

Photolysis of Indan-1,2-dione Derivatives in Oxygen-Doped Argon Matrix at Low Temperature

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Photolysis of indan-1,2,3-trion (**1a**), benzo[*b*]furan-2,3-dione (**1b**), and *N*-methylisatin (**1c**) in argon matrix either with or without oxygen at 10 K was investigated by IR spectroscopy in combination with DFT calculations. The results indicate that while **1a** and **1b** gave the products mixture as a result of α -cleavage, followed by decarbonylation, **1c** was rather photostable under similar conditions. However, when the irradiation was carried out in argon matrix doped with 20% oxygen, **1c** decomposed much more efficiently than that in argon matrix and cyclic diacyl peroxide presumably formed by trapping of initial diradical originating from α -cleavage by molecular oxygen was detected. Similar irradiation of **1b** also gave cyclic diacyl peroxide along with photodecarbonylation products, but irradiation of **1a** in oxygen-doped matrix produced not only cyclic diacyl peroxide but also products as a result of oxidation of photodecarbonylation product. The present observation reveals that photolysis of ketones in oxygen-doped matrix at low temperature provides useful information concerning the reactivities of ketones toward α -cleavage.

The chemical properties of an n, π^* excited state of a ketone is often rationalized on the basis of a simple model showing an unpaired electron in a nonbonding orbital on oxygen and an unpaired electron in a π^* antibonding orbital. One of the main reactions in this state is the homolytic cleavage of the α -bond of the carbonyl moiety to generate an acyl radical and an alkyl radical. This is often referred to as the Norrish type I cleavage.¹ The cleavage reaction parallels the cleavage of an alkoxy radical, which also has an unpaired electron in a nonbonding orbital on oxygen and breaks down to give a ketone and an alkyl radical. Norrish type I reactions have been used extensively in the field of reactive intermediates. For instance, benzoin derivatives are used as initiators for the photochemical curing of print inks, lacquers, and other surface coatings since the acyl radicals generated as a result of the type I cleavage can be diverted to initiate the polymerization of vinyl monomers.² For a saturated ketone, α cleavage is usually followed by loss of carbon monoxide (photodecarbonylation) and this results in the formation of many useful species such as diradicals,^{3,4} xylylene,^{3,4} cyclobutadiene,⁵ and so on.

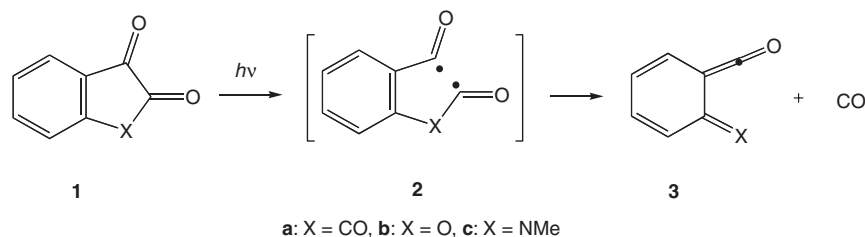
However, the efficiency of decarbonylation in acyl radicals is markedly dependent upon the strength of the bond adjacent to the carbonyl group. For instance, benzoin ethers do not undergo photodecarbonylation,⁶ while 1,3-diphenylpropanone gives 1,2-diphenylethane and CO quantitatively upon irradiation.⁷ When the decarbonylation is inefficient, the initial radicals may recombine to reproduce the original substrate and hence the ketone in this case appears rather photostable. One way to detect the initial radical pair is trapping experiments. It has been shown that acyl alkyl diradical intermediates generated in the type I cleavage of alkylketones are intercepted by 2,2,6,6-tetramethylpiperidine-1-oxyl,⁸ butanetriol,⁹ and nitric oxide¹⁰ although paraquat is unsuccessful.¹¹

We found that the diradicals are cleanly trapped by molecular oxygen especially when generated in matrix containing oxygen at low temperature and the resulting peroxides are easily detected and characterized by IR spectroscopy in combination with DFT calculations. This method provides a way to estimate the relative reactivity of ketones toward the type I reaction.

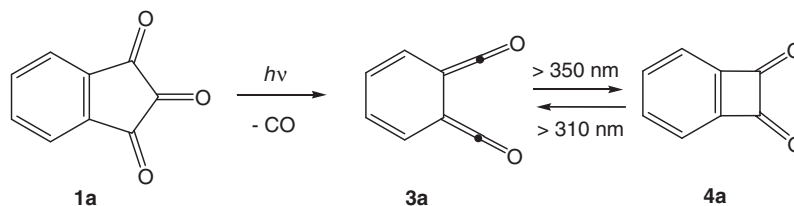
Results

Compounds which we utilized in this study were indan-1,2-dione derivatives **1**, where the component X was changed from CO (**1a**, indan-1,2,3-trion)¹² to O (**1b**, benzo[*b*]furan-2,3-dione)¹³ to NMe (**1c**, *N*-methylisatin),¹⁴ all of which are expected to undergo decarbonylation to give 6-oxomethylene-cyclohexa-2,4-diene derivatives **3** by way of diradical **2** upon photo-excitation (Scheme 1).

