

Chemiluminescence in Autoxidation of Phosphonate Carbanions. Phospha-1,2-dioxetanes as the Most Likely High-Energy Intermediates

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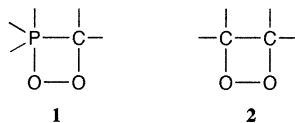
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Autoxidation of the phosphonate carbanions derived from 9-phosphono-10-hydroacridanes provided chemiluminescence ascribed to the excited acridone anion. The intramolecular CIEEL (chemically initiated electron exchange luminescence) mechanism can be applied to this chemiluminescence because of the much higher emission efficiency compared to that of 9-phosphono-10-methylacridanes. The effect of the phosphonate substituents on the emission efficiency and especially on the rates of the chemiluminescence decay can be interpreted from the valence deviation of the phosphorus atoms, which is connected with the substituent effect on the geometrical selectivity in the olefination reaction of the phosphonate carbanions. The enhanced chemiluminescence in the presence of the fluorophores was also detected in autoxidation of the carbanions of diethyl diphenylmethylphosphonate and fluorenylphosphonate. Although the evidence is circumstantial, these results strongly support the belief that phospha-1,2-dioxetane is the most likely high-energy intermediate generating the excited molecules.

Introduction

Phospha-1,2-dioxetanes (**1**) have been proposed¹ to be the most likely intermediates in the oxygenation of phosphonium ylides, sometimes called the oxy-Wittig reaction, which generates the corresponding carbonyl compounds and phosphine oxides. In a structural similarity to the well-known 1,2-dioxetanes (**2**)^{2,3} providing a peculiar phenomenon, chemiluminescence, the phospha-1,2-dioxetanes are also expected to display chemiluminescence along with decomposition, where the electronically excited carbonyl compounds would be generated similarly to thermal decomposition of 1,2-dioxetanes.



Indeed, light emission has been observed during the singlet oxygenation of suitable phosphonium ylides^{1b,c} and phosphazines,^{1d} where phospha-1,2-dioxetanes were sug-

gested as the pertinent intermediates. Recently, we reported the observation of chemiluminescence during the oxygenation of phosphonate carbanions.⁴ This chemiluminescence reaction is also expected to involve phospha-1,2-dioxetanes as the key high-energy intermediates. Elucidation of such intermediates will be significant for further understanding of the Horner–Wadsworth–Emmons (HWE) reaction,⁵ a very important olefination reaction of phosphonate carbanions, whose intermediate has been investigated less than that of the Wittig reaction.⁶ This study was conducted to explore the chemiluminescent autoxidation of phosphonate carbanions from the viewpoint of chemiluminescence, thus providing strong support for phospha-1,2-dioxetanes as the high-energy intermediates as well as supplying a new aspect for reactions of phosphonate carbanions.

Results and Discussion

The autoxidation of phosphonate carbanions derived from 9-phosphono-10-hydroacridanes (**3**) and *t*-BuOK in aprotic solvents provided chemiluminescence that lasted long enough to be spectroscopically detected, and whose

