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Photochemistry of 1,3-Bis(diazo)indan-2-one: Consecutive Decomposition and Suppression of a Wolff Rearrangement

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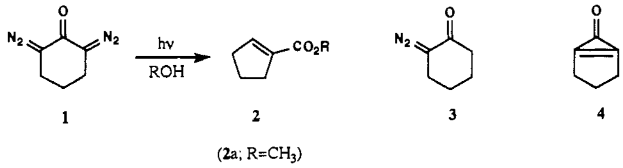
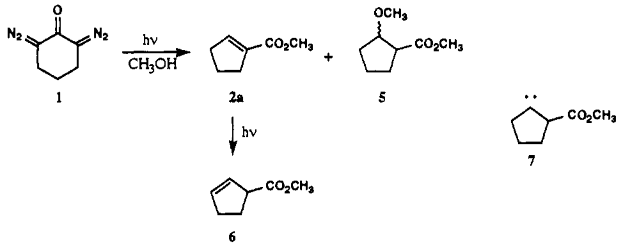
Abstract: The photodecomposition processes of 1,3-bis(diazo)indan-2-one (**19**) have been investigated by the characterization of reaction products in fluid solutions and by the direct observation of reactive intermediates in matrices at cryogenic temperatures. Irradiation of **19** in methanol gave the acetal **22**. The isolation and spectroscopic detection of intermediate photoproducts revealed that **22** was formed through the diazo ketone **24** and then the benzocyclobutene **26**. In benzene, the bis(norcaradiene) **29** was formed via the diazo ketonorcaradiene **30**. In a benzene–methanol binary solvent, a mixture of **22**, **29**, and the products derived from the photoreaction of **30** with methanol was obtained. All these products originated from the diazo ketocarbene **25**, the methanol insertion–benzene addition selectivity of which was estimated to be 0.7–0.9. The diazo ketocarbene **25** was formed by irradiation of **19** matrix-isolated at cryogenic temperatures and characterized by ESR and IR spectroscopy. Further irradiation of **25** in an Ar matrix at 10 K resulted in a Wolff rearrangement to give the diazo ketene **49**, which was converted photolytically to the cyclopropenone **20**. The cyclopropenone **20** was unreactive under short-wavelength irradiation. Thus, the synthesis of benzocyclobutenyne (**21**) was not successful. In the presence of 20% O_2 in an Ar matrix, **25** was completely trapped to give 1-diazoindan-2,3-dione (**51**). In this manner, the intermediacy of the diazo ketocarbene **25** in the photoreaction of **19** in matrices, as well as in fluid solutions, was clearly established. All these observations imply that the two diazo groups of **19** are cleaved consecutively, and that a Wolff rearrangement is suppressed in the photolytic decomposition of the first diazo group of **19**. The reason for the retardation of the rearrangement is discussed on the basis of the stereoelectronic effect of the rigid five-membered ring and the partial double-bonding character of the CO–CN_2 bond.

In 1959, Kirmse reported that irradiation of 2,6-bis(diazo)cyclohexanone (**1**) in alcoholic solutions produced cyclopentene-1-carboxylic acid derivatives **2**.[1,2] Though he explained the result through a Wolff rearrangement, several reaction paths could be considered in this ring contraction process. If the two diazo groups of **1** decomposed consecutively, the first-formed reactive intermediate would be diazo ketocarbene **3**,[3] which could react in the following four manners: Wolff rearrangement to a diazo ketene, 1,2-hydrogen migration, OH insertion with solvent, and intramolecular interaction with another diazo group to give the cyclopropenone **4**. All these routes could be candidates for the reaction pathway to the final product **2**. Moreover, the possibility of the simultaneous decomposition of the two diazo groups of **1** to produce the cyclopropenone **4** directly or the 1,3-dicarbene should be considered.[4] Thus, the involvement of various reactive intermediates and the diversity of their reactivities make it quite difficult to understand the mechanism of the photodecomposition processes of 1,3-bis(diazo) ketones. Though two reports dealing with 1,3-bis(diazo) ketones from a synthetic point of view appeared after that,[5] no mechanistic studies were reported until Trost and Whitman presented detailed results of the photolytic decompositions of 2,6-bis(diazo)cyclohexanone (**1**) in 1974.[6] They reported that irradiation of a methanolic solution of **1** at −40 °C produced predominantly methyl cyclopentene-1-carboxylate (**2a**) with a small amount of methyl 2-methoxycyclopentanecarboxylate (**5**) and that the former could isomerize to the unconjugated ester **6** under conditions of photolysis. Based on a detailed discussion of the reactivities of diazo ketocarbene **3** and β-(methoxycarbonyl)carbene **7**, which were supposed as precursors of **2a**, they excluded the mechanism involving a simple Wolff rearrangement and proposed the intermediacy of the cyclopropenone **4** in a pathway to **2a**. However, the involvement of intermediate **4** in the photolytic decompositions of **1** is quite questionable, because all attempts to isolate or trap **4** were unsuccessful, and diphenylcyclopropenone (**8**), which was isolated in the irradiation of 1,3-bis(diazo)-1,3-diphenyl-2-propanone (**9**) at visible light, was unable to be a precursor of methyl 2,3-diphenyl-3-methoxypropionate (**10**) and methyl *trans*-α-phenylcinnamate (**11**), which





