Tetrahedron Vol. 42, No 19, pp. 5273 to 5280, 1986
Printed in Great Britain.

0040-4020/86 $5.00+.00
Pergamon Journals Ltd.

SINGLET OXYGEN AND TRIAZOLINEDIONE ADDITION TO AZINES

RIKIYA SATO, HIDEKI SONOBE, TAKESHI AKASAKA, AND WATARU ANDO*

Department of Chemistry, University of Tsukuba,

Sakura-mura, Ibaraki 305, Japan

(*Received in Japan* 27 *May* 1986)

Abstract: Photooxygenation of azines, i.e., adamantanone azine (1) and benzonorborn-7-one azine (4), afforded in addition to the corresponding ketones, lactones derived from a carbonyl oxide intermediate via an electron transfer pathway. On the other hand, 4-substituted-1,2,4-triazoline-3,5-diones (TAD) react with azine 1 to give a 1,3-dipole, an azomethinimine intermediate as nitrogen analogue of a carbonyl oxide, which afforded the [2+3]-cycloadducts in treatment with dipolarophiles. The mechanistic implications are discussed.

Introduction

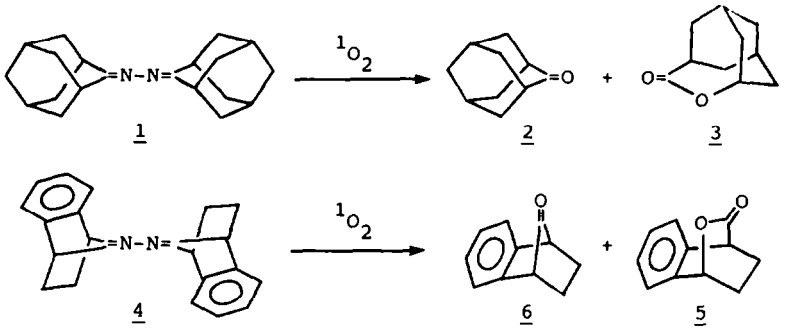
The reaction of singlet oxygen with conjugated dienes has been extensively studied and the simplest view of this reaction as a concerted [2+4]-cycloaddition is widely accepted,[1] but relatively few studies have been devoted in which azines are oxidized.[2,3] The photooxygenation of azines may have some significances in connection with chemiluminescence systems. Two types of photooxygenation of azines are revealed. Lechtken reported formation of acetone from direct decomposition of 1,2-dioxa-4,5-diazine formed by a concerted 1,4-cycloaddition of singlet oxygen to acetone azine and observed the chemiluminescence of the products.[2] Meanwhile, the Landis's proposed mechanism in photooxygenation of acetone azine involves the formation of acetone from a free-radical pathway initiated by singlet oxygen involving a linear peroxide polymer.[3] On the other hand, 4-substituted-1,2,4-triazoline-3,5-diones (TAD) exibit a wide range of reactivity and reaction types analogous to some of singlet oxygen reactions.[4-6] As reported in preliminary communications, we found that photooxygenation of cyclic azines gave not only the parent ketones but also lactones via a carbonyl oxide intermediate, formed by the elimination of a diazo compound, followed by cyclization to a dioxirane intermediate.[7] Attempted TAD addition to azines proceeded via preferential formation of a 1,3-dipole, an azomethinimine intermediate.[8] We have obtained some results that provide new insight on the nature of intermediates and on the course of these reactions.

Results and Discussion

Singlet Oxygen Addition to Azines

In a typical experiment, photooxygenation of tricyclo[3.3.1.1]decanone azine (adamantanone azine, 1) was carried out at 15°C for 5 h in methylene chloride with methylene blue (MB) as a sensitizer and use of two 500W halogen lamps. When the reaction mixture was chromatographed on silica gel, two major products were isolated, i.e., adamantanone (2, 113%) and 4-oxahomoadamantane-5-one (3,

40%).[9] Very similar results were obtained with benzonorborn-7-one azine (4) under the same condition. The photooxygenation followed by column chromatography led to the isolation of the corresponding lactone (5) in addition to the parent ketone (6).