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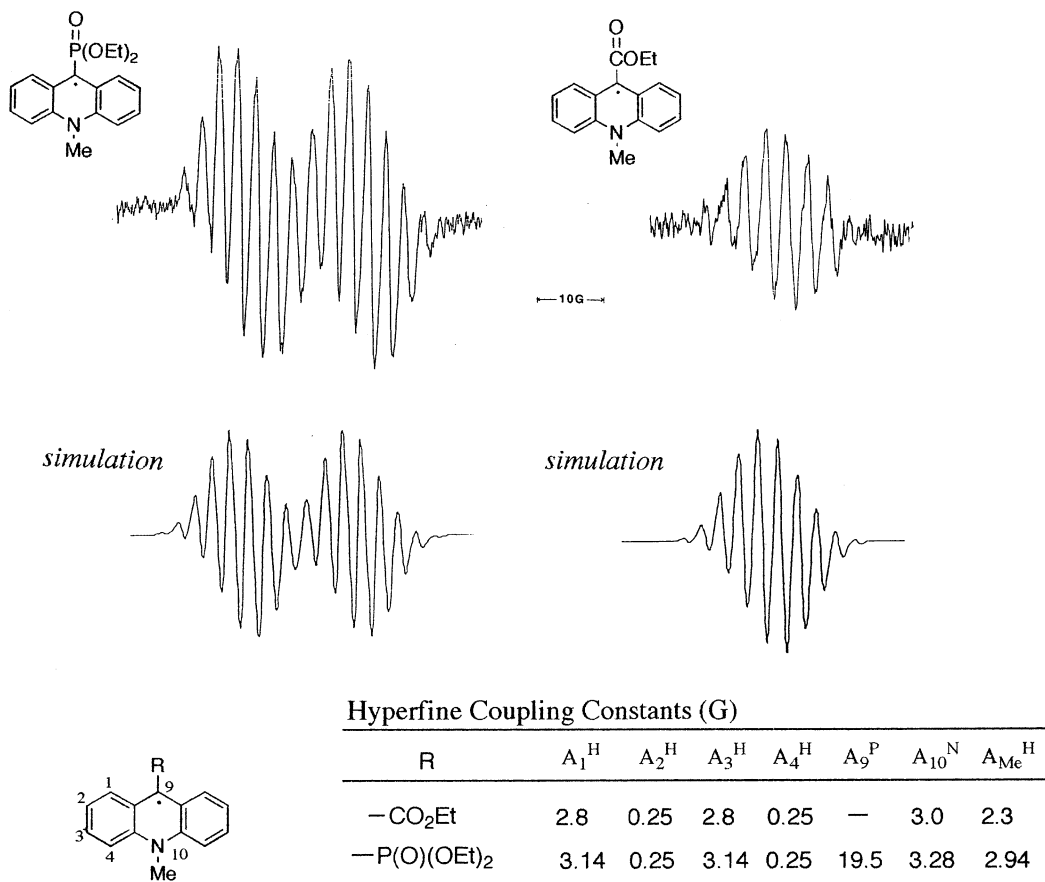
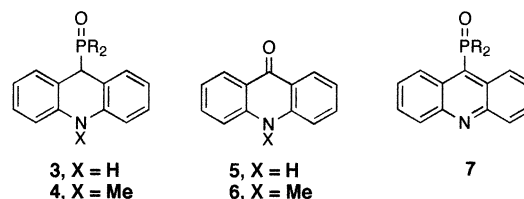


FIGURE 1. ESR spectra of the acridanyl ketyl radicals generated from 9-diethylphosphono-10-methylacridane (**4b**) and 9-ethoxycarbonyl-10-methylacridane and their computer-simulated spectra.

emission spectra were in complete agreement with the fluorescence spectrum of the anion of acridone (**5**) independently generated under basic conditions. However, the chief product in these chemiluminescence reactions was not **5** but weakly fluorescent 9-phosphonoacridine (**7**). For instance, **5** and **7a** (R = OMe) was obtained in 8% and 85% isolated yields, respectively, from the thorough autoxidation of **3a** (R = OMe) with *t*-BuOK in DMSO. On the other hand, similar reactions of **4** also showed chemiluminescence due to the fluorescence of *N*-methylacridone (**6**) as previously reported.⁴ Although one could see this weak, pale blue light emission with the naked eye in the dark when the reaction was carried out in high concentration, it was too weak to be detected spectroscopically. In the ³¹P NMR spectrum of **4f** (R = OPh) treated with *t*-BuOK in THF, the signal for **4f** at $\delta +14.67$ ppm became smaller with the increase in a new signal at $\delta -9.54$ ppm ascribed to the diphenyl phosphate anion with time. To scavenge the phosphorus fragment, a thorough autoxidation of **4f** was carried out in the presence of *t*-BuOK in THF to give **6** and potassium diphenyl phosphate in 89% and 80% isolated yields, respectively, which were those expected from the oxy-Wittig type of reaction.

Because radical species have sometimes been observed during autoxidation of stabilized carbanions,⁷ attempts







were made to detect a ketyl radical adjacent to the phosphorus atom. The ESR spectrum of the radical generated in the colored solution prepared from **4b** (R = OEt) and *t*-BuOK in aerated DMSO at room temperature was successfully recorded as shown in Figure 1, in which the *g* value was estimated to be 2.0027, and the whole spectrum was split in two. A part of the spectrum is similar to that of the 9-methyl-10-carbethoxyacridanyl ketyl radical (Figure 1) and the 9-phenylsulfenyl-10-methylacridanyl ketyl radical.⁸ The hyperfine coupling constants listed in Figure 1 were estimated by computer simulation, referring to the data documented by Janzen et al.⁹ The value, 19.5G, found for the coupling constant for the interaction of the unpaired electron and the phosphorus atom is very small compared to the values previously reported,¹⁰ and therefore, this radical is highly delocalized over the aromatic rings. The light emission from the solution of **4b** was quenched at once when

