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Photooxygenation Reaction and Chemiluminescence of (Arylmethylenehydrazono)triphenylphosphoranes. Possible Generation of Phospha-1,2-dioxetanes[1)]

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Photosensitized oxygenation of (benzylidenehydrazono)-, (diphenylmethylenehydrazono)-, (9-fluorenylidenehydrazono)-, (9-xanthenylidenehydrazono)-, and (10-methyl-9,10-dihydroacridin-9-ylidenehydrazono)triphenylphosphoranes at −78 °C gave the corresponding carbonyl compounds and triphenylphosphine oxide and also gave light emission upon warming-up to room temperature.

In the course of the studies on the 1,2-dioxetanes having a hetero atom in the ring and their chemiluminescence,[1,2)] we found that photosensitized oxygenation of (arylmethylenehydrazono)triphenylphosphoranes (**1a**—**b**) gave the corresponding carbonyl compounds (**5a**—**b**) and triphenylphosphine oxide (**6**) with chemiluminescent light emission (CL) upon warming-up to room temperature.[1)] The reactions above can be extended to the more complex (arylmethylenehydrazono)triphenylphosphoranes (**1c**—**e**). This phenomenon seems to result from the generation and the decomposition of 1,2,3-dioxaphosphetanes as the intermediates (**4**), which apparently resembles to the 1,2,3-dioxathietanes found on the oxygenation of thioketones.[2)] The former reactions were the first examples of chemiluminescent 1,2-dioxetanes containing one hetero atom in the ring. In the present paper, we wish to describe the oxygenation reactions of **1** in details (Fig. 1).

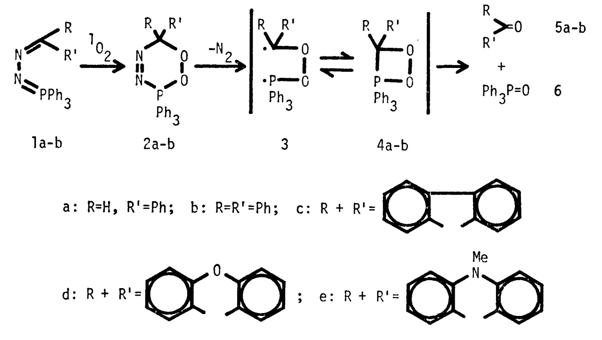
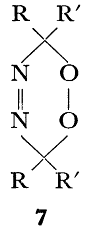


Fig. 1.

Results and Discussion

A solution of **1** (10^{-3}—10^{-2} mol/l) in CH_2Cl_2 with Methylene Blue (10^{-4}—10^{-3} mol/l) was irradiated at −78 °C with a tungsten-halogen lamp through a yellow optical filter (<510 nm cut off) with bubbling O_2. The irradiated solution gave pale-blue light emission upon warming-up to room temperature. The quantum yields of CL (ϕ_{CL}) were *ca.* 10^{-6}—10^{-7} einstein/mol relative to the luminol CL in aqueous solutions.[3)] The half life time ($\tau_{1/2}$) of CL were 8.2 s (*ca.* 0 °C) for **1b** and 5.1 s for **1c** at 10^{-4} mol/l for **1**. The CL's were so weak and the $\tau_{1/2}$ were so short that the emission spectra could not be measured, and hence, the emitters were not characterized and the ϕ_{CL} were estimated approximately, provided that the emitter would be the produced ketones or the fluorescer added into the solutions. Lechtken had reported a sensitized photooxidation of acetone azine and the CL of the photooxygenation product, which was assigned to be 3,3,6,6-tetramethyl-3,6-dihydro-1,2,4,5-dioxadiazine (**7**: R=R′=Me) from the NMR spectra of the irradiated solution.[4)] Talwar described similar photooxygenation of a several azines which could react through **7** (R=Ph, R′=H; R=Ph, R′=Me; R=R′=Ph).[5)]

Recently, Landis and Madoux claimed on Lechtken's report that the supposed peroxide was not a cyclic peroxide **7** but a linear peroxide polymer which was formed by a free-radical oxidation initiated by $^1O_2$.[6)]



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A cold photooxygenated solution in CD_2Cl_2 of **1b** was analyzed by ^{13}C-FT NMR at −78 °C: signals centered at δ 103.25 ppm (d, J_{C-P}=197.9 Hz) were assigned as the quart. C in the 6-membered peroxide (**2b**), which disappeared thoroughly upon warming up to room temperature in 5 min. In turn, signals of benzophenone (**5b**) and triphenylphosphine oxide (**6**) took place.