Several mechanisms have been suggested for the ketone and lactone formations.[2,3] The principal findings of the present study are as follows: a) Control experiments show that 1 is stable under the reaction conditions in the absence of the sensitizer or light. b) The ratios of ketone 2 : lactone 3 are moderately independent of solvents and sensitizer used as shown in Table 1. The similarity of the ratios of lactone vs. ketone in solvents capable of halogen chain reaction (run 1,3,4) and in that incapable of such reactions (run 2) indicates that a radical chain reaction initiated by a halogen atom could be ruled out.[3] c) The photooxygenation of 1 was inhibited by 0.3 eq of 1,4-diazabicyclo[2.2.2]octane (DABCO), a singlet oxygen quencher,[10] but relatively unaffected by 0.1 eq of triphenylmethane, a free-radical scavenger[11] (Table 2). d) In the presence of p-dimethoxybenzene as an electron transfer quencher,[12] the oxidation is very slow. These findings point to a reaction mechanism which is not a radical chain one initiated by singlet oxygen.[3]

One plausible rationale for these observations is closely related to that proposed by Landis for photooxygenation of acetone azine to acetone.[3] The analogous step here would be an electron transfer one from 1 to singlet oxygen generating the azine cation radical and superoxide anion radical. Subsequent recombination of these ion radicals would be expected to produce a peroxy anion 7

Table 1. Effect of Solvents on Photooxygenation of 1.

Run No.	Conditions[a]	Products and Yields(%)[b] ketone	lactone	lactone / ketone
1	CH_2Cl_2/MB	113	40	0.35
2	C_6H_6/TPP	88	21	0.24
3	CH_3CN-CH_2Cl_2/MB (2 : 1)	98	33	0.34
4	CH_3CN-CH_2Cl_2/MB (25 : 1)	98	24	0.24

a) Irradiated under an oxygen flow for 5-28 h (0.1 M azine and 1.7×10^{-2}M sensitizer); MB, methylene blue; TPP, tetraphenylporphine.
b) Determined by GLC.

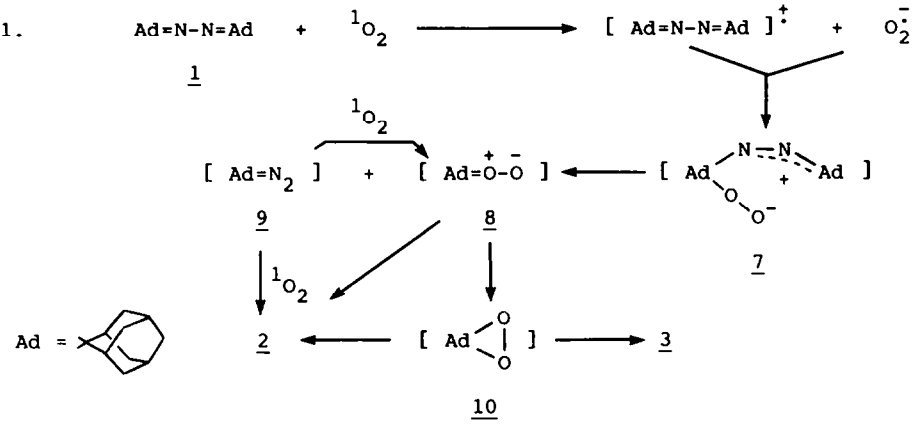
which gives carbonyl oxide 8 with elimination of diazo adamantane 9 as shown in Scheme 1. Dioxirane 10 with implication of the lactone[13,14] and ketone[15] formations may arise from the cyclization of 8.

Table 2. Effect of Additives on Photooxygenation of 1.