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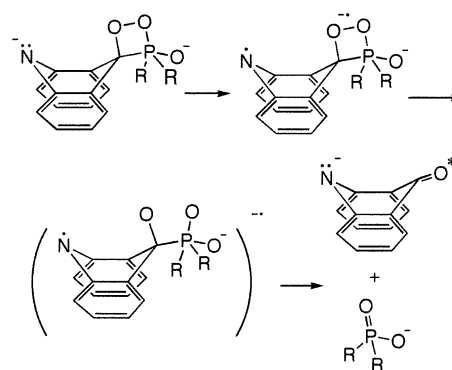
TABLE 1. Chemiluminescence Quantum Yields and Kinetic Parameters

	-P(O)R ₂	Φ _r ^a	Φ _s × 10 ⁸ ^{b, c}	rel. I _{max} ^d	rel. kinetic parameters ^e	
					k _a	k _b
3a	-P(O)(OMe) ₂	0.15	480	1.3	0.29	0.29
3b	-P(O)(OEt) ₂	0.22	110	0.76	0.40	0.35
3c	-P(O)(OCH ₂ CF ₃) ₂	0.62	1700	10.8	0.56	0.56
3d		0.21	280	30.5	108	4.1
3e		0.14	160	0.47	0.2	0.20
4a	-P(O)(OMe) ₂	0.62	2.0	1.0	3.9	1.0
4b	-P(O)(OEt) ₂	0.64	1.9	0.48	7.5	0.71
4c	-P(O)(OCH ₂ CF ₃) ₂	0.68	38	4.1	24	1.4
4d		0.61	12	7.2	24	6.9
4e		0.66	5.6	0.28	6.0	0.57

^a Determined by UV spectrum. ^b Estimated by the photon-counting method using luminol chemiluminescence as standard (einstein/mol). ^c Reference 12. ^d Arbitrary unit standardized from the value k_b for **4a**. ^e Arbitrary unit standardized from the value for **4a** determined from the curves in Figure 1. The higher values were regarded as k_a and the lower ones as k_b.

radical trapping agents such as powdered sulfur or *p*-benzoquinone were added to the solution, whereas the weak emission generated from the ionic reaction of 9-diethylphosphonoacridine (**7b**, R = OEt) and alkaline hydrogen peroxide was not interrupted. Thus, the present chemiluminescent autoxidation of the phosphonate carbanions proceeds via interaction of atmospheric oxygen and the acridanyl ketyl radical, probably generated by an electron transfer to molecular oxygen.

The remarkable effect of the phosphonate substituents on the geometric selectivity in the HWE reaction has been well documented.¹¹ This effect is believed to originate from the various rates for oxaphosphetane ring formation, namely, the acceleration of the ring formation results in an increase in the ratio of thermodynamically less favored *Z*-olefins. To explore the substituent effect on the chemiluminescence, a kinetic study based on chemiluminescence decay was done on the reactions of **3** and **4**. The collected data of the yields of the emitter (Φ_r) determined by UV spectrum and singlet excited yields (Φ_s) are listed in Table 1. There is a Φ_s value for **3** conspicuously much larger than that for **4**,¹² which explains the contribution of an intramolecular CIEEL (chemically initiated electron exchange luminescence) process as proposed for the firefly luciferin bioluminescence:¹³ namely, strong support for the CIEEL mechanism was due to the drastic decrease in the emission

SCHEME 1

efficiency when the phenolic proton of the firefly luciferin was replaced by a methyl group. As depicted in Scheme 1 similar circumstances are furnished in the present chemiluminescence if the phospho-1,2-dioxetanes could be postulated for the reaction intermediates as well as the electron acceptors such as the 1,2-dioxetanes, because an amide anion in **3** would have a much lower oxidation potential than the lone pair of the methylated nitrogen in **4**. An increase in Φ_s by an electron-attracting 2,2,2-trifluoroethyl (TFE) group was also observed, which is probably due to the promotion of ring closure (vide infra) as well as the CIEEL process.

Of interest was the drastic change in the emission profiles as shown in Figure 2. The maximum intensity appeared at about 60 s for **3a**, **3b**, and **3e**, whereas that for **3d** and **3e** occurred faster. Especially, the maximum of **3d** occurred within 1 s. The curves in Figure 2 could be matched by an equation for the combined exponential contribution of the two parameters, k_a and k_b, which is adapted to sequential reaction process. Thus, the emission intensity *I* at any time *t* is expressed by the following equation:

$$I = M\{\exp(-k_a t) - \exp(-k_b t)\}$$

where *M* is proportional to the relative maximum intensity (rel I_{max}). Such a sequential reaction can be seen in the peroxyoxalate chemiluminescence,¹⁴ in which the key species are presumed to be cyclic peroxides such as 1,2-dioxetanes. In the present system, if either kinetic parameter, k_a or k_b, corresponds to a ring-closing step producing a phospho-1,2-dioxetane, the structure of the phosphonate substituents should affect the rates, as has been found in the HWE reaction.^{15,16} Thus, an enhancement of the rates is expected for **3c**, **3d**, **4c**, and **4d**, because the formation of the phospho-1,2-dioxetane ring would be promoted by the electronegative substituents or the strained five-membered cyclic moieties.¹⁷ According to the technique used for kinetic analysis of the peroxy-

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(12) The chemiluminescence quantum yields for **4** were reinvestigated to find that the values were lower by 1 order of magnitude than those reported in ref 4b.