Indan-1,2,3-trion (**1a**) was deposited in an Ar matrix at 20 K and irradiated ($\lambda > 310$ nm) at 10 K (Figure 1). IR monitoring of the irradiation of **1a** indicated that the peaks due to **1a** decreased in intensity as new absorption bands showing strong peaks at around 1800 cm^{-1} appeared. The absorption bands due to products after 30 min irradiation were obtained by subtracting the initial spectrum from the irradiated one (Figure 1b). A comparison of the experimental spectrum with that calculated for possible products suggested that the observed bands match well with those calculated for 1,2-dihydrocyclobutabenzene-1,2-dione (**4a**) (Figure 1e). The rather weak band at 2100 cm^{-1} was assigned to carbon monoxide. When the mixture was continuously irradiated under these conditions, new bands at $2050\text{--}2150\text{ cm}^{-1}$ appeared as bands due to the dione **4a** diminished (Figure 1c). Again, a comparison of the experimental spectrum with that calculated for possible products suggested that new bands match well with those calculated for bis(ketene) **3a** (Figure 1d). Irradiation of the mixture with a



Scheme 1.



Scheme 2.

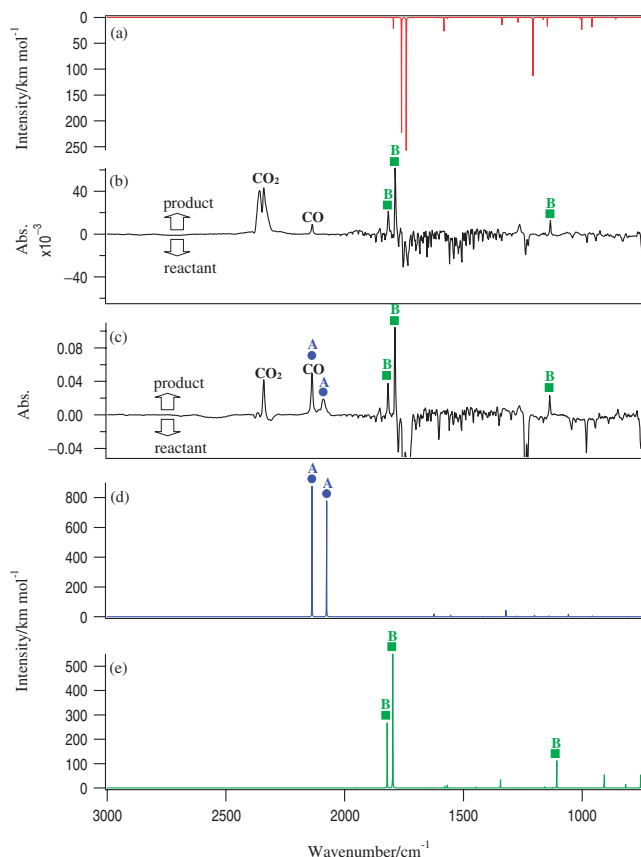


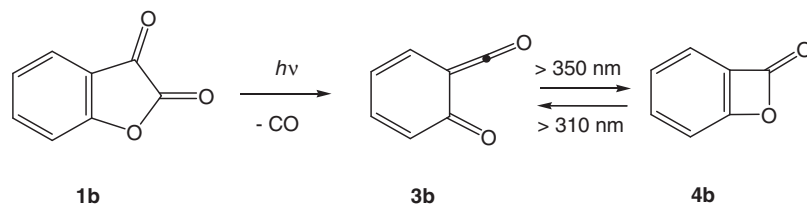
Figure 1. Photolysis of indan-1,2,3-trione (**1a**) in an Ar matrix at 10 K. (a) Calculated (B3LYP/6-31G(d)) spectra of **1a**. (b, c) Difference IR spectrum between the photo-product formed after 0.5 (b) and 3 h (c) of irradiation ($\lambda > 310$ nm) of **1a** (negative peaks) and before irradiation (positive peaks). (d and e) Calculated [B3LYP/6-31G(d)] spectra of bis(ketene) **3a** (d) and 1,2-dihydrocyclobutabenzene-1,2-dione (**4a**) (e), respectively. Note that the band at 2100 cm^{-1} of **3a** overlaps with that of CO.