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(1) Kirmse, W.; Horner, L.; Muth, K. Unpublished work, see: Kirmse, W. *Angew. Chem.* **1959**, *71*, 539.

(2) An analogous result was reported in the photolysis of 2,6-bis(diazo)-4-*tert*-butylcyclohexanone in ethanol: Tasovac, R.; Stefanović, M.; Stojiljković, A. *Tetrahedron Lett.* **1967**, 2729.

(3) For reviews of reactivities of α-ketocarbenes, see: (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; p 475. (b) Moss, R. A., Jones, M., Eds. *Carbenes*; Wiley: New York, 1973; Vol. I, p 117. (c) Meier, H.; Zeffer, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

(4) (a) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147. (b) Sugawara, T.; Inada, M.; Iwamura, H. *Tetrahedron Lett.* **1983**, *24*, 1723.

(5) (a) Cava, M. P.; Glamkowski, E. J.; Weintraub, P. M. *J. Org. Chem.* **1966**, *31*, 2755. (b) Borch, R. F.; Fields, D. L. *J. Org. Chem.* **1969**, *34*, 1480.

(6) Trost, B. M.; Whitman, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7421.

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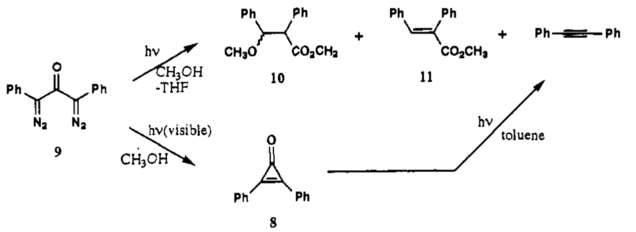
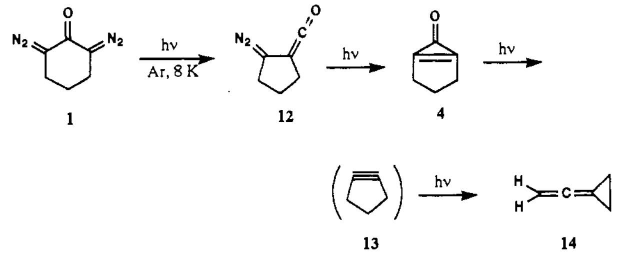


9 10 11 8

were the products in the photolysis of **9** in a methanol-tetrahydrofuran solution.[6] Thus, the mechanism of the photolytic decomposition processes of 1,3-bis(diazo) ketones still remains to be established.

On the other hand, bis(diazo) ketones have been of interest as intermediates for the synthesis of cyclopropenones, acetylenes,[6,7] and carbon oxides (C_nO_m).[8] In 1981, Chapman and his co-workers presented a pioneering work on the synthesis of the strained acetylenes by the photolysis of 1,3-bis(diazo) ketones.[7] They reported that irradiation of **1** in an Ar matrix gave diazoketene **12** and then cyclopropenone **4**. Though continued irradiation of **4** resulted in decarbonylation, they could not observe the IR spectrum of cyclopentyne (**13**) because of its rapid isomerization to vinylidenecyclopropane (**14**). They succeeded, however, in the synthesis of acenaphthyne (**15**) through the decarbonylation of the cyclopropenone **16** that was formed by the irradiation of 1,3-bis(diazo)-1,2-dihydrophenalen-2-one (**17**). The analogous pathway for the synthesis of cyclobutyne (**18**) should be quite challenging, but in spite of the theoretical prediction of the vibrational frequencies of **18**,[9] no attempt has been reported to synthesize **18** and its derivatives in frozen matrices.[10]