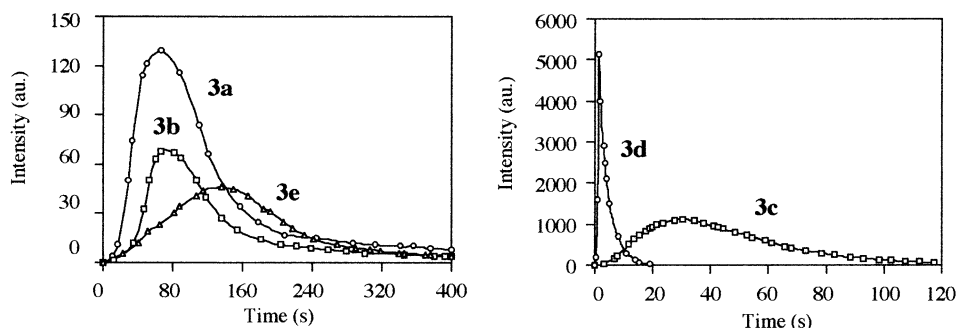
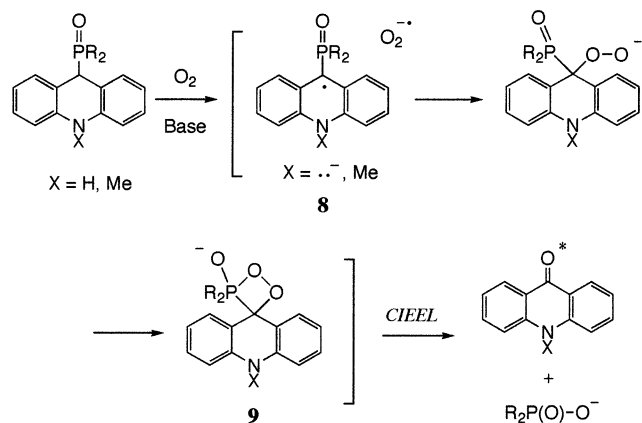


FIGURE 2. Emission profiles for the chemiluminescence reactions of **3a–e**.

SCHEME 2



oxalate chemiluminescence reaction,¹¹ computational work fitting the emission curves allowed us to estimate the relative values of both parameters k_a and k_b in each reaction, as well as relative maximum emission intensity (I_{\max}). These data are shown in Table 1. As expected, a drastic increase in k_a by some hundred times compared to the others was found in the reaction of **3d**. An appreciable acceleration in **4c** and **4d** was also found, but that for **3c** was negligible. Such a large enhancement of the rate in **3d** was also observed when the reactants and base concentrations were changed; therefore, k_a does not depend on the initial carbanion formation or the sequential oxygenation but on the valence transformation of the phosphorus atoms. This suggests that k_a is the rate corresponding to the ring-closure step. Accordingly, the light emission synchronizes with the ring formation; namely, the high-energy species providing chemiluminescence should be the phospho-1,2-dioxetanes. Therefore, we can illustrate the whole reaction path involving the acridanyl ketyl radical (**8**) and phospho-1,2-dioxetanes (**9**) as depicted in Scheme 2.

The energetic advantage for the five-membered cyclic phosphonate during the ring formation was also supported by calculations using the *ab initio* method at the RHF/6-31G(d) level of theory. Table 2 lists the energies and the valence angles of the oxyanions and the corresponding phospho-1,2-dioxetanes of **3a**, **3d**, and **3e**. The smaller valence angle for the oxyanion of **3d** compared with those of **3a** and **3e** leads to easy liberation of its strain energy by transformation into the phospho-1,2-dioxetane. Thus, a much larger energy gap between the oxyanion and the phospho-1,2-dioxetane for **3d** compared

TABLE 2. Energy Difference between Oxyanions and Phospho-1,2-dioxetanes

	ΔH (Hartree) ^a	valence angle α P-O-P (degree)	energy difference (kcal/mol)
	A - 1423.56692828 B - 1423.58948454	98.0 90.3	14.15
	A - 1422.40554758 B - 1422.44257165	93.7 92.6	23.23
	A - 1461.42762463 B - 1461.45230621	99.0 94.2	15.49

^a Calculated at the RHF/6-31G(d) level of theory.

with those for **3a** and **3e** was evaluated, which resulted in the acceleration of the ring formation, as was observed above.

