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PHOSPHA-1,2-DIOXETANES: POSSIBLE CHEMILUMINESCENT INTERMEDIATES OF PHOTOOXYGENATION OF BENZOPHENONE AND FLUORENONE TRIPHENYLPHOSPHAZINES

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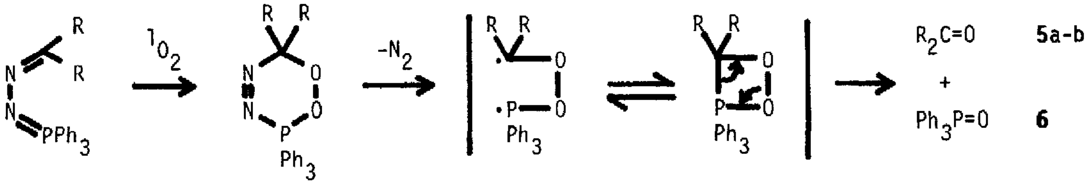
Photosensitized oxygenation of benzophenone and fluorenone triphenylphosphazines (**1a-b**) at -78 °C gave the corresponding ketones (**5a-b**) and triphenylphosphine oxide (**6**) and also gave light emission when warmed up to room temperature.

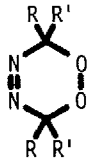
Sensitized photooxygenation of benzophenone and fluorenone triphenylphosphazines (**1a-b**), could give 3-phospha-1,2-dioxa-4,5-diazines (**2a-b**) as intermediates, which could liberate nitrogen molecule and chemiluminesce to give the corresponding ketones (**5a-b**) and triphenylphosphine oxide (**6**) as the final products through phospha-1,2-dioxetanes (**4**).



1a-b **2a-b** **3** **4a-b**

a: R=Ph **b**: R + R=

Lechtken had reported sensitized photooxidation of acetonazine and the chemiluminescence (CL) of the product, which was assigned to be tetramethyl-1,2-dioxa-4,5-diazine (**7**: R=R'=Me) from the NMR of the solution.$^{1)}$ Talwar described similar photooxygenation of a several azines which could react through **7** (R=Ph, R'=H; R=Ph, R'=Me; and R=R'=Ph).$^{2)}$ Recently Landis and Madoux claimed on Lechtken's literature 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 $^1O_2$.$^{3)}$ We now report the photo-sensitized oxygenation of **1** and the CL of the products.



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A solution of the phosphazine,$^{4,5)}$ **1** (10^{-3} – 10^{-2} mol/l) in CH_2Cl_2(dried over CaH_2) with methylene blue (10^{-4} – 10^{-3} mol/l) was irradiated at -78 °C with bubbling O_2 with a 300 W tungsten-halogen lamp (Sylvania Projector lamp; ELH 120 V/300 W at 100 V) through a yellow filter (Toshiba 0-52: < 510 nm cut off) for 5 min. The irradiated solution gave pale-blue light emission when warmed up to room temperature (quantum yield of CL (Φ_{CL}) = 3.1×10^{-6} and the half life ($\tau_{1/2}$) = 8.2 sec (ca. 0 °C) for **1a** and 7.0×10^{-7}, 5.1 sec for **1b** at 10^{-4} mol/l for **1**). As the quantum yield of fluorescence, for benzophenone (**5a**) was found as 4 x 10^{-6} on literature,6) a main part of the excited states produced on the decomposition of the peroxide (2 or 4) is supposed to be singlet (S_1). Addition of 9,10-dibromoanthracene did not affect the quantum yields. The spent solution gave only two spots on tlc; the ketones (**5a-b**) (75% and 100% yields on glc) and triphenylphosphine oxide (**6**; q.y.). These data suggest that the 4-membered peroxide, a phospha-1,2-dioxetane, **4**, could be formed as an intermediate with the reaction of $^1O_2$ and give the light emission. Energy liberated on the decomposition of the phosphadioxetane (**4**) was calculated as ca. 53.6 Kcal/mol7) which is not large enough for exciting the ketones to the S_1 states (**5a** and **b**: 75.4 and 63.2 Kcal/mol,6) resp.). Therefore, additional energy (maybe the activation energy) is needed for excitation to the singlet state.

Without methylene blue no reaction occurred on irradiation. Without irradiation with flushing oxygen **1** did not give any reactions either. On addition of KO_2 the phosphazine 1 did not give **5** and **6**. Added $^1O_2$-quenchers3) (β-carotene and DABCO) quenched the photooxygenation. 2,4,6-Tri-t-butylphenol3) did not affect the reaction. These data suggest that the present reactions are non-radical ones initiated by $^1O_2$.

From the UV data5,11) and the present 1,4-cycloaddition of $^1O_2$, phosphazine (1) may possess a 1,3-diene structure rather than a $\overset{+}{N}-\overset{-}{P}$ ylide. Apparently this phosphadioxetane derivatives, **4**, are the first chemiluminescent dioxetanes having one more hetero atom instead of the carbon atom.

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References and Footnotes

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5) **1a**: pale yellow crystalline powder ($CHCl_3$), mp 167-174° (lit4) mp 173°); m/z 456 (M^+); λ_{max} (CH_2Cl_2) 231 nm (ε20400), 323 (9900). **1b**: yellow granules (EtOH), mp 208.5-210° (lit4) mp 209-210°), m/z 454 (M^+), λ_{max} (CH_2Cl_2) 247 nm (ε27400), 257 (14200), 294 (6900), 387 (10700); m/z 454 (M^+).
6) S. L. Murov, Handbook of Photochemistry, Dekker, New York, N. Y., 1973, p. 3-4.
7) Heat of decomposition (ΔH) of **4** to a C=O and a P=O compounds was caluculated as follows assuming that the ring strain of **4** is not much different from that of ordinary 1,2-dioxetanes (26 Kcal/mol)10); $\overline{\text{C-C-O-O}} \longrightarrow \text{C=O + C=O}$; $\overline{\text{C-P-O-O}} \longrightarrow \text{C=O + P=O}$: a) 1 C-C $\rightsquigarrow$ 1 C-P (ΔHa), b) 1 C-O $\rightsquigarrow$ 1 P-O (ΔHb), c) 1 C=O $\rightsquigarrow$ 1 P=O (ΔHc), where ΔHa = 58.68) − 659) = -6.4; ΔHb = 70.08) − 869) = -16.0; and ΔHc = 152.08) − 1289) = +24; therefore, ΔH' = -(ΔHa + ΔHb) + ΔHc = +46.4 (Kcal/mol); and ΔH = ΔH (Dioxetane)10) − ΔH' = -(ca.100 − 46.4) = ca. -53.6 Kcal/mol.
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11) cf. Benzophenonazine, $Ph_2C=N-N=CPh_2$, mp 166.5-167.5° (lit.12) mp 163-163.5°); λ_{max} (CH_2Cl_2) 235 nm (ε26400), 282 (21200), 314 (19200).
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