Tetrahedron Letters,Vol.26,No.7,pp 843-846,1985
Printed in Great Britain

0040-4039/85 $3.00 + .00

REACTION OF SINGLET OXYGEN WITH INDANONE PHOSPHAZINE: FORMATION OF KETONE AND LACTONE

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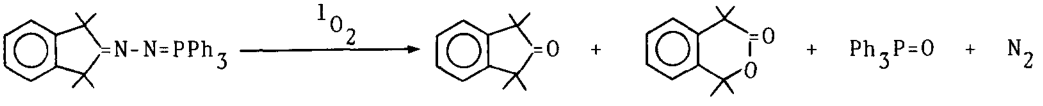
Summary: Photooxygenation of 1,1,3,3-tetramethyl-2-indanone triphenylphosphazine afforded, in addition to the parent indanone and triphenylphosphine oxide, 2,2,5,5-tetramethyl-3,4-benzo-3-penten-5-olide from a carbonyl oxide intermediate and also gave light emission.

Despite that extensive studies have been focused on the reaction of singlet oxygen with conjugated dienes,1) only little attention has been drawn to the photooxygenation of azines and phosphazines in connection with chemiluminescence system.2-5) Two types of photooxygenation of azines and phosphazines are revealed. Lechtken reported formation of acetone from direct decomposition of 1,2-dioxa-4,5-diazine formed by photooxygenation of acetone azine and observed the chemiluminescence of the products.2) Suzuki et al. also described similar type of photooxygenation of benzophenone and fluorenone triphenylphosphazines, which undergoes via formation of 3-phospha-1,2-dioxa-4,5-diazine as an intermediate, and the chemiluminescence of the products.3) Meanwhile, Landis's proposed mechanism in photooxygenation of acetone azine involves formation of acetone from a free-radical pathway initiated by singlet oxygen to give a linear peroxide polymer.4) Recently, we have found that photooxygenation of adamantanone azine gave not only the parent ketone but also the lactone via formation of a carbonyl oxide intermediate under elimination of diazo adamantane followed by cyclization to a dioxirane intermediate.5) We now report the photooxygenation of 1,1,3,3-tetramethyl-2-indanone triphenylphosphazine (1)6) to form a carbonyl oxide intermediate and chemiluminescence via a zwitterion intermediate.

A 50 ml of methylene chloride solution of phosphazine 1 (6 x 10^{-2} M) with methylene blue (6 x 10^{-3} M) as a sensitizer was irradiated at 15°C for 16 hrs with bubbling oxygen with two 500W halogen lamps. When the reaction mixture was chromatographed on silica gel, three major products were isolated.

1,1,3,3-Tetramethyl-2-indanone (2) and triphenylphosphine oxide were obtained in 68% and 99% yields, respectively. The third was 2,2,5,5-tetramethyl-3,4-benzo-3-penten-5-olide (3, 9%).[7] When a solution of 1 (1 x 10^{-2} M) in methylene chloride (sensitizer; methylene blue and polymer-bound rose bengal) was photooxygenated at -78°C for 3 hrs and warmed to room temperature, the irradiated solution gave pale-blue light emission. Since addition of 9,10-diphenylanthracene enhanced the light emission, a main part of the excited states is supposed to be singlet.[3]