The autoxidation of other phosphonate carbanions derived from diethyl diphenylmethylphosphonate (**10**) and diethyl fluorenylphosphonate (**11**) showed only a faint light emission in the absence of the fluorescent additives, but DBA (9,10-dibromoanthracene, a triplet energy acceptor) or DPA (9,10-diphenylanthracene, a singlet energy acceptor) enhanced the chemiluminescence despite the lower energy for the excited benzophenone ($E_{T1} = 68\text{--}69$ kcal/mol) and fluorenone ($E_{T1} = 53$ kcal/mol, $E_{T2} = 60$ kcal/mol, $E_{S1} = 63.2$ kcal/mol) compared with that for triplet DBA ($E_{T1} = 71$ kcal/mol) and that for singlet DPA ($E_{S1} = 72.9$ kcal/mol).¹⁸ The linear correlation in the Stern–Volmer plot of the double reciprocal of the DBA concentration and the chemiluminescence quantum yields establishes a bimolecular process between the excited species and DBA (Figure 3).

A few examples of such an upward energy transfer in the DBA-enhanced chemiluminescence from excited benzophenone have been reported previously,^{8,19} but a further study is needed to clarify this energy transfer.²⁰ The

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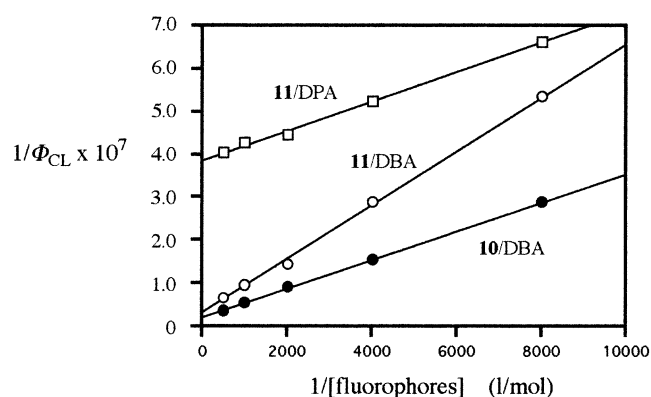
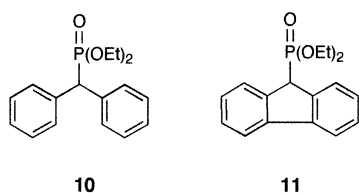


FIGURE 3. Linear relationship in double-reciprocal plot of $1/[\text{fluorophores}]$ vs $1/\Phi_{\text{CL}}$.



estimation and quantitative comparison of the quantum yields to argue the spin selectivity are therefore not as meaningful. Nevertheless, Figure 3 would be instructive to determine the excited species roughly. No enhancement by DPA in the chemiluminescence reaction of **10** suggests the predominant formation of triplet benzophenone, which is in agreement with the thermal decomposition of 3,3-diphenyl-4-methoxy-1,2-dioxetane.²¹ On the other hand, an almost equal measure of DBA enhancement in the reaction of **10** and **11** is contrary to the finding of the preferential formation of the singlet excited fluorenone in the thermal decomposition of 3,3-(9',9'-fluorenyl)-4-methoxy-1,2-dioxetane.²¹ This is probably due to an entirely different type of the counterparts formed in the reactions, namely, 1,2-dioxetanes produce two carbonyl compounds,²² whereas the present reaction forms carbonyl compounds and phosphate ions. These results show that chemiluminescence is not only a significant reaction for the acridanyl phosphonates but a general event in the autoxidation of the phosphonate carbanions if the reaction conditions are adjusted.

Conclusion

The results in the present study are indicative that phospho-1,2-dioxetanes are the most likely intermediates, although the evidence is circumstantial. The substituent effect on chemiluminescence decay was understood as a result of the different rates for the ring-closure step in the oxy-Wittig type of the reactions; namely, the

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easy phospho-1,2-dioxetane ring formation results in an increase in the rate of the light emission. On the other hand, this effect in the HWE reaction provides diversity in the geometric selectivity.

Experimental Section

General Methods. When required, all solvents were purified by standard techniques. Column chromatography was performed on silica gel. All NMR spectra were recorded in CDCl_3 . The chemiluminescence quantum yields were measured using a photomultiplier tube connected to a photon-counting system (vide infra).

