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Photosensitized Oxygenation of 1,3-Bis(diazo)indan-2-one

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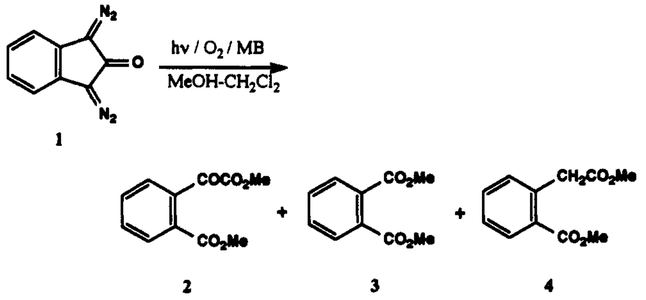
It has previously been established that photosensitized oxygenations of diazo compounds proceed through carbonyl oxides as the reactive intermediates.[1,2] Murray and co-workers reported the trapping of carbonyl oxides derived from singlet oxygen oxygenation of diazo compounds with aldehydes[3] and naphthalene.[4] They further observed that the carbonyl oxide formed by photooxygenation of 9-diazofluorene was captured intramolecularly to give 1-hydroxyfluorene.[5] Recently, carbonyl oxides generated by reaction of singlet oxygen with diazo precursors in solution were characterized by laser flash photolysis.[6] The photosensitized oxygenations of α-diazo ketones were investigated independently by Ando[7] and Foote.[8] The intermediate carbonyl oxides produced in the photooxygenation of α-diazo ketones were reported to possess more electrophilic character than carbonyl oxides derived from diphenyldiazomethane and 9-diazofluorene.[7a] We wish to report herein the first mechanistic studies of the photosensitized oxygenation of a 1,3-bis(diazo) ketone, in which the consecutive decompositions of two diazo groups were established and in which a new type of oxidative cleavage with decarbonylation was observed.

Results and Discussion

Few reports on mechanistic studies of photoreactions of 1,3-bis(diazo) ketones have appeared in the literature,[9] though they have long been of interest as intermediates for the synthesis of cyclopropenones and strained alkynes.[9,10] As a substrate for studies on the photosensitized oxygenation of a 1,3-bis(diazo) ketone, we chose 1,3-bis(diazo)indan-2-one (1), since we have found that 1 is easily prepared and purified, and its photochemical reactions in fluid solutions[11] and in Ar matrices[12] have been thoroughly investigated. A solution of 1 with methylene blue as sensitizer in methanol–dichloromethane (1:1) was irradiated at 0 °C with a tungsten–halogen lamp with oxygen bubbling. Separation by chromatography gave two main products, methyl *o*-((methoxycarbonyl)carbonyl)benzoate (2) and dimethyl phthalate (3) in 34% and 24% yields, respectively, together with small amounts of dimethyl homophthalate (4) (2%). The structure of the keto ester 2 was determined spectroscopically and confirmed by an independent synthesis from homophthalic acid. Identification of 3 and 4 was achieved by ^{1}H NMR and GC-MS comparisons with authentic samples. Control experiments revealed that none of these products were formed under the reaction conditions in the absence of sensitizer or in the presence of a singlet oxygen quencher such as 1,4-diazabicyclo[2.2.2]octane. Monitoring of the reaction as a function of irradiation time showed that there was an induction period in the formation of the products 2–4 and that all of them were stable under the irradiation conditions.



In order to investigate the mechanism of the formation of the final products 2–4, we attempted to isolate the intermediate products. Irradiation was stopped at an early stage of the reaction, and the mixture was carefully separated by chromatography after rapid filtration through silica gel to remove the sensitizer and evaporation of the solvent. Together with the final products 2–4 and the unchanged starting material 1, two diazo ketones were isolated, assigned as 1-diazoindan-2,3-dione (5) and 1-diazo-3,3-dimethoxyindan-2-one (6). The ^{1}H NMR and IR spectral data are consistent with these structures. The photosensitized oxygenation of these diazo ketones gave an informative clue concerning the mechanism for the photooxygenation of 1 in a methanol–dichloromethane solution. Irradiation of 5 under the same conditions as those described in the photosensitized oxygenation of 1 gave 2 exclusively, while 3 was produced by the photooxygenation of 6. Thus, it was concluded that the main photoproducts 2 and 3 originate from the photooxygenation of 5 and 6, respectively. Unfortunately, we were unable to reach an unambiguous conclusion concerning the origin of 4. It is thought, however, that 4 would be formed through a Wolff rearrangement of the diazo ketone 5 or 6 in the excited state or the corresponding ketocarbene, since independent irradiation (>300 nm) of 5 or 6 in methanol gave 4 as a major photoproduct.[13]

