kosei Shioji and Atsuyoshi Ohno

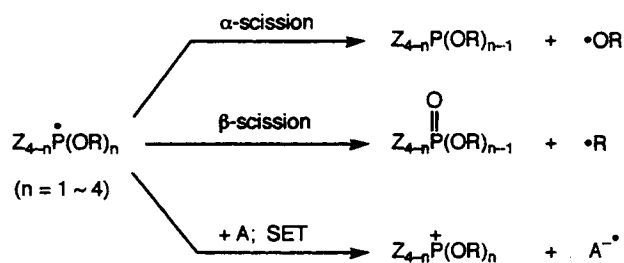
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

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ABSTRACT

Photoreaction of phenyl diphenylphosphinite (**1b**) with 10-methylacridinium iodide (**2**) in aqueous acetonitrile under an argon atmosphere gives 10-methylacridan, the reduction product from **2**, in a quantitative yield and phenyl diphenylphosphinate, the oxidation product from **1b**, in a low yield, as well as a large amount of diphenylphosphinic acid and a moderate amount of phenol. The product distribution observed here is interpreted well in terms of decomposition of a phosphoranyl intermediate through both α -scission and single electron transfer (SET) pathways.

A phosphoranyl radical which has one or more P-O bonds may decompose through either α -scission or β -scission (Scheme 1). The relative ease of these pathways depends mainly on the stability of the radical species liberated during the decomposition [1]. Thus, β -scission occurs when the substituent R on the oxygen is secondary alkyl [2], tertiary alkyl [3], or benzyl [3], whereas the phosphoranyl radical with R = aryl undergoes α -scission because

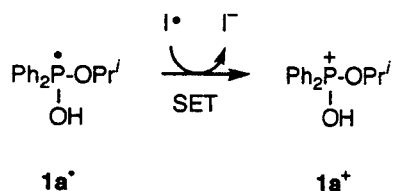


SCHEME 1

of the high stability of the aryloxy radical that is liberated [4–6]. The third path for the decomposition of a phosphoranyl radical is single electron transfer (SET) from the phosphoranyl radical to give the phosphonium ion, which takes place when a good electron acceptor exists in the system [7, 8].

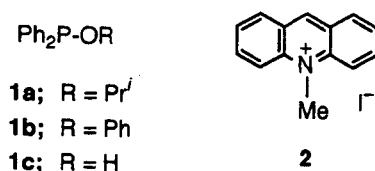
We previously reported that the photoredox reaction between isopropyl diphenylphosphinite (**1a**) and 10-methylacridinium iodide (**2**) in aqueous acetonitrile under an argon atmosphere involves the phosphoranyl radical **1a** as an intermediate, which decomposes by donating an electron to an iodine atom generated during the reaction (Scheme 2) [9]. Exclusive occurrence of SET for the decomposition of **1a** in this reaction is attributable to the insufficient stability of either the isopropoxy or the

*To whom correspondence should be addressed.



SCHEME 2

isopropyl radical which would be liberated if α - or β -scission, respectively, occurred.



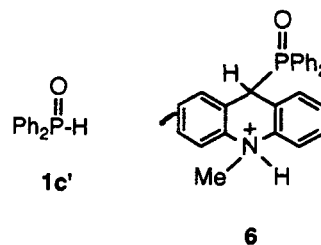
In this connection, it is interesting to examine the photoreaction of a trivalent phosphorus compound which has a phenoxyl group bonded to phosphorus with the acridinium ion **2**, since the corresponding phosphoranyl radical intermediate, if formed during the reaction, could undergo α -scission with the loss of the relatively stable phenoxyl radical [4–6]. This reaction system therefore may provide an opportunity to evaluate the relative importance of α -scission vs. SET for the decomposition of a phosphoranyl radical under these conditions. This article shows that the phosphoranyl intermediate generated from phenyl diphenylphosphinite (**1b**) during the photoreaction with **2** decomposes through both SET and α -scission.

RESULTS

When a solution of equimolar amounts of phenyl diphenylphosphinite (**1b**) and 10-methylacridinium iodide (**2**) in aqueous acetonitrile was irradiated with the light from a Xe-lamp (>360 nm with a filter) under an argon atmosphere at room temperature for 40 minutes, a small amount of phenyl diphenylphosphinate (**3b**), the oxidation product from **1b**, and a quantitative yield of 10-methylacridan (**4**), the reduction product from **2**, were obtained. A large amount of diphenylphosphinic acid (**3c**) and a moderate amount of phenol (**5**) were also produced (Scheme 3). Under aerobic conditions, the formation of **4** was largely suppressed. The results are summarized in Table 1.