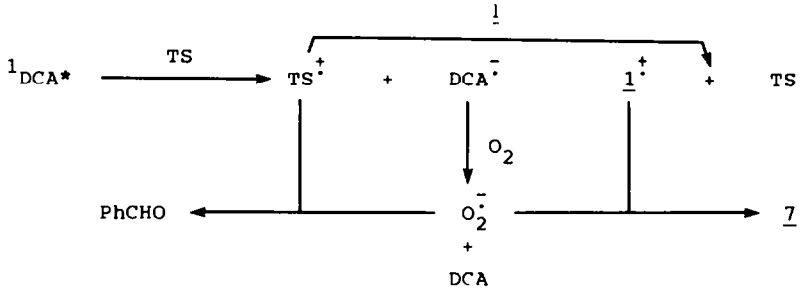
Additives	Products and Yields(%)[a]		Recovered 1 (%)[b]
	ketone	lactone	
DABCO (0.3eq)	4	none	90
Ph_3CH (0.1eq)	86	16	30
MeO-⟨⟩-OMe (3eq)	5	3	90

a) Yields were determined by GLC. b) Isolated yields.

Scheme 1.

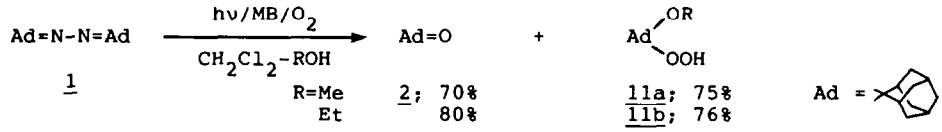


To test these possibilities, the following experiments have been done. 9,10-Dicyanoanthracene (DCA) sensitized oxygenation of 1 in the presence of an excess of trans-stilbene (TS) as a cosensitizer[16] afforded 2 and 3 in 110% and 30% yields, respectively, as was the case of singlet oxygenation. No reaction took place in the absence of the cosensitizer. The observation that TS has a large effect may be ascribed to the oxidation mediated by an electron transfer step.

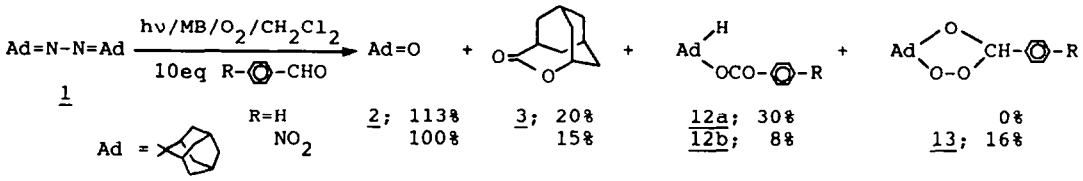


The trapping of the intermediate, 7 or 8, was carried out in the presence of 10 eq of methyl phenyl sulfoxide as a nucleophilic-oxygen atom acceptor.[17] Almost complete inhibition of the lactone formation was observed by accompaning with formation of methyl phenyl sulfone (40% yield based on 1). Addition of 10 eq of

2 did not accelerate the formation of 3 suggesting that a Baeyer-Villiger type of oxidation of adamantanone by the intermediate 7 or 8 might be ruled out. In the presence of alcohols, carbonyl oxide 8 was efficiently trapped to give hydroperoxide 11.[18]



In the presence of p-nitrobenzaldehyde, carbonyl oxide 8 was successfully converted to secondary ozonide 13 accompanied with adamantyl p-nitrobenzoate (12b).[19] It was also found that adamantyl benzoate (12a) was formed in the presence of benzaldehyde suggesting the formation of diazo adamantane (9) during the reaction.[20] These trapping experiments clearly suggest the formation of carbonyl oxide 8 in the singlet oxygenation of azine 1.



Although several routes are suggested for the carbonyl oxide formation, the results on the yields of 2 and 11 could realize direct formation of carbonyl oxide 8 from intermediate 7 but not from singlet oxygenation of 9. It is well known that photooxygenation of diazo compounds produces a carbonyl oxide with elimination of nitrogen or a ketone with that of nitrogen monooxide.[21] In a detailed product analysis by means of mass spectroscopy , evolution of nitrogen monooxide was confirmed . This means that 9 was oxygenated to 2 by singlet oxygen accompanied with loss of nitrogen monooxide.[22]

Dioxirane 10 formed by cyclization of carbonyl oxide 8 seems to be electrophilic.[23] In the presence of TS and norbornylene, the corresponding epoxides were obtained in 20% and 13% yields, respectively. One notes that electrophilic 10 can transfer one oxygen atom to olefins.