A possible reaction scheme for the photosensitized oxygenation of 1 in methanol–dichloromethane is shown in Scheme I. The isolation of diazo ketones 5 and 6 clearly

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[1] Wasserman, H. H.; Lipshutz, B. H. In *Singlet Oxygen;* Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 439.

[2] For recent papers in this field, see also: (a) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* 1981, *103,* 3832. (b) Adam, W.; Dürr, H.; Haas, W.; Lohray, B. *Angew. Chem., Int. Ed. Engl.* 1986, *25,* 101. (c) Ishiguro, K.; Hirano, Y.; Sawaki, Y. *J. Org. Chem.* 1988, *53,* 5397. (d) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* 1991, *113,* 6202.

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[4] Chaudhary, S. K.; Hoyt, R. A.; Murray, R. W. *Tetrahedron Lett.* 1976, 4235.

[5] Kumar, S.; Murray, R. W. *Tetrahedron Lett.* 1980, 4781.

[6] (a) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* 1985, *107,* 4616. (b) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* 1989, *54,* 1612.

[7] (a) Ando, W.; Miyazaki, H.; Kohmoto, S. *Tetrahedron Lett.* 1979, 1317. (b) Ando, W.; Miyazaki, H.; Ueno, K.; Nakanishi, H.; Sakurai, T.; Kobayashi, K. *J. Am. Chem. Soc.* 1981, *103,* 4949.

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[9] Trost, B. M.; Whitman, P. J. *J. Am. Chem. Soc.* 1974, *96,* 7421.

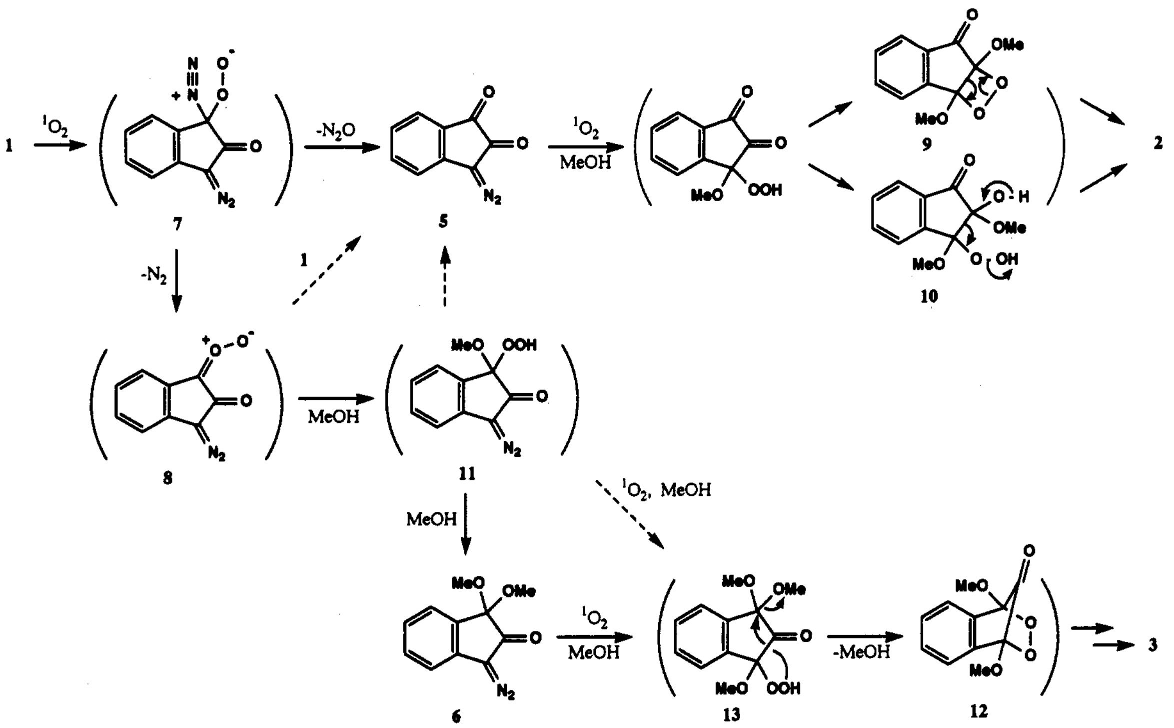
[10] Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* 1981, *103,* 7033.