The progress of the reaction was followed by HPLC and GC. As shown in Figure 1, large amounts of diphenylphosphine oxide (**1c'**) and the cationic adduct **6** from **1c'** and **2**, besides phosphinate **3b** and phenol **5**, were detected at the initial stage of the reaction. The amounts of **1c'** and **6** decreased with an increase in the amounts of **3c** and **4** formed,

whereas the amounts of **3b** and **5** remained constant for the rest of the reaction.

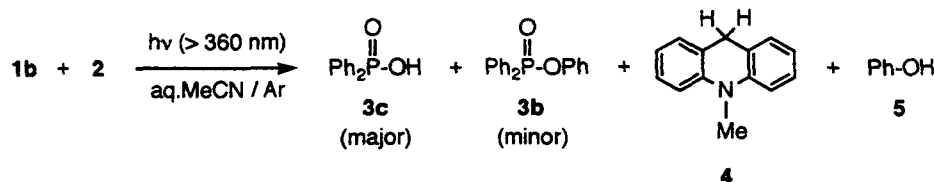


The water content in the solvent used was estimated to be about 0.1% by the Karl–Fisher method.

DISCUSSION

In the present reaction, phenyl diphenylphosphinite (**1b**) does not absorb the light of wavelengths longer than 360 nm, and the acridinium ion **2** is the sole species that is photoexcited under these conditions. Therefore, there is no doubt that the photoreaction of **1b** with **2** is triggered by SET from the former to the latter in the photoexcited state, with the cation radical **1b⁺⁺** and the dihydroacridinyl radical **2'** being generated (Scheme 4, R = Ph). Similar processes in which trivalent phosphorus compounds, **1a** [9], diphenylphosphinous acid (**1c**) [10], and triphenylphosphine [11], donate an electron to **2** in the photoexcited state are well-known (Scheme 4; R = Pr^f, H). The participation of radical species in this reaction is revealed by the observation that the formation of **4** is largely suppressed under aerobic conditions (Entry 2, Table 1).

As has been reported previously, **2'** thus formed is converted to the final product **4** according to the reaction sequence represented by Scheme 5 [10]. On the other hand, cation radical **1b⁺⁺** reacts with water in the solvent to afford the phosphoranyl radical **1b'** (Scheme 6; R = Ph) [9–15]. It is unlikely that **1b'** decomposes via SET only to give the phosphonium ion **1b⁺**. The phosphonium ion **1b⁺**, if formed, would eliminate a proton in preference to a phenyl cation to afford phenyl diphenylphosphinate (**3b**) as the exclusive product from **1b** (refer to Scheme 2). This is not the case; **3b** is obtained in a low yield, while a large amount of diphenylphosphinic acid (**3c**) is formed. Thus, for the decomposition of phosphoranyl radical **1b'**, SET is only a minor pathway and there must be another route available. As seen in Figure 1, phosphine oxide **1c'** is detected at the early stage of the reaction. The compound **1c'** is the pentavalent tautomer of phosphinous acid **1c**, and the former is much more stable than the latter [16]. Therefore, the fact that a large amount of the former tautomer **1c'** is detected implies the formation of **1c** in a large amount during the reaction. This strongly



SCHEME 3

 TABLE 1 The Photoreaction of **1b** with **2**^a

Entry	Time (Min)	Yield/pct				
		3b	3c	1c'	4	5
1	40	6	78	2	97	45
2 ^b	50	3	48	0	3	48
3 ^c	130	0	0	14	—	16
4 ^d	60	—	100	0	59	—

^a[**1b**]₀ = [**2**]₀ = 1.25 × 10⁻² M; Xe-lamp (>360 nm with a glass filter); at 20°C; under Ar atmosphere.

^bUnder the aerobic conditions.

^cControl experiment in the dark in the absence of **2**. 70 pct of **1b** was recovered.

^dThe reaction of **1c'** with **2**; data from Ref. [10].

suggests that rapid α -scission occurs as a major pathway for the decomposition of phosphoranyl radical **1b'**, giving **1c** as well as the phenoxyl radical (path b in Scheme 7).

