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REACTION OF SINGLET OXYGEN WITH AZINES: IMPLICATIONS FOR DIOXIRANE INTERMEDIATE

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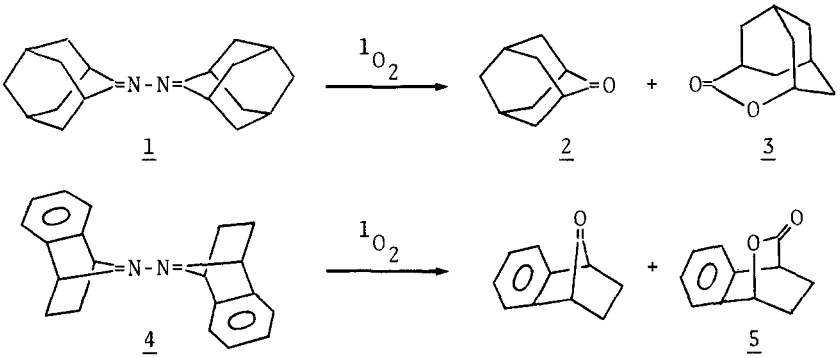
Summary: Photooxygenation of tricyclo[3.3.1.1]decanone azine (adamantanone azine) afforded, in addition to adamantanone, 4-oxahomoadamantan-5-one derived from a dioxirane intermediate via a non-radical pathway.

The reaction of singlet oxygen with conjugated dienes has been extensively studied,1) but relatively few studies have been devoted in which azines are oxidized.2,3) The oxidation of azines may have some significances in connection with bioluminescence system.4) Two types of photooxygenation are revealed. One of these is ketone formation from direct decomposition of 1,2-dioxa-4,5-diazine formed by a concerted 1,4-cycloaddition of singlet oxygen to acetone azine2) and the other is that from a free-radical pathway initiated by singlet oxygen.3)

We now report that the photooxygenation of several cyclic azines gave not only ketones but also lactones via a new type of singlet oxygen reaction.

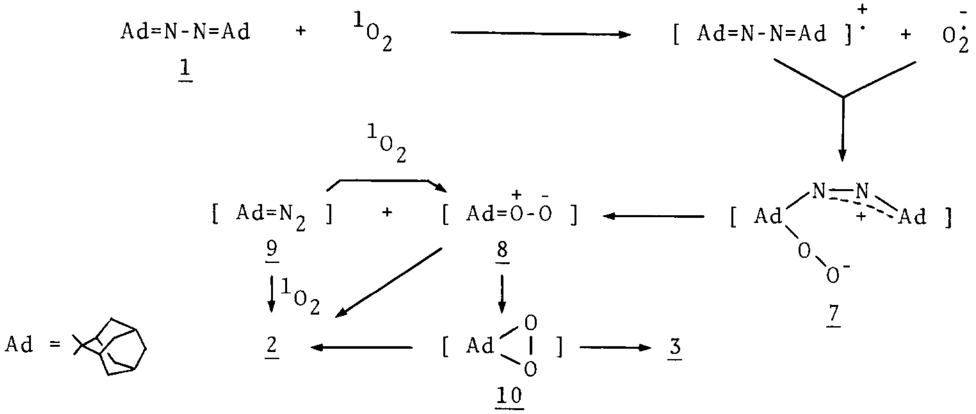
The photooxygenation of tricyclo[3.3.1.1]decanone azine5) (adamantanone azine, 1, 0.1M) was carried out at 15°C for 5 hrs in methylene chloride with methylene blue (1.7×10^{-2}M) as a sensitizer and use of two 500W halogen lamps. When the reaction mixture was chromatographed on silica gel, two major products were isolated. The first was adamantanone 2 (113%). The other (40%) has mp 286-289°C [m.e 166(M^+); IR(CCl_4) ν 2925, 2850, 1725, 1175 cm^{-1}; ^{1}H-NMR(60MHz,CCl_4) δ 4.42(m,1H), 2.29(m,1H), 1.63-2.27 ppm (m,12H)]. These data are consistent with the structure of 4-oxahomoadamantan-5-one 3.6)

Very similar results were obtained with benzonorbornone azine 4. The photooxygenation followed by column chromatography led to the isolation of lactone 5[7] (9%) in addition to benzonorbornone (135%). The photooxygenation of cyclopentanone azine 6 and cyclohexanone azine gave several products involving the corresponding ketone as a major product and a trace amount of lactone and α-chloroketone.