[11] (a) Murata, S.; Yamamoto, T.; Tomioka, H. *J. Am. Soc.* In press. (b) Lee, H.-K.; Kim, H.-R.; Tomioka, H. *Bull. Korean Chem. Soc.* 1988, *9,* 399; *Chem. Abstr.* 1989, *111,* 133742a.

[12] Murata, S.; Yamamoto, T.; Tomioka, H.; Lee, H.-K.; Kim, H.-R.; Yabe, A. *J. Chem. Soc., Chem. Commun.* 1990, 1258.

[13] It was reported that irradiation of 2-diazoindan-1,3-dione in methanol also gave 4 as a major photoproduct: (a) Cava, M. P.; Spangler, R. J. *J. Am. Chem. Soc.* 1967, *89,* 4550. (b) Spangler, R. J.; Kim, J.-H.; Cava, M. P. *J. Org. Chem.* 1977, *42,* 1697.

Scheme I



demonstrated that the decomposition of two diazo groups of 1 by the attack of singlet oxygen occurs stepwise to give the intermediate 7. In analogy with photosensitized oxygenations of diazoalkanes,[2,3] decomposition of 7 with loss of nitrogen gave the diazo carbonyl oxide 8,[14] while cyclization of 7, followed by loss of dinitrogen monoxide, produced 5.[15] No evidence was obtained for the intramolecular interaction of the carbonyl oxide moiety with the adjacent diazo group in 8. The oxidative cleavage of 5 with singlet oxygen to give 2 is regarded as an analogous reaction to the formation of dimethyl adipate by the photosensitized oxygenation of 2-diazocyclohexanone in methanol.[7b] Dioxetane 9 and hemiacetal 10 would be postulated as possible transient intermediates. It should be pointed out that indan-1,2,3-trione could not be obtained from the photosensitized oxygenation of 1 in methanol–dichloromethane. This observation suggests that in the adduct formed by the reaction of 5 with singlet oxygen, formation of the carbonyl oxide and nucleophilic attack of methanol on the carbonyl oxide carbon occurs in preference to loss of dinitrogen monoxide which would lead to the high energy 1,2,3-triketone.[16]

On the other hand, nucleophilic attack of methanol on the carbonyl oxide carbon in 8 afforded the α-keto methoxy hydroperoxide 11. It is thought that 6 is obtained by methanolysis of 11, presumably catalyzed by acid which might be present in the reaction mixture.[17] In the course of the photooxygenation of 6 to 3, decarbonylation should be involved. Though the endoperoxide 12,[18] which could be formed by nucleophilic attack of the hydroperoxide oxygen on the dimethoxy-substituted β-carbon in the hydroperoxide 13, appears to be an intermediate in the decarbonylation process, the detailed mechanism of decarbonylation has not been elucidated yet.[19] The oxidative cleavage with decarbonylation seems to be a characteristic mode in the photooxygenation of 1,3-bis(diazo) ketones. Further work to elucidate the general scheme of the photosensitized oxygenation of 1,3-bis(diazo) ketones is ongoing in our laboratory.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 100 or 400 MHz. GC-MS spectra were recorded with a GC column prepared from 5% silicone OV-17 on Diasolid L (5.0 mm × 1.0 m). The GC analyses were performed on a column prepared from 5% silicone OV-17 on Diasolid L (5.0 mm × 1.0 m) or 5% PEG-20M on Diasolid L (5.0 mm × 1.0 m). Gel permeation liquid chromatography (GPC) was carried out on a JASCO HLC-01 high-pressure liquid chromatograph equipped with a Shodex GPC H-2001 column. TLC was carried out on a Merck kieselgel 60 PF$_{254}$.