longer wavelength light (>350 nm) resulted in the increase of the band due to **4a** at the expense of that of **3a**. Thus, **1a** is shown to undergo photodecarbonylation rather efficiently to produce a mixture of **3a** and **4a**, which were found to be in a photoequilibrium (Scheme 2).^{12a,12b}

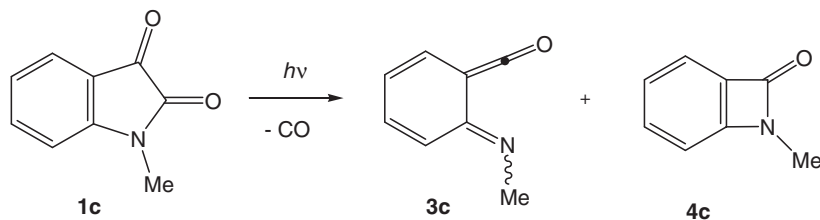
Similar irradiation (>310 nm) of benzo[*b*]furan-2,3-dione (**1b**) matrix-isolated in Ar at 10 K gave a mixture of oxoketene **3b** and benzopropiolactone (**4b**). The irradiation of the mixture with a longer wavelength light (>350 nm) again resulted in the increase of the bands due to **4a** at the expense of that of **3a**, indicating that the two products were in a photoequilibrium.^{13c} However, the irradiation of **1b** with shorter wavelength light (>310 and >350 nm) resulted in rather rapid decrease in the bands due to **3b** and **4b** concomitant with the formation of the bands presumably ascribable to the secondary photodecomposition products (Scheme 3). Since this process makes subsequent analysis very difficult, the irradiation of **1b** was carried out with a longer wavelength light (>390 nm) so that we could monitor the initial photoreaction process more precisely (Figure 2).

Irradiation of *N*-methylisatin (**1c**) gave somewhat different results. Thus **1c** did not undergo appreciable decomposition upon irradiation in Ar matrix at 10 K at least under conditions (at >310 nm for 5 h) where both **1a** and **1b** were appreciably photodecomposed. Only after irradiation for 24 h were observed weak absorption bands due to ketene **3c** (Scheme 4, Figures 3c and 3d).

However, when the irradiation was carried out in the presence of oxygen, the appreciable disappearance of the bands due to **1c** was observed. Thus, when **1c** matrix-isolated in argon doped with 20% oxygen was irradiated at 10 K (Figure 3a), the bands due to **1c** diminished much more efficiently than that in an undoped matrix (Figure 3b). New bands were completely different from those observed in the irradiation of **1c** in undoped matrix and hence they are most probably ascribable to oxidation products. If one assumes that **1c** also undergoes α -cleavage upon excitation by way of an n,π^* excited state, it is possible that the resulting diradical **2c** is trapped by molecular oxygen to form cyclic peroxide **5c**. It is also known that diradicals from small cyclic ketones generate oxocarbenes by



Scheme 3.



Scheme 4.

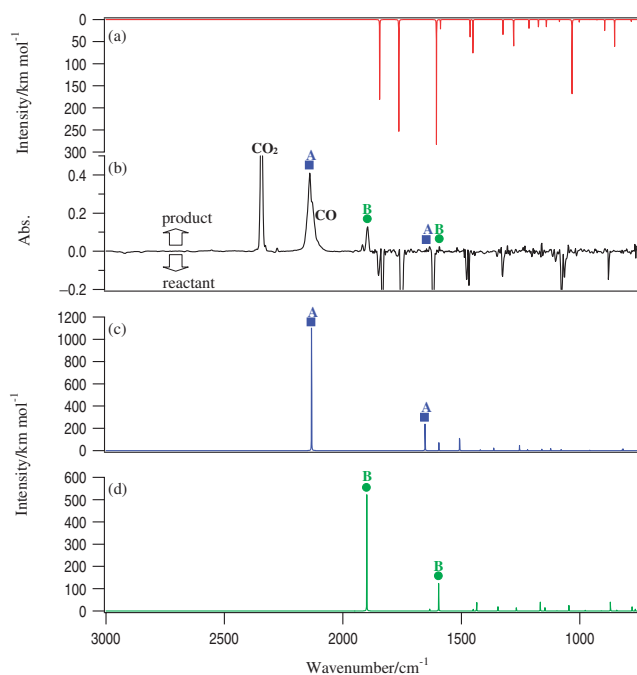


Figure 2. Photolysis of benzo[*b*]furan-2,3-dione (**1b**) in an Ar matrix at 10 K. (a) Calculated (B3LYP/6-31G(d)) spectra of **1b**. (b) Difference IR spectrum between the photoproduct formed after 0.5 h of irradiation ($\lambda > 390$ nm) of **1b** (negative peaks) and before irradiation (positive peaks). (c and d) Calculated (B3LYP/6-31G(d)) spectra of oxoketene **3b** (c) and benzopropiolactone (**4b**) (d), respectively.

attack of the oxygen of the acyl radical on the other radical centers.¹ This ring-expansion reaction in **2c** will result in the generation of oxacarbenes **6c** and/or **6'c**. Most oxacarbenes have a singlet ground state,¹⁵ which are rather unreactive toward oxygen.¹⁶ However, it has been shown that some singlet carbenes unreactive toward oxygen in solution in a short time scale react with oxygen under matrix conditions.¹⁷ Thus, oxidation product **7c** from oxacarbenes **6c** or **6'c** is also considered (Scheme 5).