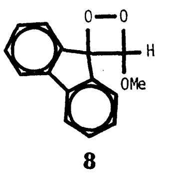
The spent solutions gave only two spots on TLC; the ketones (**5**) and triphenylphosphine oxide (**6**) almost quantitatively (GLC). These data suggest that the 6-membered peroxide (**2**) could be formed as an intermediate with the reaction of $^1O_2$ to **1** and the successive extrusion of N_2 from **2** resulted in the 4-membered peroxide (**4**) which gave the light emission.

Energy liberated on the decomposition of the supposed dioxaphosphetane (**4**) was calculated as *ca.* 66.1 kcal/mol[7)] which is not large enough for exciting some of the ketones (**5**) or **6** to the S_1 states (82.3 kcal/mol for **5a**; 68.9 for **5b**; 56.0 for **5c**; 68.8 for **5d**; 65.5 for **5e**; 65.3 kcal/mol for **6**). Therefore, additional energy (maybe the activation energy) is needed for excitation of **5a**—**b** and **5c** to the singlet state.

Methylene Blue, irradiation, and O_2 were essential for the present photooxygenation. On addition of

KO_2, **1** did not give **5** and/or **6**. Addition of $^{1}O_2$-quenchers[6] (β-carotene and 1,4-diazabicyclo[2.2.2]-octane (DABCO)) quenched the reaction. A radical scavenger (2,4,6-tri-*t*-butylphenol)[6] did not affect the reaction. These data suggest that the present photooxygenation reactions are non-radical ones initiated by $^{1}O_2$ and seems to support the Lechtken's mechanism rather than the Landis' one.

Apparently, the "dioxaphosphetane" derivatives, **4**, were the first chemiluminescent dioxetanes having one additional hetero atom instead of the carbon atom.[8]



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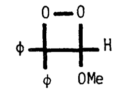

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Nearly all the dioxetanes studied so far give carbonyl products with lowest excited states of n,π^* configuration.[9] It is conceivable that a dioxetane giving excited carbonyls in which the excitation energy was more delocalized (in a π,π^* state) may be less stable and give relatively more singlet products (greater ϕ_{CL}). A switch from a stepwise mechanism of decomposition (*via* a short-lived diradical-like intermediate as is now generally accepted) to a concerted cleavage may then take place.[9]

Wilson *et al.*[10] compared dioxetanes (**8** and **9**), which produce fluorenone [**5c**: S_1 (π,π^*)] and benzophenone [**5b**: S_1 (n,π^*)] and found significant difference between them: *i.e.*, **8** has much smaller E_a (activation energy) and log A than **9** has. Moreover, **8** gives the singlet excited product, while **9** the triplet one. They suggested that the difference in the electronic configuration of the two ketones (π,π^* instead of n,π^*) allows a change of mechanism of dioxetane cleavage (from a two-step radical mechanism to perhaps a concerted cleavage).[10]

The present results on **1b** and **1c**, however, did not satisfy the expectation of the effect of the electronic configurations of the products on the chemiluminescence efficiency. This might be explained by the fact that **2** may give the radical intermediate (**3**) first, which decomposes directly to the products (**5** and **6**) or indirectly through the dioxaphosphetane (**4**). The direction of the decomposition is in a reverse order to the decomposition of the ordinary 1,2-dioxetanes.