Our preference for Scheme 1 is based on these observations for trapping and quenching reactions.

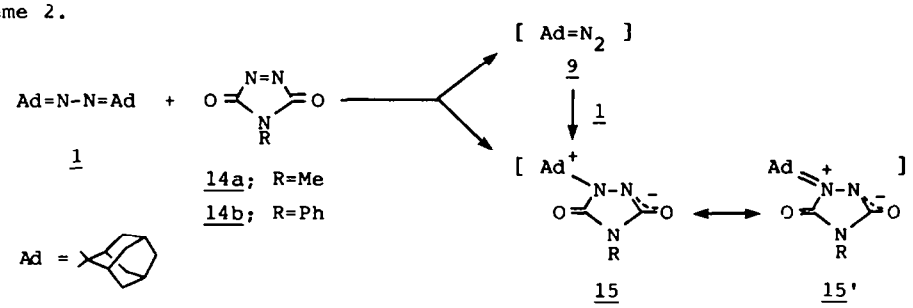
The results of singlet oxygenation have prompted us to investigate the reactivity of azines toward TAD.[4-6]

Triazolinedione Addition to 1

To 4-methyl-1,2,4-triazoline-3,5-dione (14a, 1 mmol) was added a methylene chloride solution of 1 (1 mmol) at room temperature under nitrogen atmosphere. An exothermic reaction[24] immediately took place with evolution of nitrogen and the red color of reaction mixture turned to dark green. When the reaction mixture was chromatographed on silica gel, 2 and N-methylurazole were obtained in 75% and 73% yields, respectively, accompanied with recovered 1 (43%). When 2 mmol of 14a was used under the same conditions, 1 was completely consumed (2; 180%, N-methylurazole;95%). Similar results were also obtained with 4-phenyl derivative (14b). It is well known that azines derived from aromatic aldehydes or hexafluoroacetone undergo the so-called criss-cross addition with two equivalents

of dienophile to give diazabicyclooctane derivatives.[25] None of the criss-cross addition products was, however, obtained at all in the present reaction. A suspected intermediate would be a 1,3-dipolar, azomethinimine (15),[24,26,27] which was stable in anhydrous solution as seen by NMR Spectroscopy but could not be isolated (Scheme 2).

Scheme 2.



A characteristic feature of 15 is seen in the ^{1}H-NMR spectra, where the resonances due to the α-hydrogen atoms adjacent to the cationic carbon appear at 3.92-4.30(m,1H) and 4.70-5.0(m,1H) ppm (Fig.1); in the ^{13}C-NMR spectra, the cationic carbon and anionic carbon resonances are assigned at 181.6 and 156.5 ppm, respectively, by comparison with those found for the corresponding benzil derivatives (16)[24](Fig.2). These spectral data may demonstrate the large contribution of the structure 15'.[28] One plausible rationale for these observations is that the reaction of 1 with TAD 14 would initially form 15 by eliminating 9 as was the case of singlet oxygenation of 1. A subsequent reaction[24,26] of 9 with another molecule of 14 might also produce 15 as shown in Scheme 2, followed by formation of the hydrolyzed products, i.e., 2 and N-methylurazole. To test these possibilities, the following experiments have been done. In order to trap the dipole intermediate 15, the cycloaddition with some dipolarophiles was attempted (Scheme 3). The reaction of 1 with 2 eq of 14 in the presence of phenylisocyanate and acetylenedicarboxylic acid dimethyl ester[24] afforded the corresponding adducts, 17 and 18, in substantial yields, respectively. Both are regarded as a nitrogen analogue of secondary ozonide 13. When the reaction mixture was quenched with methanol, the corresponding urazole 19 as a nitrogen analogue of hydroperoxide 11 was obtained. these results clearly show the actual existence of 15.

Thus, a new type of reaction of the azines with singlet oxygen and TAD 14 actually afforded 1,3-dipoles, i.e., a carbonyl oxide and an azomethinimine intermediate, respectively.