Irradiation for Preparative Experiments. A solution of 150 mg (820 μmol) of 1[12] and 15 mg of methylene blue trihydrate in 60 mL of methanol–CH$_2$Cl$_2$ (1:1, v/v) was placed in a Pyrex tube and purged with O$_2$ for 15 min. The solution was irradiated

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[14] The diazo carbonyl oxide (8) has been directly observed by IR spectroscopy, which is formed by the reaction of the corresponding carbene with oxygen in an Ar matrix at 35 K.[12]

[15] It is known that carbonyl oxides formed by photosensitized oxygenation of diazoalkanes react with diazo compounds to give two molecules of ketones.[6] If this process can be applied to carbonyl oxides derived from α-diazo ketones, 5 could also be produced in the oxidation of 1 by 8. Moreover, since it was reported that α-keto methoxy hydroperoxides decomposed to give diketones,[8] 5 might also be formed from 11.

[16] It is known that a cyclic vicinal triketone structure is unstable because of the unfavorable arrangement of the three dipolar carbonyl groups: Laird, T. *Comprehensive Organic Chemistry*; Pergamon Press: Oxford, 1979; Vol. 1, p 1203.

[17] α-Keto methoxy hydroperoxides formed by photosensitized oxygenation of α-diazo ketones in methanol–dichloromethane were reported to decompose upon warming to room temperature.[8] Though the isolation of 11 was unsuccessful, the possibility that 11 is a real precursor of 3 under the reaction conditions and that 6 is an artifact of the workup procedure cannot be ruled out.

[18] The intermediacy of analogous endoperoxides has been postulated in the oxidative cleavage of furans and thiophenes by singlet oxygen: (a) Schenck, G. O. *Chem. Ber.* **1947**, *80*, 289. (b) Wasserman, H. H.; Liberles, A. *J. Am. Chem. Soc.* **1960**, *82*, 2086. (c) Lutz, R. E.; Welstead, W. J., Jr.; Bass, R. G.; Dak, J. I. *J. Org. Chem.* **1962**, *27*, 1111. (d) Skold, C. N.; Schlessinger, R. H. *Tetrahedron Lett.* **1970**, 791.

[19] Attempts to detect carbon monoxide were unsuccessful at the present stage. The possibility that carbon monoxide is eliminated as other species, such as formaldehyde, during workup cannot be excluded. We thank a referee for pointing out this possibility.

at 0 °C with a tungsten–halogen lamp filtered by aqueous sodium chromate solution for 12 h with oxygen bubbling. After the solvent was evaporated under reduced pressure, the residue was dissolved in CH_2Cl_2 and filtered through silica gel to remove methylene blue. After evaporation of the solvent, the residue was separated into four fractions by the use of GPC with chloroform eluent. The products in each fraction were identified by ^1H NMR, IR, and GC-MS. From the first eluted fraction 18 mg of methyl *o*-((methoxycarbonyl)carbonyl)benzoate (**2**) was obtained as colorless granules: mp 67–68 °C (hexane); ^1H NMR ($CDCl_3$) δ 3.80 (3 H, s), 3.85 (3 H, s), 7.40–7.65 (3 H, m), 7.85–7.95 (1 H, m); IR (NaCl) 1735, 1715, 1700, 1295, 1210, 710 cm^{-1}; GC-MS *m/z* (rel intensity) 163 ($M^+ - CO_2Me$, 100), 131 (11), 77 (28). Anal. Found: C, 59.42; H, 4.62. Calcd for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54. The second fraction (2 mg) was obtained as a light yellow oil, which was composed of 1-diazo-3,3-dimethoxyindan-2-one (**6**) and small amounts of dimethyl homophthalate (**4**). Further purification of **6** was not successful because of its thermal and chemical lability. **6**: ^1H NMR ($CDCl_3$) δ 3.43 (6 H, s), 7.00 (1 H, d, J = 8.1 Hz), 7.25 (1 H, t, J = 8.1 Hz), 7.48 (1 H, t, J = 8.1 Hz), 7.53 (1 H, d, J = 8.1 Hz); IR (NaCl) 2110, 1715, 1330 cm^{-1}. From the third fraction 17 mg of dimethyl phthalate (**3**) was obtained as colorless liquid, which was identified by comparison of the spectroscopic data with those of authentic material. The fourth fraction was obtained as orange-red granules, composed of the unchanged starting material (**1**) and 1-diazoindan-2,3-dione (**5**). Separation of the mixture by preparative TLC with hexane-$CHCl_3$ (2:1) gave 20 mg of **5**, together with 22 mg of **1**. **5**: orange-red needles; mp 122–124 °C dec (hexane–ethanol); ^1H NMR ($CDCl_3$) δ 7.10–7.30 (2 H, m), 7.50–7.75 (2 H, m); IR (KBr) 2105, 1735, 1700, 1605, 750 cm^{-1}. Anal. Found: C, 62.78; H, 2.47; N, 16.26. Calcd for $C_9H_4N_2O_2$: C, 62.80; H, 2.34; N, 16.27.