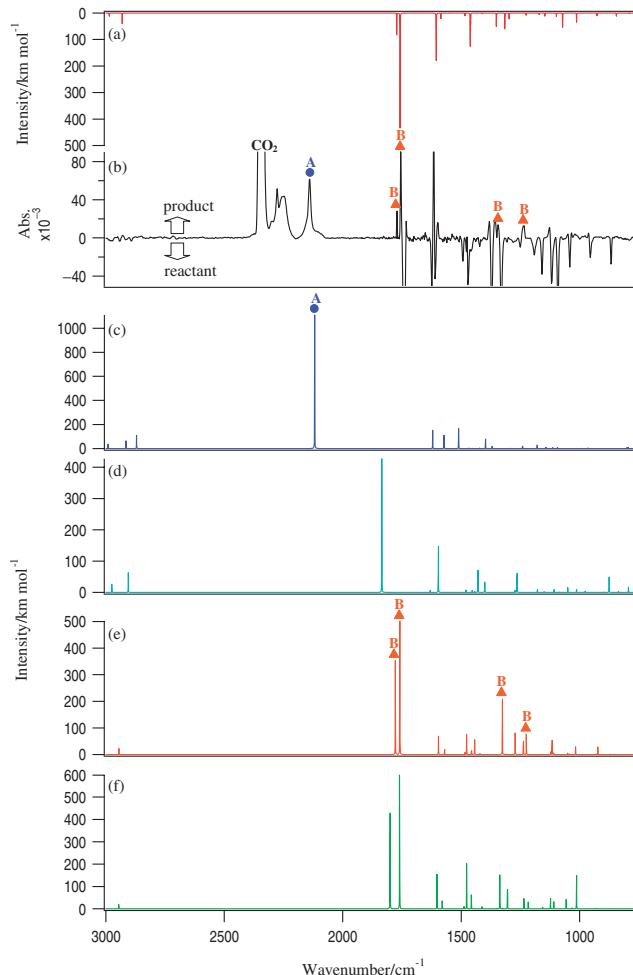
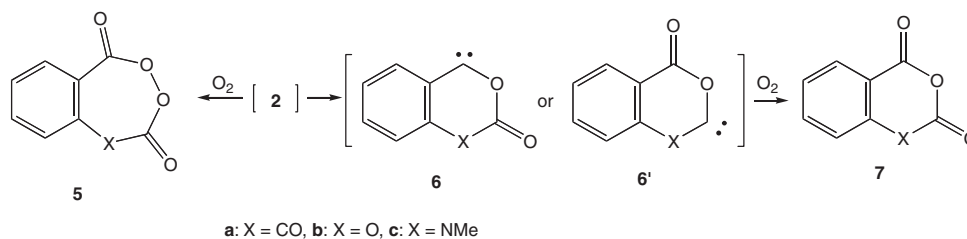


Figure 3. Photolysis of *N*-methylisatin (**1c**) in 20% O₂-doped Ar matrix at 10 K. (a) Calculated (B3LYP/6-31G(d)) spectra of **1c**. (b) Difference IR spectrum between the photoproduct formed after 24 h of irradiation ($\lambda > 310$ nm) of **1c** (negative peaks) and before irradiation (positive peaks). (c, d, e, and f) Calculated (B3LYP/6-31G(d)) spectra of ketene **3c** (c) and lactam **4c** (d), cyclic peroxide **5c** (e), and cyclic anhydride **7c** (f), respectively.



Scheme 5.