A phosphoranyl radical with an aryloxy group bonded to phosphorus has been reported to undergo readily α -scission to liberate a relatively stable aryloxy radical [4–6]. Thus, as represented in Scheme 7, phosphoranyl radical **1b'** decomposes through both SET (path a) and α -scission (path b) to give

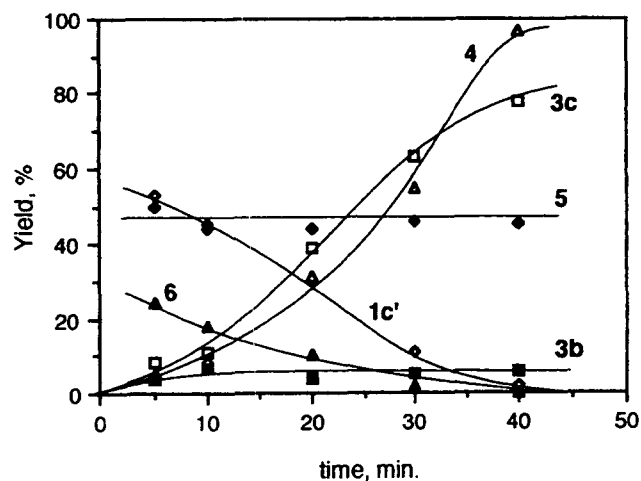
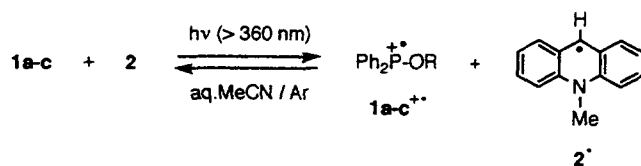
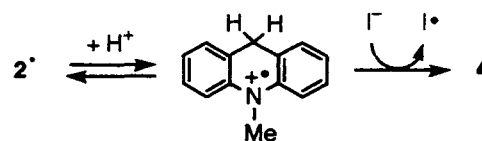


FIGURE 1 Time course of the photoreaction of **1b** with **2**. Plots of the yields of **3b** (■), **3c** (□), **4** (△), **5** (◆), **1c'** (◇), and **6** (▲) against reaction time.

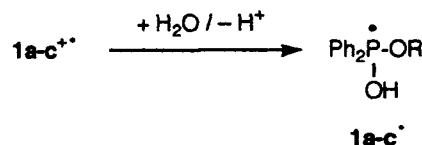


SCHEME 4

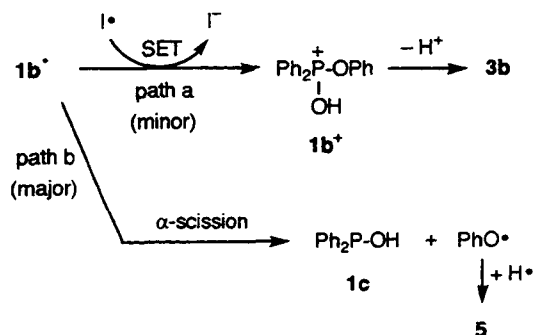
1b' and **1c**, respectively; the latter process is much more favorable than the former. That the amount of phenol **5** remains constant during the reaction is consistent with this mechanism; that is, phenoxyl radical formed via α -scission decomposes rap-



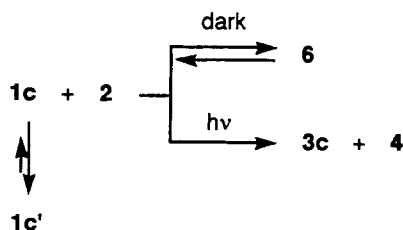
SCHEME 5



SCHEME 6



SCHEME 7



SCHEME 8

idly through hydrogen abstraction from the solvent to give **5** as a major product [4].

Figure 1 shows that **1c'** gradually disappears and so does the adduct **6**, which is in thermal equilibrium with **1c** and **2**, as **3c** gradually appears. This indicates that **1c'** is converted to **3c** under the reaction conditions. Apparently, this conversion results from a photoredox reaction between **1c**, the trivalent tautomer of **1c'**, and **2** (Scheme 8), as has been reported [10, 17]; the reaction of **1c'** with **2** under these photochemical conditions gives a quantitative yield of **3c**, with **4** being obtained as well (Entry 4, Table 1). The mechanism proposed here thus includes the oxidation of **1b** to **1b^{••}** (Scheme 4) and of **1c** to **3c** (Scheme 8), both of which are coupled to the reduction of **2** to **4**, which predicts that quantitative conversion of **1b** to the products **3b** and **3c** is accomplished by more than one equivalent amount of **2**.

