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PHOTOSENSITISED OXYGENATION OF (ARYLIDENEHYDRAZONO)-TRIPHENYLPHOSPHORANES AND CHEMILUMINESCENT INTERMEDIATES

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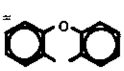
Sensitised photooxygenation of (arylidenehydrazono)-triphenylphosphoranes (**1**a-d) could give 3-phospha-1,2-dioxa-4,5-diazines (**2**a-d) as intermediates, which could liberate nitrogen molecule and chemiluminesce (CL) to give the corresponding ketones (**5**a-d) and triphenylphosphine oxide (**6**) as the final products through phospha-1,2-dioxetanes (**4**). We report here the photo-sensitised oxygenation of **1** and the CL of the products.

A solution of **1** (10^{-3}-10^{-2}mol/l) in CH_2Cl_2 (dried over CaH_2) with methylene blue (MB: 10^{-4}-10^{-3} mol/l) was irradiated at -78°C with bubbling O_2 with a 300W tungsten-halogen lamp through a yellow filter (<510 nm cut off) for 5 min. The irradiated solution gave pale-blue light emission when warmed up to room temp. Addition of 9,10-dibromo- or diphenyl-anthracene or rubrene did not affect the quantum yields. The spent solution gave only two spots on tlc; the ketones (**5**) and **6** (see Table). These data suggest that the 4-membered peroxide, **4**, could be formed as an intermediate with the reaction of $^1O_2$ and give the light emission. Energy liberated on the decomposition of **4** was calculated as ca. 54 Kcal/mol which is not large enowgh for exciting the ketones or phosphine oxide to the S_1 states (77.1, 75.4, 63.2, and 77.6 for **5**a-d, 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 O_2 **1** did not give any reactions either. On addition of KO_2 **1** did not give **5** and **6**. Added $^1O_2$-quenchers (β-carotene and DABCO) quenched the photooxygenation. 2,4,6-Tri-t-butylphenol, a radical scavenger, did not affect the reaction. These data suggest that the present reactions are non-radical ones initiated by $^1O_2$.

Photooxygenation of Aryl ketone Phosphazines (**1**)

1	C=O (**5**)(%)	P=O (**6**)(%)	Φ_{CL}	τ_{CL}(ca. 0°)
a: R = **Ph**, R'= **H**	99	65	3.0×10^{-6}	
b: R = R'=**Ph**	75	q.y.	3.1×10^{-6}	8.2 sec
c: R + R'= 	100	q.y.	7.5×10^{-7}	5 1 sec
d: R + R'= 	100	67	7.5×10^{-7}	