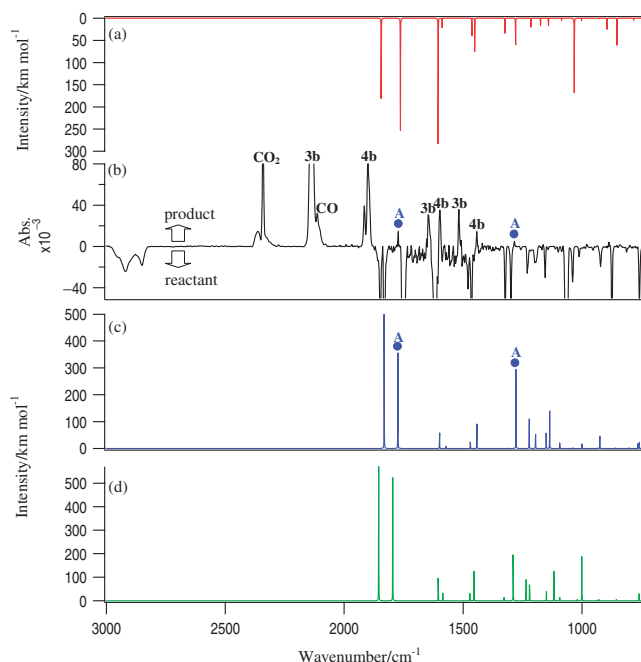


Figure 4. Photolysis of benzo[*b*]furan-2,3-dione (**1b**) in 20% O₂-doped Ar matrix at 10 K. (a) Calculated (B3LYP/6-31G(d)) spectra of **1b**. (b) Difference IR spectrum between the photoproduct formed after 0.5 h of irradiation ($\lambda > 390$ nm) of **1b** (negative peaks) and before irradiation (positive peaks). (c, d) Calculated (B3LYP/6-31G(d)) spectra of cyclic peroxide **5b** (c) and cyclic anhydride **7b** (d), respectively.

We have optimized the structures of those oxidation products and the vibration frequencies for those oxidation products were compared with the experimental values. The observed spectrum match better with that predicted for **5c** (Figure 3e), which is expected to form by the direct trapping of initial diradical **2c** by oxygen, rather than that for **7c** (Figure 3f).

Irradiation of **1b** under similar conditions also gave the oxidation products but photodecarbonylation products **3b** and **4b** were also observed in this case. Comparison of the spectra with those calculated for possible oxidation products, i.e., **5b** and **7b** indicates that the spectra match better with that calculated for **5a** rather than that for **7a** (Figure 4).

Irradiation of **1a** in oxygen-doped matrix gave somewhat different results from that observed for **1b** and **1c** (Figure 5a). There were at least three major products, designated A, B, and C, all of which were detected only in the photolysis in oxygen-doped matrix (Figure 5b). Comparison of the observed bands with those calculated suggested that A is most likely cyclic

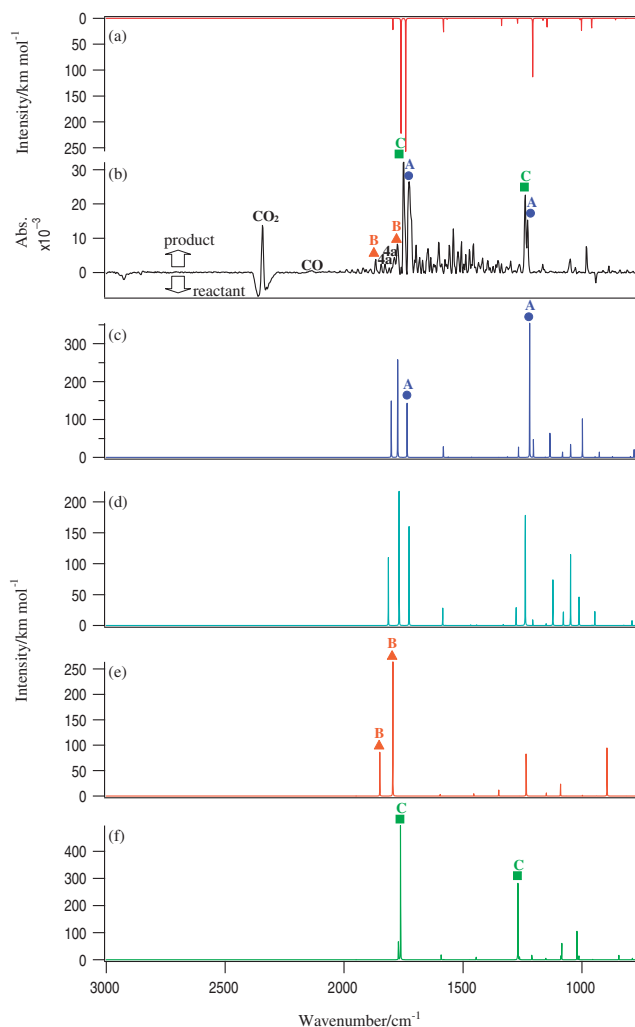


Figure 5. Photolysis of indan-1,2,3-trione (**1a**) in 20% O₂-doped Ar matrix at 10 K. (a) Calculated (B3LYP/6-31G(d)) spectra of **1a**. (b) Difference IR spectrum between the photoproduct formed after 0.5 h of irradiation ($\lambda > 310$ nm) of **1a** (negative peaks) and before irradiation (positive peaks). (c, d, e, and f) Calculated (B3LYP/6-31G(d)) spectra of cyclic peroxide **5a** (c), cyclic anhydride **7a** (d), phthalic anhydride (**8**) (e), and diacylperoxide **9** (f), respectively.