However, **3b** and **3c** are formed in nearly quantitative yields in total when the initial amount of **2** is equivalent to that of **1b** (Entry 1, Table 1). This is explainable in the terms of "catalysis" by **2**. It is well-known that **2** is regenerated through the thermal oxidation of acridan **4** by iodine present in the system [18], and, as a result, it contributes to the reaction catalytically. Our previous research revealed that the reaction of **1a** [9] or **1c'** [10] with **2** affords the oxidation and the reduction products **3** and **4**, respectively, roughly in the ratio of **3:4** = **2:1**, although these products are expected to be formed in equimolar amounts (see Entry 4, Table 1). The quantitative formation of **4** observed in the present reaction is therefore an indication that there are plural processes which bring about the reduction of **2** to **4**. This is consistent with the presently proposed mechanism.

Based on the redox potentials, a previous report has revealed that the initial SET from **1a-c** to **2** in the photoexcited state is considerably exothermic [10], suggesting that nucleophilic attack of water upon cation radical **1a-c^{•+}** is rate-limiting for the formation of phosphoranyl radical **1a-c[•]** (Scheme 6). Thus, the higher electronegativity of the phenoxy group than the hydroxyl group results in more rapid formation of **1b[•]** from **1b** than the formation of **1c[•]** from **1c**, which accounts well for the observation that **1b** affords **1c** rapidly while

1c is gradually converted to **3c**. The phosphoranyl-decomposition steps, α -scission and SET, are certainly fast.

It may be argued that **1c'** (or **1c**) is produced simply by the hydrolysis of **1b**. The fact that the yield of phosphinic acid **3c** is much higher than that of phenol **5** (Entry 1, Table 1), however, rules out the possibility that the hydrolysis of **1b** is the sole path to produce **1c** and **5**; the hydrolysis of **1b** produces **1c** and **5** in equal amounts, and therefore the amount of **3c**, the oxidation product from **1c**, cannot exceed the amount of **5** [19]. Furthermore, if **1b** is hydrolyzed quantitatively to **1c**, then **1c** is the sole species which reduces **2** to **4** in the system, and the apparent yield of **4** would be much lower than quantitative owing to the oxidation of **4** to **2** under the reaction conditions (vide supra). A control experiment showed that the extent of hydrolysis of **1b** to **1c** is only 14% for a prolonged reaction in the dark (Entry 3, Table 1), and the addition of **2** brought about no appreciable acceleration of the hydrolysis of **1b**.

Taking into account that less than 14% of **1c** is produced by the hydrolysis of **1b** within the period tested and that **1c** is oxidized quantitatively to **3c** under the same conditions, we can assume that at least 64% out of the 78% total yield of **3c** is formed via α -scission of **1b[•]**. Comparison of this yield with that of **3b** (6%) allows us to estimate that α -scission of **1b[•]** is at least 10 times more rapid than SET from **1b[•]** under the conditions examined. This ratio, of course, changes depending on several factors, including, the concentration of an electron acceptor. Therefore, this number by itself has no significant physical meaning. Nevertheless, this estimation manifests that a phosphoranyl radical having a phenoxy group bonded to phosphorus readily undergoes α -scission. α -Scission of alkoxy-substituted diphenylphosphoranyl radicals, on the other hand, is not observed under these conditions; the phosphoranyl radical, such as **1a[•]** [9] or **1c[•]** [10], which is formed from **1a** or **1c**, respectively, in the similar photoreaction with **2**, exclusively undergoes SET to an iodine atom generated during the reaction, giving the corresponding phosphonium ion (see Scheme 2).

Finally, the thermal reaction of phosphinite **1b** with an equimolar amount of acridinium ion **2** was briefly examined in acetonitrile-*d*₃ solution by ³¹P NMR spectroscopy. The signal for **1b** (δ = 111.4 from H₃PO₄) disappeared within 20 minutes with an incipient appearance of a small and transient signal at δ = 57.4, a new signal finally appearing at δ = 31.6. Based on the comparison with the reported values of chemical shifts for similar phosphonium ions (**7**, R = alkyl) [20], the former signal is assignable to phosphonium salt **7b** (R = Ph). On the other hand, the chemical shift of the latter is different from those of **1c'** (δ = 21.7) and **6** (δ = 33.8), and we tentatively assign this to ylide **8** [21]. Thus,

this result assumes path c in Scheme 9 to be a thermal reaction of **1b** with **2**.