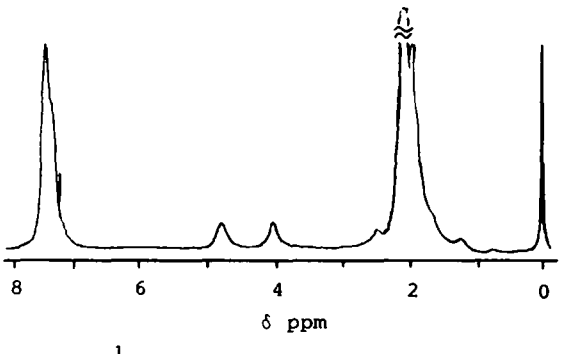


Fig.1. ^{1}H-NMR Spectrum of 15b.

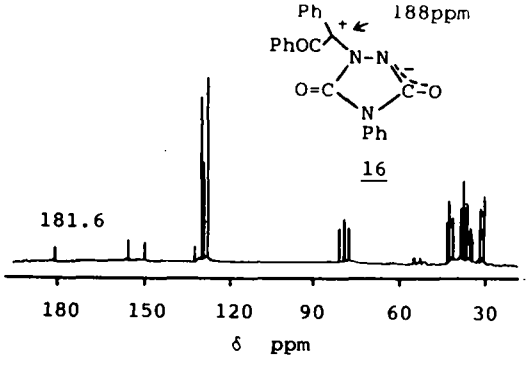
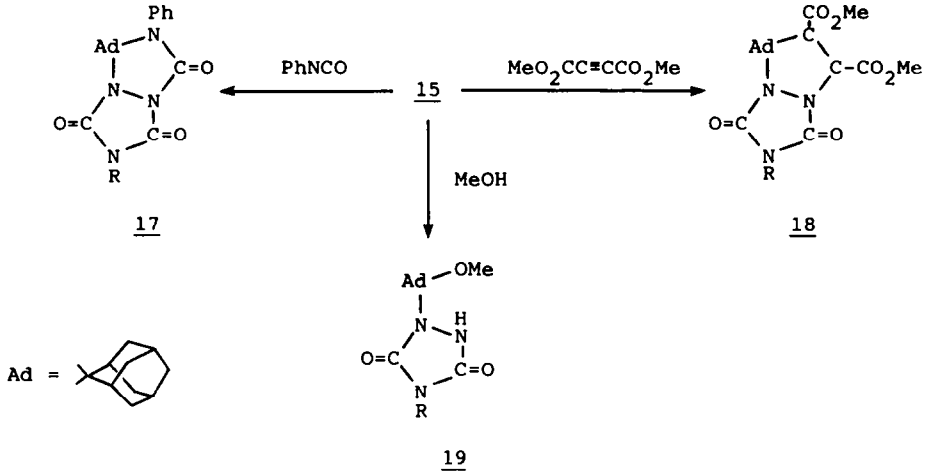


Fig.2. ^{13}C-NMR Spectrum of 15b.

Scheme 3.



Experimental

All melting points are uncorrected. IR spectra were recorded with a Hitachi 260-50 infrared spectrometer, ^{1}H-NMR spectra recorded with a Varian EM 360A spectrometer, ^{13}C-NMR recorded with a JEOL JNM FX100 spectrometer (solvent, deuteriochloroform; tetramethylsilane as an internal standard), and Mass spectra recorded with a Hitachi RMU-6M Mass spectrometer. The light source was two 500W halogen lamps with a Pyrex filter. Irradiations were carried out in an ice-water bath while passing oxygen. Preparative column chromatography was performed with columns packed with Merck Kieselgel (70-230 mesh). Gel permeation chromatography (GPLC) was performed on a series of JAIGEL 1H and 2H columns with a flow of 3.5 ml min-1 of chloroform on an LC-08 liquid chromatograph of Japan Analytical Industry Co. Ltd.