peroxide **5a** formed by trapping the diradical **2a** (Figure 5c), while B and C are assignable to phthalic anhydride **8** (Chart 1 and Figure 5e) and diacylperoxide **9** (Chart 1 and Figure 5f), respectively. Again **7a** is not likely to be produced in this case (Figure 5d). Continued irradiation of the mixture resulted in the

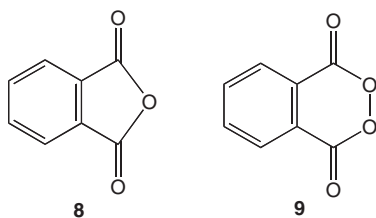


Chart 1.

decrease of the bands ascribable to **5a** with concomitant increase of the bands due to **8** along with CO_2 , suggesting that **5a** undergoes photodecarboxylation to give **8**.

Discussion

The photooxidation of diketones in solution at room temperature have been studied in some detail.¹⁸ A mechanism involving initial formation of the ketone–oxygen adduct as a result of attack of oxygen on to the carbonyl carbon is most frequently proposed. It has been demonstrated that such adduct is detected by using time-resolved UV spectroscopy.¹⁹

Present results demonstrate that acyl–acyl diradicals generated by the type I cleavage of indan-1,2-diones **1** can be trapped by oxygen to form cyclic diacylperoxide **5** when generated in oxygen-doped matrix at low temperature. It has been shown that quantum yields and rate constants for type I α -cleavage of triplet n,π^* states are generally greater than from singlet states if the structure is the same.²⁰ This difference is rationalized by the use of state correlation diagrams.²¹ Thus the nascent diradical should have a triplet state, which is expected to be trapped efficiently by oxygen. Intervention of diacylperoxide **5a** is postulated in the photolysis of indan-1,2,3-trion in solution in the presence of oxygen.^{12a}

The present trapping experiments also provide information concerning reactivities toward α -cleavage in the n,π^* excited state of diketones. It is very difficult to estimate relative reactivities of photodecarbonylation among different runs under matrix conditions since it is difficult to control the concentration of the starting ketones and also the light absorbed by the sample under our experimental conditions (see Experimental section). So, we roughly estimated the trends in the reactivity based on the average amount of photodecarbonylation products per irradiation time formed in the irradiation of indan-1,2-diones **1** in Ar matrix from several runs, which imply that the reactivities toward photodecarbonylation in argon matrix decreased from indan-1,2,3-trion (**1a**) which efficiently gives the decarbonylation products immediately after irradiation, to benzo[*b*]furan-2,3-dione (**1b**) to *N*-methylisatin (**1c**), which produces a very small amount of the decarbonylation products even after prolonged irradiation. In the irradiation in 20% oxygen-doped matrix, all three indan-1,2-diones **1** were found to decrease at a similar rate. It should be noted that product ratios of oxidation vs. decarbonylation are somewhat different. Thus, **1c** gave only oxidation products, while **1a** and **1b** gave both oxidation and decarbonylation products. This order is roughly in the same direction with the strength of the bond that undergoes subsequent cleavage. For instance, the bond strength increases in the order of $\text{MeCO-COMe} < \text{MeCO-OH} < \text{MeCO-NH}_2$.²² This suggests that, even if the

ketones undergo α -cleavage upon photoexcitation, the resulting diradicals undergo recombination to return back to the starting ketones unless the bond undergoing subsequent cleavage is weak.

It has been pointed out that stability of the resulting diradical is an important factor to enhance the photodecarbonylation.²⁰ For instance, 2-indanone, when irradiated in cyclohexane, yields mainly photoreduction products, while 1,3-diphenyl-2-indanone gives a good yield of carbon monoxide under the same conditions.²³ Present observations however suggest that decarbonylation is also affected by the strength of the bond that subsequently undergoes cleavage generating CO.