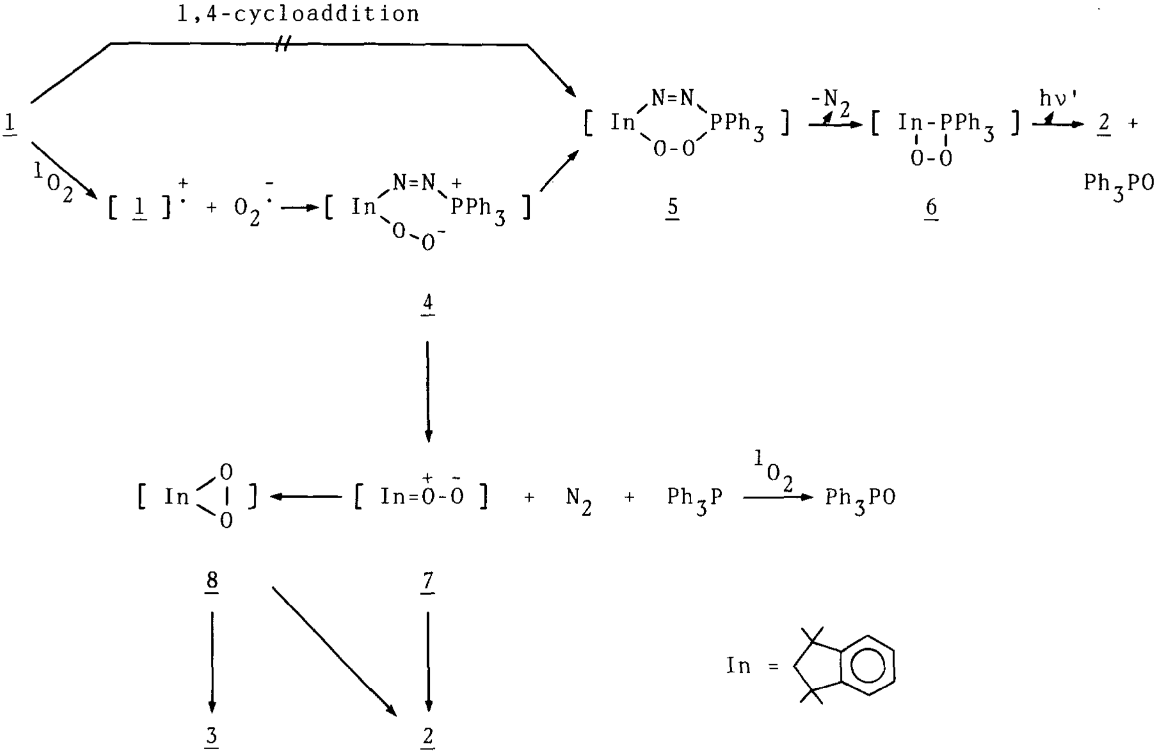
1 2 3

Control experiments show that phosphazine 1 is stable under the reaction conditions in the absence of the sensitizer or light. The product ratios of ketone 2 : lactone 3 are moderately independent of the solvent and the sensitizer used ($CDCl_3$/MB, CD_3CN/MB, C_6D_6/TPP, and CD_3COCD_3/RB).[4,8] The photooxygenation of 1 was inhibited by DABCO, a singlet oxygen quencher,[9] but unaffected by triphenylmethane, a free-radical scavenger.[10] Furthermore, addition of p-dimethoxybenzene as an electron transfer quencher[11] suppressed the oxidation of 1. These data might suggest that the present reaction is not a radical-chain one initiated by singlet oxygen.[4] One plausible rationale for these observations seems that the oxidation would involve an electron transfer step from phosphazine 1 to singlet oxygen, generating a cation radical and superoxide anion radical.[4,5] Subsequent recombination of these ion radicals may produce a peroxy anion intermediate 4[12] followed by cyclization of 3-phospha-1,2-dioxa-4,5-diazine intermediate 5, which could liberate nitrogen and chemiluminesce to give indanone 2 and triphenylphosphine oxide as the final products through phospha-1,2-dioxetane intermediate 6 proposed by Suzuki et al.[3,13] This mechanism seems to be true since phosphazine 1 cannot possess a cisoid-form by steric hindrance and therefore is not able to undergo 1,4-cycloaddition with singlet oxygen to form 5.[1,3] The formation of lactone 3 might be explained as follows. A peroxy anion intermediate 4 produces carbonyl oxide 7 and triphenylphosphine liberating nitrogen. Carbonyl oxide 7 can cyclize to a dioxirane intermediate 8 followed by rearrangement to lactone 3 similar to the case of adamantanone azine.[5] Triphenylphosine can be oxidized to the corresponding oxide with singlet oxygen[14] as shown in Scheme.

To test these possibilities, the following experiments have been done. In order to trap the nucleophilic intermediate, 4 or 7, the photooxygenation of 1 was carried out in the presence of methyl phenyl sulfoxide as a nucleophilic-oxygen atom acceptor.[15)] Almost complete inhibition of the lactone formation (3; 1%) was observed by accompaning with formation of methyl phenyl sulfone (13%). A Baeyer-Villiger type oxidation of indanone 2 by the intermediate, 4 or 7, might be ruled out by the evidence that addition of excess amounts of indanone 2 did not alter the yield of lactone 3.

Thus, new type of photooxygenation of phosphazine 1 afforded a zwitterion intermediate 4 followed by either formation of carbonyl oxide 7 or phospha-dioxadiazine 5 which decomposes to chemiluminesce through phosphadioxetane 6.

Scheme



References and Notes:

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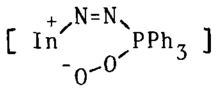
2) Lechtken, P., Z. Naturforsch. B: Anorg. Chem., Org. Chem., 1976, 31, 1436.
3) Suzuki, N.; Wakatsuki, S.; Izawa, Y., Tetrahedron Lett., 1980, 21, 2313.
4) Landis, M. E.; Madoux, D. C., J. Am. Chem. Soc., 1979, 101, 5106.
5) Ando, W.; Sato, R.; Sonobe, H.; Akasaka, T., Tetrahedron Lett., 1984, 25, 853.
6) Cullen, E. R.; Guziec, Jr., F. S.; Hollander, M. I.; Murphy, C.J., ibid., 1981, 22, 4563; oxidation potential (E_p vs. SCE; 0.1M Bu_4NClO_4/CH_3CN) of 1 is +0.77 V.
7) 3; m/e 204(M^+); IR(CCl_4) ν 1710 cm^{-1}; NMR(CCl_4) δ 7.20-7.77(m,4H), 1.73 (s,6H), 1.60(s,6H) ppm.
8) MB; methylene blue, TPP; tetraphenylporphine, RB; rose bengal.
9) Foote, C. S.; Peterson, E. R.; Lee, K. -W., J. Am. Chem. Soc., 1972, 94, 1032.
10) Russell, G. A., ibid., 1956, 78, 1047.
11) Eriksen, J.; Foote, C. S., ibid., 1980, 102, 6083.
12) It may be considered that an alternative route for recombination of ion radicals involves another peroxy anion intermediate 9 followed by formation of perphosphine oxide 10[14] and diazo indane 11.[6] This pathway, however, could be ruled out by the evidence that the photooxygenation[16] of diazo indane 11[17] under the same condition did not afford lactone 3 at all (indanone 2; 24%, 1,2,3,3-tetramethylindene[18]; 36%).



9

$[\ Ph_3P=\overset{+}{O}-\overset{-}{O}\ ]$

10

$In=N_2$

11

13) Recently, we have succeeded to observe both intermediates, 5 and 6, at low temperature by high-field ^{31}P-NMR spectroscopy. Details will be reported elsewhere.
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17) IR(CCl_4) ν 2000 cm^{-1}; ref. 6.
18) m/e 172(M^+); NMR(CCl_4) δ 7.04-7.30(m,4H), 2.01(s,3H), 1.85(s,3H), 1.17 (s,6H) ppm.

(Received in Japan 4 October 1984)