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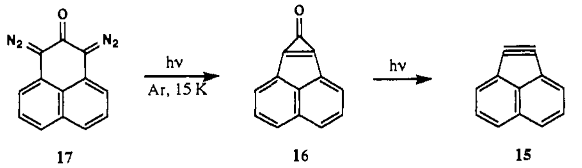

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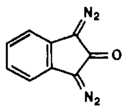

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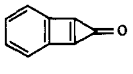

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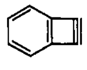

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Thus, we have been interested in the photochemistry of 1,3-bis(diazo)indan-2-one (**19**), which is the first 1,3-bis(diazo) ketone, one ketone and two diazo groups of which are incorporated in a five-membered ring, and is a potential precursor of unknown, highly strained compounds, e.g., the cyclopropenone **20** and benzocyclobutenyne (**21**). In this paper, we wish to report our detailed studies of the photochemical reactions of **19** in fluid solutions and in matrices,[11] where the consecutive decomposition of the two diazo groups and the retardation of a Wolff rearrangement in the first stage of the photolytic decomposition process could be established.

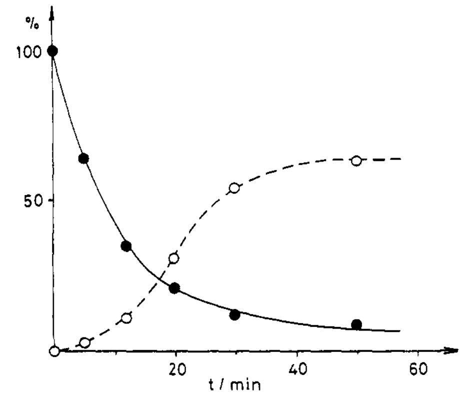


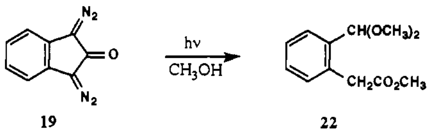
Figure 1. Change in the proportion of the material **19** (●) and the product **22** (○) with irradiation time in the photoreaction in methanol.

Results and Discussion

Preparation of 1,3-Bis(diazo)indan-2-one (19). We could obtain **19** in 47% yield by the acid-catalyzed reaction of indan-2-one with isopentyl nitrite, followed by treatment of the resulting bisoximino ketone with an alkaline chloramine solution. Purification was achieved by silica gel column chromatography with dichloromethane, followed by recrystallization from hexane-ethanol. Further purification was accomplished by sublimation under 10^{-6} Torr at ca. 40 °C to give bright orange-red needles, which decomposed at 127 °C.

The IR spectrum, measured in a KBr disk, showed a medium intensity absorption at 2100 cm^{-1} and a very strong absorption at 2080 cm^{-1}, both of which were assigned to diazo stretching vibrations. The carbonyl stretching band with a medium intensity appeared at 1645 cm^{-1}. The splitting of the diazo stretching band into a doublet and the appearance of the carbonyl absorption band at the lower wavenumber are known as the important features of the IR spectrum of 1,3-bis(diazo) ketones.[5a,6]

Photoreactions of 1,3-Bis(diazo)indan-2-one (19) in Methanol. Irradiation of **19** in methanol with a high-pressure mercury lamp exclusively afforded methyl *o*-(dimethoxymethyl)phenylacetate (**22**, 69%). The acetal structure of **22** was characterized by its ^1H NMR spectrum and confirmed by the hydrolysis to methyl *o*-formylphenylacetate. The change in the proportion of the material **19** and the product **22** with irradiation time was examined by GC. The result shown in Figure 1 displays the presence of the induction period in the formation of **22**, which strongly suggests that **22** is not a primary photoproduct of **19**.



19 22

In order to reveal the mechanism of the formation of **22**, we tried to isolate the intermediates. At first, the photolysis was stopped at the early stage of the reaction, and the reaction mixture was examined by ^1H NMR spectroscopy after the rapid removal

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(7) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033.

(8) (a) Maier, G.; Reisenauer, H. P.; Schäfer, U.; Balli, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 566. (b) Maier, G.; Reisenauer, H. P.; Balli, H.; Brant, W.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 905.

(9) Fitzgerald, G.; Saxe, P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1983**, *105*, 690.