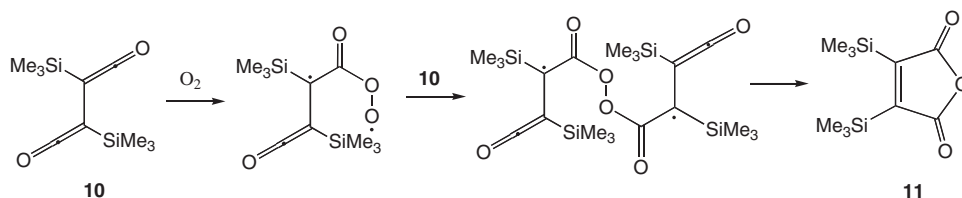
It should be noted here that oxidation products from indan-1,2,3-trion (**1a**) are somewhat different from the others. Thus, not only cyclic peroxide **5a** formed by trapping the diradical but also phthalic anhydride (**8**) and diacylperoxide **9** are formed in this case. Since the latter two types of oxidation products are not formed in the photolysis of the other ketones i.e., **1b** and **1c** in oxygen-doped matrix and since photodecarbonylation products **3a** and **4a** are significantly decreased in the irradiation of **1a** in O_2 -doped matrix, it is likely that the oxidation products **8** and **9** are derived from **3a** and/or **4a**. 1,2-Bis(ketenes) generated by photolysis of 1,2-cyclobutenediones have been shown to react with oxygen to form maleic anhydrides in solution.²⁴ The formation of unsaturated anhydride is also reported in the photolysis of pyracycloquinone in the presence of oxygen, where bis(ketene) is postulated as an intermediate.²⁵ Thus the formation of phthalic anhydride (**8**) can be explained in terms of oxidation of bis(ketene) **3a**, which should be formed from diacyl radical **2a** in competition with quenching by oxygen.

What is the origin for diacylperoxide **9** then? The formation of diacylperoxide is postulated in the photolysis of camphor-quinone but direct addition of oxygen to the quinone carbonyl group rather than the intervention of ketene is proposed in this case.²⁶

A mechanism of oxidation of bis(ketene) forming anhydride proposed by using stable bis(ketene) is interesting in this connection. Bis(ketene) **10** generated from 1,2-bis(trimethylsilyl)-3,4-cyclobutenedione is shown to be stable in the absence of oxygen due to stabilization effect by silylmethyl groups, but reacts with oxygen to give maleic anhydride **11**. A proposed mechanism includes initial attack of oxygen on the carbonyl carbon of ketene group to generate diradical, oxygen radical of which then attacks carbonyl carbon of another ketene group.²⁷ This is mainly because these bis(ketenes) have transoid form and hence the oxygen radical cannot undergo intramolecular attack of adjacent ketene carbonyl oxygen (Scheme 6).

The situation is completely different for bis(ketene) **3a** where two ketene groups are fixed on a cyclic framework and hence are expected to undergo trapping by oxygen relatively easily leading to **9**.

Finally it is worth noting that the rate of photodecomposition of **1** was markedly increased in the O_2 -doped matrix compared to that in the undoped matrix. This may be partly due to the intervention of the quenching pathway of the diradical by oxygen. However, apparent formation of **3c** in the photolysis of **1c** in relatively short irradiation time in the presence of oxygen may indicate that the photodecomposition process itself is



Scheme 6.

accelerated by oxygen. Oxygen is known to enhance the overall $S_1 \rightarrow T_1$ process.²⁰ Thus, in the presence of oxygen, the intersystem crossing efficiency of initially generated singlet state to the triplet is accelerated, which results in the increase in population of the triplet n, π^* state from which α -cleavage of the ketones takes place.

Conclusion

The present observation reveals that photolysis of ketones in oxygen-doped matrix at low temperature provides useful information concerning the reactivities of ketones toward type I cleavage. It has been suggested that even a ketone which appears completely inert toward the cleavage may be analyzed by employing this method.

Experimental

General Methods. ¹H NMR and ¹³C NMR spectra were recorded on a Varian GEMINI 200 FT/NMR spectrometer in CDCl₃ with Me₄Si as an internal reference. IR spectra were measured on a Shimadzu FTIR-4800S spectrometer, and UV-vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. The mass spectra were recorded on a Hitachi MS-80B mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO model HLC-01 instrument. The GPC column was a Shodex H-2001. Thin-layer chromatography was carried out on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was performed on silica gel (Nacalai tesque) for column chromatography.

Indan-1,2,3-trione (1a). **1a** was prepared by heating ninhydrin at 120 °C for a few hours under reduced pressure and was purified by sublimation as dark reddish-violet needles, yield 93%, mp 254–255 °C, Lit. mp 255 °C;²⁸ ¹H NMR (CDCl₃): δ 8.24–8.18 (m, 2H), 8.12–8.06 (m, 2H); IR (KBr) $\nu_{\max}$ (cm⁻¹): 1771, 1740, 1711; IR (Ar, 10 K) ν (cm⁻¹): 1774 (m), 1751 (s), 1729 (s), 1600 (m), 1239 (m), 1228 (m), 979 (m), 750 (m); UV $\lambda_{\max}$ (CH₂Cl₂) nm (ϵ /M⁻¹ cm⁻¹): 335.5 (2419), 327.5 (2350), 258.0 (19619). MS m/z 160 [M]⁺.