9-Dimethylphosphono-10-hydroacridane (3a). A mixture of *N*-hydroacridinium bromide (2.00 g, 7.68 mmol) and trimethyl phosphite (1.81 mL, 15.4 mmol) was stirred for 2 h at room temperature. The product was collected, washed with petroleum ether, and recrystallized from benzene to give white crystals (0.80 g, 53%): mp 166–168 °C; ^1H NMR δ 3.54 (d, 6H, $J_{\text{PH}} = 11$ Hz), 4.58 (d, 1H, $J_{\text{PH}} = 25$ Hz), 6.67–7.22 (m, 8H); ^{13}C NMR δ 43.03 (d, $J_{\text{PC}} = 140$ Hz), 53.59 (d, $J_{\text{PC}} = 8$ Hz), 114.03, 114.40, 120.77, 128.27, 130.08, 140.28; ^{31}P NMR δ 24.81; MS (m/z) 289 [M^+] (22.6), 180 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_3\text{P}$: C, 62.28; H, 5.58; N, 4.84. Found: C, 62.40; H, 5.57; N, 4.65.

9-Diethylphosphono-10-hydroacridane (3b). A mixture of *N*-hydroacridinium bromide (5.00 g, 19.2 mmol) and triethyl phosphite (6.60 mL, 38.40 mmol) was heated for 10 min at 80 °C. The product was collected, washed with petroleum ether and recrystallized from benzene to yield a white powder (3.42 g, 70%): mp 190–192 °C; ^1H NMR δ 1.16 (t, 6H, $J = 7$ Hz), 3.82–3.90 (m, 4H), 4.54 (d, 1H, $J_{\text{PH}} = 25$ Hz), 6.64–7.24 (m, 8H); ^{13}C NMR δ 16.75 (d, $J_{\text{PC}} = 5$ Hz), 43.79 (d, $J_{\text{PC}} = 139$ Hz), 63.17 (d, $J_{\text{PC}} = 7$ Hz), 114.28, 115.26, 120.97, 128.47, 130.59, 140.63; ^{31}P NMR δ 22.45; MS (m/z) 317 [M^+] (18.2), 180(100). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{P}$: C, 64.35; H, 6.35; N, 4.41. Found: C, 64.06; H, 6.46, N, 4.27.

9-Bis(2',2',2'-trifluoroethyl)phosphono-10-hydroacridane (3c). A solution of *N*-hydroacridinium bromide (3.00 g, 11.5 mmol) and tris(2,2,2-trifluoroethyl) phosphite (5.68 g, 17.3 mmol) in dimethyl formamide (DMF) (10 mL) was heated for 12 h under reflux. Removal of DMF under reduced pressure, addition of brine, extraction with chloroform, and removal of the solvent after drying over anhydrous Na_2SO_4 gave the crude product, which was purified by column chromatography (eluant AcOEt/hexane = 3/2) to afford white crystals (2.14 g, 44%): mp 147–150 °C; ^1H NMR δ 3.96–4.03, 4.11–4.19 (m, 4H), 4.76 (d, 1H, $J_{\text{PH}} = 25$ Hz), 6.27 (s, 1H), 6.72–6.74, 6.92–6.96, 7.16–7.26 (m, 8H); ^{13}C NMR δ 43.28 (d, $J_{\text{PC}} = 140$ Hz), 62.61 (dq, $J_{\text{FC}} = 38$ Hz, $J_{\text{PC}} = 7$ Hz), 122.88 (dq, $J_{\text{FC}} = 276$ Hz, $J_{\text{PC}} = 8$ Hz), 112.75, 114.35, 121.18, 129.03, 130.02, 140.70 (Ar C); ^{31}P NMR δ 24.67; MS (m/z) 425 [M^+] (8.0), 180 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{P}$: C, 64.35; H, 6.35; N, 4.41. Found: C, 64.06; H, 6.46, N, 4.27.