(10) Attempts to generate a cyclobutyne derivative in solution were unsuccessful: (a) Montogomery, L. K.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 4750. (b) Wittig, G.; Wilson, E. R. *Chem. Ber.* **1965**, *98*, 451.

(11) For preliminary reports of the photochemistry of **19**, see: (a) Lee, H. K.; Kim, H. R.; Tomioka, H. *Bull. Korean Chem. Soc.* **1988**, *9*, 399; *Chem. Abstr.* **1989**, *111*, 133742a. (b) Murata, S.; Yamamoto, T.; Tomioka, H.; Lee, H. K.; Kim, H. R.; Yabe, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1258.

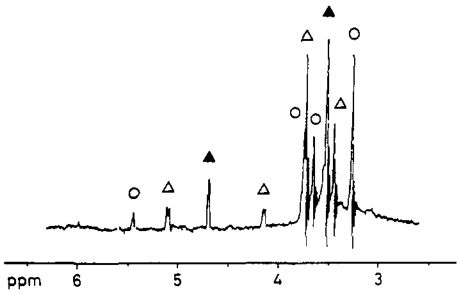


Figure 2. ^{1}H NMR spectrum in $CDCl_3$ of the photoreaction mixture obtained after irradiation of **19** in methanol. The conversion of **19** was ca. 50%. The signals marked with ▲, △, and ○ are due to the intermediates A (= **24**) and B (= **26**) and the final product **22**, respectively.

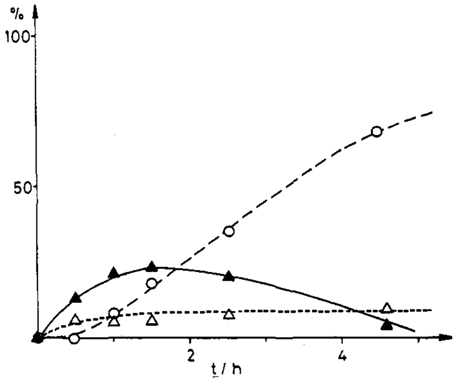
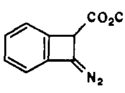


Figure 3. Change in the proportion of the photoproducts of **19** in methanol with irradiation time, which was estimated on the basis of the relative intensity of the methine peaks in the ^{1}H NMR spectrum of the photoreaction mixture: A (= **24**) (▲) δ 4.80; B (= **26**) (△) δ 5.10; **22** (○) δ 5.44.

of the solvent at low temperature. Figure 2 shows the spectrum of the reaction mixture obtained after irradiation of **19**, the conversion of which was estimated to be ca. 50% by GC. The signals marked with open circles in Figure 2 are unambiguously due to the final product **22**. By following the change in intensity of the signals with irradiation time (Figure 3), we were able to identify two other independent reaction components. The concentration profile shown in Figure 3 exhibits that the first-formed intermediate should be the product A, with the signals marked with full triangles in Figure 2, and that between A and the final product **22**, there is another intermediate B, exhibiting the signals with the open triangles, with a low steady concentration.

After chromatographic separation of the reaction mixture, the first intermediate A could be isolated, though it could not be completely purified. In its ^{1}H NMR spectrum, the methoxy signal and the methine signal appeared at δ 3.56 and 4.80, respectively, and in the IR spectrum, the diazo and the carbonyl stretching absorptions were observed at 2090 and 1695 cm^{-1}, respectively. We could exclude the presence of an ester group in A, because of the lower wavenumber of the carbonyl stretching band than that expected for an ester group and the absence of intense absorptions in the range of 1100–1300 cm^{-1}, where an ester group should show a C–O stretching band. Methyl 2-diazobenzocyclobutene-1-carboxylate (**23**) as a possible structure for A was



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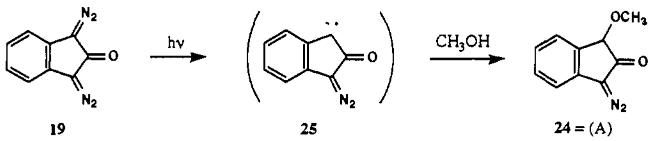
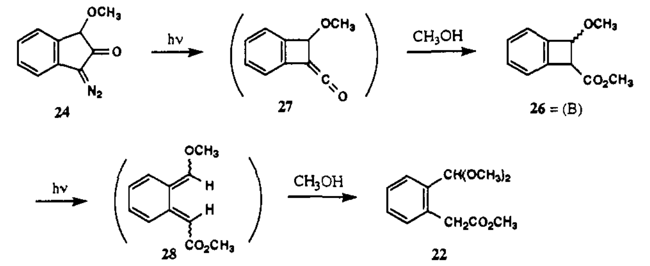
ruled out based on the above discussion. Thus, we identified the first intermediate A as 1-diazo-3-methoxyindan-2-one (**24**). The spectroscopic data are in agreement with this structure, and the formation of diazo ketone **24** is rationalized by the OH insertion of the diazo ketocarbene **25** with methanol (Scheme I). The intermediacy of **24** in the formation of the final product **22** was confirmed by the fact that an independent irradiation of **24** in methanol exclusively yielded **22**.