Benzo[b]furan-2,3-dione (1b). To a solution of isatin (1.47 g, 0.01 mol) in 1 M aqueous sodium hydroxide (150 mL) was added sodium nitrite (0.7 g) and the mixture was stirred under cooling with an ice bath. To the cold solution, 15 mL of 2.5 M sulfuric acid was added slowly. The solution was stirred for 10 min and then warmed to 60 °C and allowed to stand for 1 h with occasional shaking. The solution was filtered from activated charcoal (0.1 g) and extracted with ethyl acetate (30 mL). Drying and removal of the solvent left crude 2-hydroxyphenylglyoxylic acid. The entire preparation of acid was dissolved in 30 mL of benzene and 20 mL of heptane. Phosphorus pentoxide (1.5 g) was added and the mixture was refluxed for 30 min. The solution was filtered and evaporated to 5 mL. Addition of heptane produced a yellow solid. Recrystallization from benzene–heptane gave **1b**, yield 46%, mp 128–130 °C, lit. 132 °C;²⁹ ¹H NMR (CDCl₃): δ 8.12 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.61 (dd, J = 8.0 Hz, J = 2.0 Hz,

1H), 7.05 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H), 6.99 (dd, J = 8.0 Hz, J = 2.0 Hz, 1H); IR (KBr) $\nu_{\max}$ (cm⁻¹): 1741 (s), 1618 (s). IR (Ar, 10 K) ν (cm⁻¹): 1832 (s), 1753 (s), 1616 (s), 1466 (m), 1325 (m), 1300 (m), 1070 (m), 1062 (m), 856 (m). UV $\lambda_{\max}$ (CH₂Cl₂) nm (ϵ /M⁻¹ cm⁻¹): 360 (2140), 287.0 (10200). MS m/z 148 [M]⁺.

1-Methylisatin (1c). Sodium hydride (0.48 g, 12 mmol) free from mineral oil was added to isatin (1.47 g, 10 mmol) in DMF (20 mL) under an inert atmosphere. After stirring for 30 min, a solution of methyl iodide (0.68 g, 11 mmol) in DMF (2 mL) was added and the solution was stirred at room temperature for 1 h to give a dark red solution. The reaction was quenched by careful addition of water (30 mL) and was extracted with dichloromethane. The dichloromethane layer was washed with distilled water. After drying the dichloromethane layer and removal of solvent, the residue was purified by column chromatography. 1-Methylisatin (**1c**) was recrystallized from ethanol as yellowish solid, yield 95%, mp 132–133 °C. Lit. 132–134 °C;³⁰ ¹H NMR (CDCl₃): δ 7.65 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.60 (td, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.14 (td, J = 7.8 Hz, J = 1.6 Hz, 1H), 6.92 (dd, J = 7.8 Hz, J = 1.6 Hz, 1H); IR (KBr) $\nu_{\max}$ (cm⁻¹): 1747, 1725; IR (Ar, 10 K) ν (cm⁻¹): 1751 (s), 1641 (s), 1475 (m), 1371 (m), 1331 (m), 1159 (w), 1117 (m), 1009 (w), 754 (m) cm⁻¹. UV $\lambda_{\max}$ (CH₂Cl₂) nm (ϵ /M⁻¹ cm⁻¹): 426.5 (820), 299.0 (3620), 242.5 (29760). MS m/z 161 [M]⁺.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques^{31,32} using a closed-cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fitted with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and a quartz outer window were used. The temperature of the matrix was maintained by a controller (gold vs. chromel thermocouple).

All the samples used in this study were not easily vaporized and hence were directly deposited on the window from a glass tube equipped with a ceramic heater under the stream of argon. Therefore, the concentration of the sample on the window was different at each run.

Irradiations were carried out with a 500-W xenon high-pressure arc lamp. For broad-band irradiation, cutoff filters were used (50% transmittance at the specified wavelength). For monochromatic light irradiation, a monochromator was used.

Computational Procedures. DFT calculations were carried out using the Gaussian 94,³³ programs. Optimized geometries were obtained at the B3LYP/6-31G(d)³⁴ levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.³⁵ Transition states were located using Gaussian program (Rational Function Optimization-pseudo-Newton-Raphson method).³⁶ The nature of each stationary point was confirmed with harmonic frequency calculations, i.e., minima have exactly one imaginary frequency related to the expected movement.

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Supporting Information

Supporting Information is expanded version of Figure 4 and plot of the intensity of absorption bands due to cyclic peroxide **5a**, phthalic anhydride (**8**), and CO as a function of irradiation time. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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