Reagent grade benzene, methanol and acetonitrile were distilled in the presence of appropriate drying reagents before use. Dichloromethane was washed with water, dried over calcium chloride and then distilled. Methylene blue (MB, KANTO CHEMICAL) and meso-tetraphenylporphine (TPP, STREM CHEMICALS) were used as received. DABCO and triphenylmethane were used after purification by sublimation and recrystallization, respectively. All other chemicals were used as accepted after drying when necessary. 4-Methyl- (14a, MeTAD) and 4-phenyl-1,2,4-triazoline-3,5-dione (14b, PhTAD) were prepared according to the literature procedure.[29] Azines 1 and 4 were prepared from the corresponding ketones (2 and 6[30]) according to the procedure reported previously.[31] 4: mp 244.5-245.5°C; IR(KBr) ν 1695, 1460cm^{-1}; ^{1}H-NMR δ 7.29-7.59(m,4H), 4.31(d,1H,J=3Hz), 3.72(d,1H,J=3HZ), 1.95-2.38(m,2H), 1.23-1.51(m,2H); m/e 312(M^+), 150, 128. Anal Calcd for $C_{22}H_{20}N_2$: C,84.58; H,6.45; N,8.96. Found C,84.41; H,6.45; N,8.96.

Photooxygenation of Azines

In a typical experiment, 1 (5 mmol) was dissolved in 50 ml of dichloromethane with MB (0.85 mmol) as a sensitizer. After this solution was photooxygenated, the products were separated by column chromatography using benzene as an eluent. The first fraction was 2 in 130% yield. The second fraction was 3[29] in 40% yield. 3: mp 286-289°C; IR($CDCl_3$) ν 2925, 2850, 1725, 1175cm^{-1}; ^{1}H-NMR δ 4.42(m,1H), 2.29(m,1H) and 1.63-2.27(m,12H); m/e 166(M^+).

In the case of 4, both 5 and 6 were analyzed by GLC. 5: oil; IR(KBr) ν 1740 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 7.16-7.42(m,4H), 5.53-5.68(m,1H), 3.83-3.98(m,1H), 1.56-2.62(m,4H) ppm; m/e 174(M^+). Exact Mass Calcd for $C_{11}H_{10}O_2$: 174.0679. Found: 174.0664. GLC analysis was performed with a Hitachi 164 Gas Chromatograph with a FID detector. (4 mm x 2 m glass column packed with 10% SF-96 on Chromosorb, column temperature; 220°C).

Photooxygenation of 1 in the presence of several additives was also carried out in the same manner.

Analysis of Gases Evolved from Photooxygenation of 1

Photooxygenation was carried out in a closed vessel with a rubber septum containing 1 (0.1 mmol), 1 mg of MB in 10 ml of methylene chloride. The reaction vessel was filled with oxygen. After the irradiations, gases in the system were syringed out and directly analyzed by means of a GLC-Mass spectrometer system (4 mm x 1 m glass column, 1% OV-1 on Chromosorb).

Photooxygenation of 1 in the Presence of Methyl Phenyl Sulfoxide

0.1 mmol of 1 in 1 ml of methylene chloride containing 3 mg of MB and 1 mmol of methyl phenyl sulfoxide was photooxygenated under an oxygen flow until disappearance of 1 (5h). The yield of methyl phenyl sulfone was determined by GLC (4 mm x 3 m glass column, 10% SF-96 on Chromosorb, column temperature; 120°C).

In the Presence of Alcohols: 1 mmol of 1 and 5 mg of MB were dissolved in 20 ml of methylene chloride and 20 ml of methanol. The resulting solution was irradiated for 5 h under an oxygen flow. After removal of solvent in vacuum, the products were separated and purified by GPLC. 2-Hydroperoxyadamantyl methyl ether (11a, 75%): oil; IR($CDCl_3$) ν 3370, 2970, 2930, 2850, 1115 cm^{-1}; ^{1}H-NMR δ 7.89(brs,1H), 3.40(s,3H), 1.44-2.37(m,14H) ppm; m/e 181(M^+-OH), 165(M^+-OOH). Anal Calcd for $C_{11}H_{18}O_3$: C,66.63; H,9.15. Found C,66.57; H,9.02; 11a showed a positive iodide test with potassium iodide solution. 2; 70% yield. In the presence of ethanol, 2-hydroperoxyadamantyl ethyl ether (11b, 76%) was obtained. 11b: oil; IR($CDCl_3$)ν3400, 2950, 2830, 1170 cm^{-1}; ^{1}H-NMR δ 7.76(brs,1H), 3.57(q,2H,J=7.2Hz), 1.44-2.33(m,14H), 1.26(t,3H,J=7.2Hz)ppm; m/e 195(M^+-OH), 179(M^+-OOH); 11b showed a positive iodide test with potassium iodide solution. 2; 80% yield.