Previously, we have reported that **1a** and the related alkyl esters of diphenylphosphinite undergo the Arbuzov-type reaction with **2** thermally to afford phosphine oxide **9** (path d in Scheme 8) [20]. It seems possible that, while an alkoxy-substituted phosphonium ion (**7**, R = alkyl) readily eliminates an alkyl cation, phosphonium ion **7b** (R = Ph) is reluctant to eliminate a phenyl cation even in the presence of iodide ion, which brings about the loss of the 9-proton to afford ylide **8**. As clearly shown in Figure 1, the photoreaction between **1b** and **2** is so fast that this thermal process is not observed under the photochemical conditions.

EXPERIMENTAL

Instruments

HPLC analysis 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 analysis 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. ³¹P NMR spectra were obtained on a Varian XL 200 NMR spectrometer under proton decoupling conditions. The water content in the solvent was determined by use of a Kyoto Electronics MFG Karl-Fisher moisture content meter Model MK-AII.

Materials

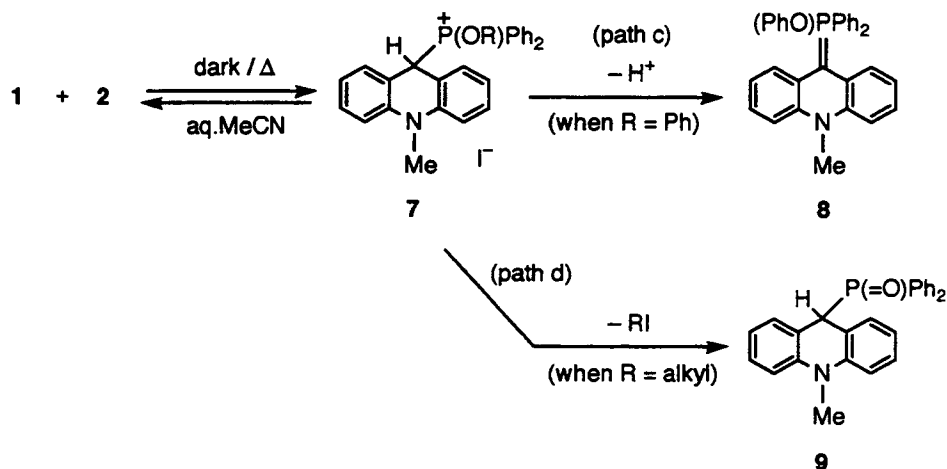
Phenyl diphenylphosphinite (**1b**) was prepared by the procedure described for the preparation of al-

kyl diphenylphosphinites [7b]. To the solution containing 1.41 g (0.0150 mol) of phenol and 1.20 g (0.0152 mol) of pyridine in dry ether placed in an ice-salt bath was added 3.50 g (0.0159 mol) of chlorodiphenylphosphine through an addition funnel. The reaction mixture was stirred at room temperature overnight and then concentrated in vacuo. Crude material thus obtained was subjected to repeated purifications by use of a medium pressure liquid chromatograph (silica gel; ethyl acetate as the eluent) to give 0.23 g (6% yield) of the pure material as a colorless liquid (>99% on GC). ³¹P NMR (in CD₃CN, δ from H₃PO₄) 111.4. MS *m/z* 277, 201, 183, 77. On exposure to air, this material was quantitatively converted to phenyl diphenylphosphinate (**3b**).

10-Methylacridinium iodide (**2**) was prepared according to the procedure described in the literature [22].

Photoreaction of **1b** with **2**

A solution of equimolar amounts (1.25 × 10⁻² M) of **1b** and **2** in aqueous acetonitrile was irradiated with light from an Ushio xenon short arc lamp UXL-500D-0 (>360 nm with a Toshiba glass filter L-311) under an argon atmosphere at room temperature. After an appropriate reaction time, a 50 μl aliquot was subjected to analyses by an HPLC apparatus equipped with a photodiode array detector as well as a GC. GCMS analysis was also performed, when necessary. The products were identified based on the comparisons of the retention times as well as UV-vis and mass spectra on HPLC and GCMS, respectively, with those of the authentic samples. The cationic adduct **6**, formed from **1c'** and **2**, was detected in the form of a conjugate base on an HPLC apparatus, as has been described previously [10].



SCHEME 9

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