9-(4',5'-Dimethyl-2'-oxo-2',2',5-[1',3',2']dioxaphospholan-2'-yl)-10-hydroacridane (3d). A mixture of *N*-hydroacridinium bromide (2.64 g, 10.1 mmol) and 4,5-dimethyl-2-methoxy-1,3,2-dioxaphospholane (3.04 g, 20.3 mmol), prepared from the reaction of methyl dichlorophosphite and 2,3-butanediol (mixture of stereoisomers) in the presence of triethylamine in benzene, was stirred for 1.5 h at room temperature. The product was collected, washed with petroleum ether, and recrystallized from acetonitrile to give white crystals (2.37 g, 74%): mp 208–214 °C; ^1H NMR δ 0.77, 0.93, 1.18, 1.19 (d, 6H, $J_{\text{PH}} = 6$ Hz), 2.96–3.04, 3.72–3.81, 4.05–4.12, 4.67–4.72 (m, 2H), 4.79, 4.84 (d, 1H, $J_{\text{PH}} = 25$ Hz), 6.69–6.72, 6.89–6.93, 7.12–7.16, 7.28–7.34 (m, 8H), 8.55 (s, 1H); ^{13}C NMR δ 14.75, 16.20, 17.18, 17.83, 42.84, 43.23 (d, $J_{\text{PC}} = 129$ Hz), 77.43, 78.32, 80.38, 83.32, 113.81, 121.06, 128.49, 130.33, 130.78, 140.30; ^{31}P NMR δ 39.00, 39.26, 39.45 (mixture of stereoisomers); MS (m/z) 315 [M^+] (2.4), 180 (100). Anal. Calcd for

$C_{17}H_{18}NO_3P$: C, 64.76; H, 5.75; N, 4.44. Found: C, 64.54; H, 5.76; N, 4.32.

9-(5',5'-Dimethyl-2'-oxo-2' λ^5 -[1',3',2']dioxaphosphorinan-2'-yl)-10-hydroacridane (3e). This was prepared similarly to the above procedure using *N*-hydroacridinium bromide (2.00 g, 7.68 mmol) and 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (1.89 g, 11.5 mmol), obtained from the reaction of methyl dichlorophosphite and 2,2-dimethyl-1,3-propanediol in the presence of triethylamine in benzene. The product was recrystallized from acetonitrile (1.68 g, 67%): mp 187–188 °C; 1H NMR δ 0.53, 0.93 (s, 6H), 3.48–3.53, 3.92–3.97 (m, 4H), 4.70 (d, 1H, $J_{PH} = 26$ Hz), 6.69–6.71, 6.89–6.91, 7.10–7.14, 7.29–7.31 (m, 8H); ^{13}C NMR δ 18.83, 19.73 ($J_{PC} = 7$ Hz), 41.36 (d, $J_{PC} = 137$ Hz), 74.51 (d, $J_{PC} = 8$ Hz), 112.05, 112.51, 119.13, 126.54, 128.57, 138.34; ^{31}P NMR δ 16.71; MS (m/z) 329 [M^+] (2.5), 59 (100). Anal. Calcd for $C_{18}H_{20}NO_3P$: C, 65.65; H, 6.12; N, 4.25. Found: C, 65.72; H, 6.08; N, 4.07.

9-Dimethylphosphono-10-methylacridane (4a), 9-diethylphosphono-10-methylacridane (4b), 9-bis(2',2',2'-trifluoroethyl)phosphono-10-methylacridane (4c), and 9-diphenylphosphono-10-methylacridane (4f) are known compounds and were prepared by the established procedure.^{4b}

9-(4',5'-Dimethyl-2'-oxo-2' λ^5 -[1',3',2']dioxaphospholan-2'-yl)-10-methylacridane (4d). This was prepared similarly to the above procedure using *N*-methylacridinium iodide (1.60 g, 5.00 mmol) and 4,5-dimethyl-2-methoxy-1,3,2-dioxaphospholane (1.60 g, 5.00 mmol, mixture of stereoisomers). The product was recrystallized from benzene/hexane (0.37 g, 49%): mp 201–202 °C; 1H NMR δ 0.66, 0.85, 1.17 (d, 6H, $J = 6$ Hz), 2.85–2.92, 4.02–4.08, 4.61–4.68 (m, 2H), 3.35 (s, 3H), 4.78 (d, 1H, $J_{PH} = 22$ Hz), 6.86–6.98, 7.22–7.35 (m, 8H); ^{13}C NMR δ 15.11, 17.49, 18.05, 33.54, 43.92, 45.20 (d, $J_{PC} = 129$ Hz), 80.41, 83.66, 112.89, 118.50, 121.28, 128.84, 130.40, 143.25; ^{31}P NMR δ 39.49, 39.71, 40.42 (mixture of stereoisomers); MS. m/z 329 [M^+] (4.3), 180 (100). Anal. Calcd for $C_{18}H_{20}NO_3P$: C, 65.65; H, 6.12; N, 4.25. Found: C, 65.63; H, 6.31; N, 4.48.