In the Presence of Aryl Aldehyde: 1 mmol of 1, 2 ml of benzaldehyde and 5 mg of MB were dissolved in 10 ml of methylene chloride, and the resulting solution was irradiated for 6 h under an oxygen flow. After removal of solvent in vacuum, the products were separated by column chromatography using benzene as an eluent. The first and second fractions were 2 (113%) and 3 (20%), respectively. 12a; mp 57-58 °C; IR($CDCl_3$) ν 2940, 1720, 1280, 1275, 1115 cm^{-1}; ^{1}H-NMR δ 8.18(m,2H), 7.57(m,3H), 5.25(m,1), 1.44-2.40(m,14H) ppm; m/e 256(M^+). Anal Calcd for $C_{17}H_{20}O_2$: C,79.65; H,7.86. Found C,79.54; H,7.89. The reaction in the presence of 10 eq of p-nitrobenzaldehyde afforded the following products. The first fraction on column chromatography was 12b (8%). 12b ; mp 142-143°C; IR($CDCl_3$) ν 3040, 2920, 2870, 1720, 1530, 1350, 1280 cm-1; ^{1}H-NMR δ 8.47(s,4H), 5.33(m,1H), 1.50-2.34(m,14H) ppm; m/e 301(M^+). Anal Calcd for $C_{17}H_{19}N_1O_4$: C,67.75; H,6.35; N,4.64. Found C,67.71; H,6.44; N,4.64. The second fraction was ozonide 13 (16%). 13; mp 92° C(dec); IR($CDCl_3$) ν 3100, 3070, 2920, 2850, 1520, 1340, 1310, 1120 cm^{-1}; ^{1}H-NMR δ 8.38(d,2H,J=9.8Hz), 7.78(d,2H,J=9.8Hz), 6.24(s,1H), 1.44-2.39(m,14H) ppm. Anal Calcd for $C_{17}H_{19}NO_5$: C,64.34; H,6.03; N,4.41. Found C,64.30; H,6.12; N,4.18. The third fraction was 3 (15%). The forth one was 2 (100%).

In the Presence of Olefins: 0.1 mmol of 1, 1 mmol of trans-stilbene and 2 mg of MB were dissolved in 2 ml of methylene chloride. The resulting solution was irradiated for 3 h under an oxygen flow. The reaction mixture was directly analyzed by GLC (4 mm x 3 m glass column, 10% SF-96 on Chromosorb, column temperature; 180°C). trans-Stilbene oxide was obtained in 20% yield. 0.1 mmol of 1, 0.8 ml of norbornylene, and 3 mg of MB were dissolved in 0.5 ml of methylene chloride. The resulting solution was irradiated for 5 h under an oxygen flow. The reaction mixture was directly analyzed by GLC (4 mm x 4 m glass column, 10% SF-96 on Chromosorb, column temperature; 20°C). Exo-norbornylene oxide[32] was obtained in 13% yield.

Reaction of 1 with TAD

Into a 100 ml round-bottomed flask was placed 1 mmol of 1 in 20 ml of methylene chloride. While stirring at room temperature, 1 mmol of MeTAD was added portionwise over a period of 20 min. After stirring for additional 5 min, the products were separated by column chromatography by using chloroform as an eluent. 2 (75%) and N-methylurazole (73%) were obtained accompanied with recovered 1 (43%). When 2 eq of MeTAD was used, 2 and N-methylurazole[29] were obtained in 180% and 95% yields, respectively.