Scheme I



Scheme II



Attempts to isolate the second intermediate B were not successful at the present stage, but on the basis of its NMR spectrum, the intermediate B was tentatively identified as methyl 2-methoxy-1,2-dihydrobenzocyclobutene-1-carboxylate (**26**). In the ^{1}H NMR spectrum of the photoreaction mixture (Figure 2), the intermediate B showed two methoxy signals at δ 3.47 and 3.75 and two methine doublets centered at δ 4.16 and 5.10. This spectrum is in complete accord with the proposed structure, though we could not determine the geometric configuration by a coupling constant of 3 Hz. Furthermore, the photolability of B shown in Figure 3 supports the benzocyclobutene structure, since the photochemical cleavage of benzocyclobutene derivatives in alcoholic solutions is known.[12] In Scheme II is summarized the mechanism explaining the formation of the final product **22** from the diazo ketone **24** through the benzocyclobutene intermediate **26**. The photolysis of **24** causes an extrusion of dinitrogen, followed by a Wolff rearrangement to give the methoxy ketene **27**, which is immediately captured by the solvent to afford **26**. Subsequently, the conjugate addition of methanol to the *o*-quinodimethane **28**, which is thought to be formed photochemically from the benzocyclobutene **26**, produces the final product **22**.

Thus, the route from the bis(diazo) ketone **19** to the final acetal **22** can be revealed (Schemes I and II). We should emphasize the following three points concerning these schemes. First, as shown in Figure 3, the reaction components are formed sequentially, which indicates that the two diazo groups of the bis(diazo) ketone **19** decompose stepwise to give the diazo ketocarbene **25** as the first-formed transient intermediate. Second, **25** does not undergo Wolff rearrangement but inserts into the OH bond of methanol. On the other hand, the photolysis of the α-methoxy diazo ketone **24** affords the ring contraction product **26** through a Wolff rearrangement. A detailed discussion concerning a retardation of rearrangement in **25** is given in a subsequent section. Finally, there is no evidence for an involvement of the cyclopropenone **20** or benzocyclobutenyne (**21**) in this photoreaction.

Photoreactions of 1,3-Bis(diazo)indan-2-one (19) in Benzene. A solution of **19** in dry benzene was irradiated with a high-pressure mercury lamp. After separation by chromatography, two reaction products were obtained together with the unchanged starting material (11%). The main product was identified as the bis(norcaradiene) **29** (51%). The ^{1}H NMR spectrum of **29** showed three sets of multiplets centered at δ 3.20, 6.11, and 6.49, which

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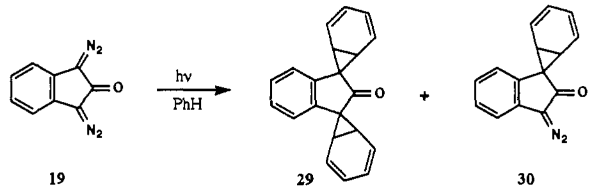
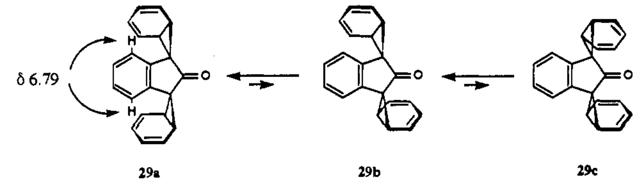
[12] (a) Staab, H. A.; Ipaktschi, J. *Tetrahedron Lett.* **1966**, 583. (b) Cava, M. P.; Spangler, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 4550. (c) Spangler, R. J.; Henscheid, L. G.; Buck, K. T. *J. Org. Chem.* **1977**, *42*, 1693. (d) Spangler, R. J.; Kim, J. H.; Cava, M. P. *J. Org. Chem.* **1977**, *42*, 1697.