Experimental

Instrumentation. All mp were uncorrected. Following spectrophotometers were used for spectral measurements: IR: JASCO IR-G and A-100; UV: Shimadzu UV-200; NMR JEOL JNM-MH-100 (100 MHz) and FX-100 (99 MHz for ^1H and 25.05 MHz for ^{13}C); MS: JEOL JMS-D-100; Fluorescence: Hitachi MPF-2A. The spectral data are presented as follows: IR in cm^{-1}; UV: in nm (ε given in parentheses); NMR: δ in ppm from int. TMS and J in Hz (accuracy ± 0.5 Hz); MS in m/z; fluorescence: $\lambda_{\max}$ in nm. GLC were carried out by Yanagimoto Yanaco G-80FP and G-180F.

Materials. Ketones (**5a**—**e**) and $Ph_3P{=}O$ (**6**) were purchased. (Arylmethylenehydrazono)triphenylphosphoranes (**1a**—**c**) were prepared according to the literatures. **1a**: Yellow-green granules, mp 141—142 °C (lit,[11] 141—142 °C); $\lambda_{\max}$ (KBr) 1435, 1100, 840 cm^{-1}; δ ($CDCl_3$) 7.42 (20H, m), 8.36 (1H, d); m/z 380 (M^+); UV: $\lambda_{\max}$ (CH_2Cl_2) 328 nm (ε 23000); FL: $\lambda_{\max}$ (CH_2Cl_2) 483 nm. **1b**: pale-yellow crystalline powder ($CHCl_3$), mp 167—174 °C (lit,[11] mp 173°); m/z 456 (M^+); UV: $\lambda_{\max}$ (CH_2Cl_2) 231 (ε 20400), 323 nm (9900). **1c**: yellow granules (EtOH), mp 208.5—210 °C (lit,[12] mp 209—210 °C); m/z 454 (M^+); UV: $\lambda_{\max}$ (CH_2Cl_2) 247 (ε 27400), 257 (14200), 294 (6900), 387 nm (10700).

*(9-Xanthenylidenehydrazono)triphenylphosphorane (**1d**)*: A solution of triphenylphosphine (3 g: 1.2×10^{-2} mol) in abs. benzene (50 ml) was cooled in an ice–salt bath under argon streams. Into the solution was added bromine (1 ml: *ca.* 1.0×10^{-2} mol) and then triethylamine (2 g: 2.0×10^{-2} mol). After the resulted solution was stood for a while at room temperature, 9-xanthenone hydrazone[13] (2.1 g: 1.0×10^{-2} mol) in abs. benzene (50 ml) was added and the mixture was stirred overnight at room temperature. After removing triethylamine·HBr with suction and evaporation of benzene gave a redish-brown oil, which resulted in crude crystals of **1d** after crystallization from $CHCl_3$, ether, and pet. ether at 0 °C. Orange-yellow granules, 0.9 g (19.1%). Main parts of the crystals were recrystallized from $CHCl_3$ and pet. ether, purified with Nylon-column chromatography (Woelm Silicagel: *ca.* 30 cm, ϕ 1.9 cm; CH_2Cl_2), and then recrystallized from EtOAc.

Yellow granules, mp 196—199 °C, Found: C, 78.88; H, 4.66%. Calcd for $C_{31}H_{23}N_2PO$: C, 79.14; H, 4.93%. m/z 470 (M^+); $\nu_{\max}$ (KBr) 1450, 1030, 900 cm^{-1}; δ ($CDCl_3$) 7.26 (m), 10.20 (d); UV: $\lambda_{\max}$ (CH_2Cl_2) 394 (ε 14000), 296 nm (ε 6400).

*(10-Methyl-9,10-dihydroacridin-9-ylidenehydrazono)triphenylphosphorane (**1e**)*: A solution of 9-(N'-formylhydrazono)-10-methyl-9,10-dihydroacridine[14] (0.7 g: 2.8×10^{-3} mol) in 15% $HClO_4$ (12 ml) was heated at 100 °C for 2 min and then cooled to room temperature. The resulted perchlorate was collected and recrystallized from EtOH containing a few drop of $HClO_4$ to give dark-tan needles, mp>300 °C. Yield 0.51 g (56.7%). $\nu_{\max}$ (KBr) 1590, 1465, 760 cm^{-1}; δ (DMSO-d_6) 7.82 (d), 7.40 (m), 3.94 (s). This was used immediately for the following preparation.