Control experiments show that 1 is stable under the reaction conditions in the absence of the sensitizer and the ratios of ketone 2 : lactone 3 are moderately independent of solvent (CH_2Cl_2, C_6H_6, CH_3CN/CH_2Cl_2) and sensitizer (methylene blue, tetraphenylporphyrin).[3] The photooxygenation of 1 was inhibited by 0.3 eq of DABCO, a singlet oxygen quencher,[8] but relatively unaffected by 0.1 eq of triphenylmethane, a free-radical scavenger.[9] Furthermore, addition of 1 eq of p-dimethoxybenzene as an electron transfer quencher[10] suppressed the oxygenation of 1. One plausible rationale for these observations seems that the oxidation would involve an electron transfer step from azine to singlet oxygen,[3] generating azine cation radical and superoxide anion radical. Subsequent recombination of these ion radicals may produce a peroxy anion intermediate 7 followed by the formation of a carbonyl oxide intermediate 8[11] and diazo adamantane 9 as shown in Scheme. The carbonyl oxide 8 may cyclize to a dioxirane intermediate 10 followed by rearrangement to lactone 3[12,13] and adamantanone 2 can be produced either from the decomposition of carbonyl oxide 8 and/or dioxirane 10 or the oxidation of diazo adamantane 9.[14] To test these possibilities, the following experiments have been done. In

Scheme



order to trap the intermediate 7 or 8, the photooxygenation of 1 was carried out in the presence of 10 eq of methyl phenyl sulfoxide which had been demonstrated as a nucleophilic-oxygen acceptor.15) Almost complete inhibition of the lactone formation was observed by accompaning with a formation of methyl phenyl sulfone (40% yield based on azine). A Baeyer-Villiger type oxidation of adamantanone by the intermediate 7 or 8 might be ruled out by the evidence that the addition of 10 eq of adamantanone did not alter the yield of lactone 3. Further, in the presence of benzaldehyde diazo adamantane 9 was trapped as adamantyl benzoate 11 16) by trace amount of benzoic acid generated during the reaction.

The yields of lactones may have some relations with their oxidation potentials17) or conformations, and the free-radical path may become important for the case of azines which have higher oxidation potentials.

References and Notes

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7) 5: m/e 174(M$^+$); IR(NaCl) ν 1745 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 7.39-7.55(m,4H), 5.74(m,4H), 4.02(m,1H), 1.60-2.20 ppm (m,4H).

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11) Another possibility for a direct formation of dioxirane 10 would be ruled out since intramolecular substitution on the intermediate 7 to afford 10 seems to be sterically quite hard.

12) The similar rearrangement of a dioxirane intermediate in gas phase has been reported for the ozonolysis of olefins and the reaction of CH$_2$: with oxygen; (a) Suenram, R. D.; Lovas, F. J., J. Am. Chem. Soc., 1978, 100, 5117; (b) Martinez, R. I.; Huie, R. E.; Herron, J. T., Chem. Phys. Lett., 1977, 51, 457; (C) Martinez, R. I.; Huie, R. E.; Herron, J. T., J. Chem. Phys., 1981, 75, 5975.

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16) 11: m/e 256(M$^+$); IR(CCl$_4$) ν 2940, 2920, 2860, 1720, 1280, 1275, 1115 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 8.18(m,2H), 7.57(m,3H), 5.25(m,1H), 1.44-2.40 ppm (m,14H).

17) Oxidation potentials (E_p vs. SCE (V)) are +1.47, +1.67 and +1.76 for 1, 4 and 6, respectively. Oxidation potentials were measured by means of cyclic voltammogram in acetonitrile containing 0.1 N (n-Bu)$_4$NClO$_4$ as an electrolyte.

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