are characteristic of norcaradiene structures,[13] and only two kinds of aromatic protons, one of which appeared in a highly shielded area (δ 6.79). Moreover, no other signals were detected in the ^{1}H NMR spectrum recorded at −90 °C. These data imply that **29** was present exclusively in the bis-endo conformation as depicted in **29a**, excluding the presence of the endo-exo **29b** and



the bis-exo conformation **29c**. Norcaradiene is well known to be in equilibrium with cycloheptatriene, and structural factors to shift this valence tautomerism toward norcaradiene have been presented.[14] Though it is known that substitution of a π-acceptor group at the 7-position in cycloheptatriene shifts the equilibrium to a norcaradiene form, the reason why the equilibrium lies exclusively to the bis-*endo*-norcaradiene in the case of **29** cannot be satisfactorily explained at the present stage.

The second photoproduct, which showed an intense diazo stretching band at 2080 cm^{-1} in the IR spectrum, was identified as the diazo ketonorcaradiene **30** (21%). The ^{1}H NMR spectrum of **30** resembled that of **29**, except that it showed four kinds of aromatic protons. The presence of a shielded proton at δ 6.73 indicated that the norcaradiene **30** also existed in the endo conformation. The concentration profile of the products with increasing irradiation time shown in Figure 4 exhibits that **29** was formed from the irradiation of **30**, which was a primary photolysis product of **19**. This speculation was supported by the observation that an independent photolysis of **30** in dry benzene exclusively afforded **29**.

The facile isolation of norcaradiene derivatives formed in the photolysis of diazo ketones in benzene is quite unusual. In general, the irradiation of diazo ketones in benzene gives a complex mixture from which nothing can be identified, except for carboxylic acids, which are formed by the reaction of the ketene generated through a Wolff rearrangement with a contaminating water. It has been reported, however, that irradiation of a benzene solution of diazo ketones, which generates the ketocarbene reluctant to undergo a Wolff rearrangement, gives an adduct of the ketocarbene with benzene.[15-17] The route from the bis(diazo) ketone **19** to the bis(norcaradiene) **29** is illustrated by Scheme III. Irradiation of **19** gives the diazo ketocarbene **25**, which is captured by benzene to afford the diazo ketonorcaradiene **30**. The subsequent photodecomposition of **30** produces the ketocarbene **31**, which reacts with benzene again to give the final product **29**. In the photoreaction in benzene, it should be noted that the two diazo groups of the bis(diazo) ketone **19** decompose consecutively as indicated in the photoreaction in methanol and that the intermediate ketocarbenes **25** and **31** are reluctant to undergo a Wolff rearrangement. However, even if the ketocarbenes **25** and **31** rearranged to the corresponding ketenes, they could not be captured by benzene but could polymerize to yield a tar. Thus, in order to examine the possibility of a Wolff rearrangement in the photoreaction in benzene, we carried out the photoreaction in a benzene–methanol binary solvent.

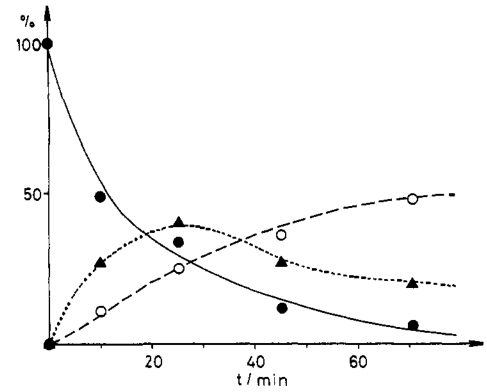


Figure 4. Change in the proportion of the material **19** (●) and the products **29** (○) and **30** (▲) with irradiation time in the photoreaction in benzene.

Photoreaction of 1,3-Bis(diazo)indan-2-one (19) in a Benzene–Methanol Binary Solvent. A solution of **19** in benzene containing 5% (v/v) methanol was irradiated with a high-pressure mercury lamp. When ca. 90% of the starting material was consumed, the reaction mixture was examined by GC. Methyl *o*-(dimethoxymethyl)phenylacetate (**22**) and bis(norcaradiene) **29** were obtained in 7% and 32% yield, respectively, together with diazo ketonorcaradiene **30**. Thus, the products obtained in dry benzene were mainly formed in benzene containing a small amount of methanol. This result strongly suggested that a Wolff rearrangement was retarded in the first-formed carbene **25**, which underwent addition to benzene in competition with insertion into the OH bond of methanol. Even in a 1:1 (v/v) binary mixture of benzene and methanol, irradiation of **19** gave a considerable amount of **29** and **30** (6% and 12%, respectively), which implied that the reactivity of **25** with benzene was comparable to that with methanol (vide infra).