To a solution of the perchlorate (565 mg: 1.75×10^{-3} mol) and KOH (1.2 g: 2.1×10^{-2} mol) in EtOH (100 ml) was added HgO (red: 0.4 g: 1.85×10^{-3} mol) and the mixture was stirred overnight at room temperature under argon streams. To the filtrate of the mixture was added a solution of Ph_3P (0.46 g: 1.76×10^{-3} mol) saturated in ether under argon streams and the resulted mixture was stirred overnight at room temperature. After evaporation, the mixture was chromatographed on silica gel (Woelm: 30 cm, ϕ 1.9 cm; CH_2Cl_2). Reddish-brown needles, mp $\approx$189 °C: Yield, 75.4 mg (19.5%). Found; C, 79.66; H, 5.30%. Calcd for $C_{32}H_{26}N_3P$: C, 79.485; H, 5.420%. m/z 277 (M^+ −206); $\nu_{\max}$ (KBr) 1595, 1360, 1180, 740 cm^{-1}; δ ($CDCl_3$) 8.62 (d), 7.56 (m), 3.80 (s); UV: $\lambda_{\max}$ (CH_2Cl_2) 400 (ε 16000), 382 (12000), 306 (4700), 293 nm (7400).

*Sensitized Photooxygenation of **1a**—**e**.* A solution of **1** (10^{-3}—10^{-2} mol/l) in CH_2Cl_2 (dried over CaH_2: 5 ml) containing Methylene Blue (10^{-4}—10^{-3} mol/l) was irradiated in a Pyrex cell (ϕ 10 mm) or a quartz cell (ϕ 10 mm) at −78 °C with bubbling O_2 with a 300 W tungsten-halogen lamp (Kondo/Sylvania Projector lamp; ELH 120 V/300 W at 100 V) through a yellow optical filter (Toshiba

Table 1. Photooxygenation of **1** and the CL

1	**5**(%)	**6**(%)	Φ_{CL} (einstein/mol)[a]	τ_{CL} (*ca.* 0 °C)
a:	89	89	3.0×10^{-6}	
b:	75	g.y.[b]	3.1×10^{-6}	8.2 s
c:	91	75	4.5×10^{-6}	5.1 s
d:	100	67	7.5×10^{-7}	
e:	85	86	4.1×10^{-6}	

a) Relative to the CL of luminol (Ref. 3). b) Quantitative yield.

Table 2. Effect of inhibitors on photooxygenation of **1**

Inhibitor(In)	[In]/[**1**]	**1a**	**1b**	**1c**	**1d**
DACCO	25	Q[a]	Q	Q	Q
β-Carotene	5	Q	Q	Q	Q
2,4,6-Tri-*t*-butylphenol	25	N[b]	N	N	N

a) Q: Quenched. b) N: Not effected.

O-52: <510 nm cut off) for 60 min.

Chemiluminescence with/without Fluorescer. The irradiated solutions as above were warmed up to room temperature with/without fluoresceres (9,10-dibromo- and 9,10-diphenylanthracene, or rubrene: 10 mmol/l) in the cell chamber of MPF-2A and the light emitted was recorded. The quantum yields are shown in Table 1.

*^{13}C-NMR of the Irradiated Solution of **1b** in CD_2Cl_2.* CD_2Cl_2 Solution irradiated as above in a Pyrex NMR tube was analysed by ^{13}C-FTNMR at −78 °C. δ (TMS) 103.25 (d, J=197.9) at −78 °C, disappeared when warmed-up to room temperature for 5 min.

Product Analyses. The spent solutions of the irradiated samples were analysed by GLC and TLC: only two spots on TLC were appeared and identified as the ketones and Ph_3PO, which were estimated by GLC as shown in Table 1.

Effect of Inhibitors on CL. Inhibitors were added into the solutions and the effect on the photochemical reactions and the CL was estimated (Table 2).

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