Preparation of Methyl *o*-((Methoxycarbonyl)carbonyl)benzoate (2) from Homophthalic Acid. A mixture of homophthalic acid (1.0 g, 5.6 mmol) and SeO_2 (0.68 g, 6.1 mmol) in xylene (30 mL) was refluxed for 5 h. After removal of selenium by filtration, the reaction mixture was extracted with a saturated aqueous solution of Na_2CO_3. After acidification of the extract with dilute HCl, the organic material was extracted with ether and the extract was dried (Na_2SO_4). The solvent was removed under reduced pressure, and $CHCl_3$ was added to the oily residue which crystallized immediately. The crystals were collected by filtration to give 0.38 g (35%) of *o*-(carboxycarbonyl)benzoic acid as colorless granules, which melted at 141–145 °C (lit.[20] mp 144 °C). An ethereal solution of the dicarboxylic acid was treated with excess diazomethane generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and KOH in the usual manner.[21] After removal of the solvent under reduced pressure, **2** was obtained as colorless granules in almost quantitative yield. The melting point and spectroscopic data were thoroughly consistent with those of the product obtained by the photosensitized oxygenation of **1**.

Irradiation for Analytical Experiments. (1) Photosensitized Oxygenation of 1. A solution of **1** (5 mg) and methylene blue trihydrate (0.5 mg) in 5 mL of methanol–CH_2Cl_2 (1:1, v/v) was irradiated under the same conditions as those described in the preparative-scale irradiation. The reaction was monitored by GC. Identifications of the products **2–4** were established by GC-MS comparison with authentic samples. Product yields were determined by GC on the basis of the reacted material after irradiation for 4 h, where the conversion of **1** was 86%. Control experiments demonstrated that no reaction occurred in the absence of methylene blue or in the presence of 1,4-diazabicyclo[2.2.2]octane (30 mg).

(2) Photosensitized Oxygenation of 5 or 6. Photosensitized oxygenation of **5** was carried out under the same conditions as those described in the photooxygenation of **1**. GC and GC-MS analyses of the irradiation mixture showed that **2** was formed in 84% yield and that small amounts of **3** or **4** were produced. The photooxygenation of **6**, though contaminated by small amounts of **4**, gave **3**, whose structure was established by GC-MS.

(3) Direct Photolysis of 5 or 6 in Methanol. A solution of **5** (2.5 mg) in 1 mL of methanol was placed in a Pyrex tube, purged with argon for 10 min, and irradiated with a high-pressure mercury lamp at rt. GC and GC-MS analyses of the irradiated mixture demonstrated that **4** was formed in 88% yield, together with small amounts of methyl 2-oxobenzocyclobutene-1-carboxylate (4%).[13] Though the material **6** contained as impurities small amounts of **4**, GC analyses established that **4** was formed by irradiation of **6** in methanol, together with the product, GC-MS of which exhibited the peaks at *m/z* (rel intensity) 194 (10), 179 (100), 163 (39), and 133 (33). The structure of the latter photoproduct remains unidentified, though methyl 2,2-dimethoxybenzocyclobutene-1-carboxylate and methyl *o*-(trimethoxymethyl)phenylacetate are possible structures.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, which is gratefully acknowledged.

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(21) de Boer, Th. J.; Backer, H. J. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. IV, p 250.