9-(5',5'-Dimethyl-2'-oxo-2' λ^5 -[1',3',2']dioxaphosphoran-2'-yl)-10-methylacridane (4e). This was prepared similarly to the above procedure using *N*-methylacridinium iodide (1.12 g, 3.50 mmol) and 5,5-dimethyl-2-methoxy-1,3,2-dioxaphosphorinane (2.22 g, 12.5 mmol). The product was recrystallized from benzene/hexane (0.90 g, 75%): mp 242–243 °C; 1H NMR δ 0.52, 0.95 (s, 6H), 3.38 (s, 3H), 3.39–3.43, 3.89–3.94 (m, 4H), 4.67 (d, 1H, $J_{PH} = 26$ Hz), 6.87–6.98, 7.23–7.36 (m, 8H); ^{13}C NMR δ 21.06, 21.95, 32.60 (d, $J_{PC} = 7$ Hz), 33.58, 44.92 (d, $J_{PC} = 136$ Hz), 76.71–76.99 (m), 112.77, 118.63, 121.31, 128.76, 130.37, 143.23; ^{31}P NMR δ 16.20; MS (m/z) 343 [M^+] (3.6), 194 (100). Anal. Calcd for $C_{19}H_{22}NO_3P$: C, 66.46; H, 6.46; N, 4.08. Found: C, 66.51; H, 6.48; N, 4.28.

9-Dimethylphosphonoacridine (7a). A solution of **3a** (3.80 g, 13.1 mmol) and chloranil (3.88 g, 15.8 mmol) in benzene (150 mL) was heated under reflux for 4 h. After removal of the solvent, purification by column chromatography (eluant hexane/AcOEt = 6/1) gave the product, which was recrystallized from chloroform/hexane (2.44 g, 65%): mp 164–166; 1H NMR (60 MHz) δ 3.85 (d, 6H, $J_{PH} = 11.4$ Hz), 7.27–7.94 (m, 4H), 8.18–8.40 (m, 4H); MS (m/z) 315 [M^+] (100), 286

(29), 206 (51). Anal. Calcd for $C_{15}H_{14}NO_3P$: C, 62.72; H, 4.88; N, 4.88. Found: C, 62.60; H, 4.91; N, 5.27.

9-Diethylphosphonoacridine (7b). This was prepared similarly to the above procedure using **3b** (1.72 g, 5.42 mmol) and chloranil (1.60 g, 6.51 mmol). The crude product was recrystallized from ether (0.70 g, 41%): mp 82–84 °C; 1H NMR (60 MHz) δ 1.28 (t, 6H, $J = 7.2$ Hz), 4.18 (dq, 4H, $J = 7.2$ Hz, $J_{PH} = 14.4$ Hz), 7.41–7.86 (m, 4H), 9.11–9.27 (m, 4H); MS (m/z) 315 [M^+] (100), 286 (29), 206 (51). Anal. Calcd for $C_{17}H_{18}NO_3P$: C, 64.76; H, 5.75; N, 4.44. Found: C, 64.64; H, 5.66; N, 4.81.

Calibration of Photomultiplier. It is known²³ that autoxidation of a luminol solution having an absorbance of 1.0 produces photons of 1.62×10^{-6} mol/L in the reaction with excess *t*-BuOK in *t*-BuOH; therefore, the correction value (G) for the photomultiplier is defined by

$$G = (1.62 \times 10^{-6}) \text{Abs}_{\text{lumi}} \frac{V_{\text{lumi}}}{N_{\text{lumi}}}$$

where Abs_{lumi} is the absorbance, V_{lumi} is the volume of the luminol solution, and N_{lumi} is the count number determined by an average of at least five measurements. Because a luminol solution of a certain concentration suitable for the capacity of the photomultiplier used in this study was required, the absorbance at 359.5 nm of a stock luminol solution (1.6×10^{-7} M) in distilled DMSO was determined to be 1.22×10^{-3} from a calibration curve of the luminol solution. To this luminol solution (2.0 mL) in a quartz cell was added *t*-BuOK solution (0.3 mL, 2.0×10^{-2} M) in *t*-BuOH, and the photons generated immediately were counted. The G value was calculated according to the above equation.

Measurement of CL Quantum Yields. The total CL quantum yields (Φ_{CL}) were calculated according to

$$\Phi_{\text{CL}} = GN \left(\frac{R_{\text{photo}}}{M} \right)$$

where N is the average number of the counts, R_{photo} the correction factor given by the manufacturer for the fluorescence emission maximum of the fluorophores, and M is the moles of phosphonoacridanes. For a typical run, a solution (1.0 mL) containing **3** or **4** (1.00×10^{-3} M) in distilled DMSO was placed in a 1×1 cm² quartz cuvette in front of the photomultiplier in exactly the same geometry. Photon-counting was initiated simultaneously with the injection of a solution (0.5 mL) of *t*-BuOK (2.00×10^{-1} M) in DMSO into the cuvette, and the data collection was continued for 512 s. The total CL quantum yields were calculated according to the above equation.

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