In the Presence of Phenylisocyanate: Into a 100 ml round-bottomed flask was placed 2.5 mmol of TAD and 20 mmol of phenylisocyanate in 20 ml of methylene chloride. While stirring at room temperature, 1 mmol of 1 in 20 ml of methylene chloride was added portionwise over a period of 20 min. After the reaction mixture was kept to stand overnight with stirring, the solvent was removed in vacuum, and the products were separated by GPLC. Adduct with MeTAD, 17a: 76% yield, mp 186-188° C; IR($CDCl_3$)ν1750, 1720 cm^{-1}; ^{1}H-NMR δ 7.28-7.60(m,5H), 3.13(s,3H), 2.39-2.86(m,4H), 1.50-2.10(m,10H) ppm; m/e 366(M^+); Anal Calcd for $C_{20}H_{18}O_3N_4$: C,65.24; H,6.01; N,15.16. Found: C,65.55; H,6.05; N,15.29. Adduct with PhTAD, 17b: 79% yield, mp 140-142°C; IR(KBr)ν1780, 1720 cm^{-1}; ^{1}H-NMR δ 7.35-7.70(m,10H), 2.50-3.0(m,4H), 1.50-2.10(m,10H) ppm; m/e 428(M^+). Exact Mass Calcd for $C_{25}H_{24}N_4O_3$: 428.1847. Found: 428.1832.

In the Presence of Acetylenecarboxylic Acid Dimethyl Ester: The photooxygenation in the presence of 8 eq of acetylenecarboxylic acid dimethyl ester was carried out in the same manner as mentioned above. Adduct with MeTAD, 18a: 36% yield, mp 179.5-181°C; IR(KBr)ν1810, 1740 cm^{-1}; ^{1}H-NMR δ 3.95(s,3H), 3.87(s,3H), 3.08(s,3H), 2.30-3.0(m,4H), 1.55-2.10(m,19H) ppm; m/e 389(M^+); anal Calcd for $C_{19}H_{23}O_6N_3$: C,58.60; H,5.95; N,10.79. Found: C,58.12; H,5.96; N,10.65. Adduct with PhTAD, 18b: 57% yield; mp 176-178°C; IR(KBr)ν1780, 1720 cm^{-1}; ^{1}H-NMR δ 7.45-7.65(m,5H), 3.97(s,3H), 3.87(s,3H), 2.30-3.0(m,4H), 1.50-2.10(m,10H) ppm; m/e 451(M^+). Exact Mass Calcd for $C_{24}H_{25}N_3O_6$: 451.1743. Found: 451.1744.

In the Presence of Methanol: The azomethinimine 15 generated as mentioned above was treated with an excess of methanol. After removal of solvent in vacuum, the products were separated by GPLC. Adduct with MeTAD, 19a: quant.; mp 68-69°C(dec); IR(KBr) ν 3175, 2910, 1755, 1680, 1085 cm^{-1}; ^{1}H-NMR δ 3.28(s,3H), 3.10(s,3H), 1.60-2.20(m,14H) ppm. Adduct with PhTAD, 19b: quant.; mp 68-70°C(dec); IR(KBr) ν 3150, 3040, 2900, 1750, 1680, 1090 cm^{-1}; ^{1}H-NMR δ 7.30-7.65(m,5H), 3.30(s,3H), 1.25-2.20(m,14H) ppm.

^{1}H-NMR and ^{13}C-NMR Spectra of 1 and 15

^{1}H-NMR (JEOL JNM FX100 Spectrometer), 1: 3.12-3.34(m,2H), 2.50-2.68(m,2H), 1.70-2.10(m,24H) ppm. N-Phenyl azomethinimine 15b: 7.10-7.75(m,5H), 4.70-

5.0(m,1H), 3.92-4.30(m,1H), 1.60-2.60(m,12H) ppm. ^{13}C-NMR, 1: 170.8, 78.3, 77.0, 75.7, 39.5, 39.2, 37.9, 36.5, 31.6, 27.8 ppm. 15b: 181.6, 156.5, 150.8, 131.4, 129.0, 128.2, 125.5, 78.4, 77.1, 75.8, 40.6, 39.8, 39.3, 37.3, 35.7, 34.2, 26.8 ppm.

Acknowledgment. This work was supported by a Grant-in-Aid for Environmental Science (NO.59035011) from the Ministry of Education, Science and Culture of Japan.

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