In the reaction mixture resulting from the photolysis of **19** in a benzene–methanol binary solvent, several kinds of additional products were detected, each of which had a molecular weight equal to the sum of the molecular weights of the dicarbene generated from **19**, methanol, and benzene. We concluded that these products were derived from the photoreaction of diazo ketonorcaradiene **30** with methanol, because an independent irradiation of **30** in methanol equally gave a mixture of these products while no identifiable products were formed by the photolysis of 1-diazo-3-methoxyindan-2-one (**24**) in dry benzene. The assignment of the structures of these products will be presented in a following section.

The product distribution in the photoreaction in a benzene–methanol binary system is summarized in Table I, where X stands for a mixture of products derived from the photoreaction of **30** with methanol as described above. The possible reaction scheme for the formation of the products in a binary solvent is shown in Scheme IV. It is thought that all products originate from the diazo ketocarbene **25**, which either undergoes insertion into the O–H bond of methanol or adds to the π electron of benzene.

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[13] (a) Ciganek, E. *J. Am. Chem. Soc.* **1965**, *87*, 652. (b) Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1454.

[14] For reviews, see: (a) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 402. (b) Takeuchi, K. *Yuki Gosei Kagaku Kyokaishi* **1985**, *43*, 40. See also: (c) Takeuchi, K.; Arima, M.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 3081. (d) Takeuchi, K.; Fujimoto, H.; Kitagawa, T.; Fujii, H.; Okamoto, K. *J. Chem. Soc., Perkin Trans. II* **1984**, 461. (e) Takeuchi, K.; Kitagawa, T.; Ueda, A.; Senzaki, Y.; Okamoto, K. *Tetrahedron* **1985**, *41*, 5455. (f) Schwager, M.; Wilke, G. *Chem. Ber.* **1987**, *120*, 79. (g) Hannemann, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 284.

[15] (a) Bannerman, C. G. F.; Cadogen, J. I. G.; Gosney, I.; Wilson, N. H. *J. Chem. Soc., Chem. Commun.* **1975**, 618. (b) Chang, S.-J.; Ravi Shankar, B. K.; Shechter, H. *J. Org. Chem.* **1982**, *47*, 4226.

[16] (a) Trost, B. M.; Kinson, P. L. *Tetrahedron Lett.* **1973**, 2675. (b) Trost, B. M.; Kinson, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 2438.

[17] The ketocarbenes photolytically generated from ethyl diazoacetate and methyl (*p*-nitrophenyl)diazoacetate also give adducts with benzene: (a) Schenel, G. O.; Ziegler, H. *Justus Liebigs Ann. Chem.* **1953**, *584*, 221. (b) Tomioka, H.; Hirai, K.; Tabayashi, K.; Murata, S.; Izawa, Y.; Inagaki, S.; Okajima, T. *J. Am. Chem. Soc.* **1990**, *112*, 7692.

Scheme III

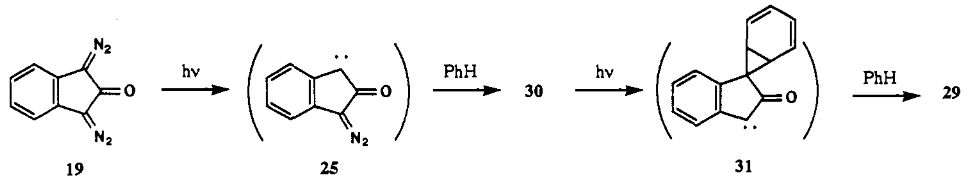


Table I. Photoproducts of **19** in a Benzene–Methanol Binary System

	yield (%)[b]			
PhH:CH₃OH[a]	**22**	**29**	**30**	X[c]
100:0		51	21	
95:5	7	32	10	38
50:50	61	6	12	12
0:100	69			

[a] v/v. [b] Determined by GC. [c] See text.

Assuming that Scheme IV is correct, the OH insertion–benzene addition selectivity ($k_{\mathrm{ins}}/k_{\mathrm{add}}$) of **25** can be estimated. The selectivity is calculated by eq 1, where p_i and p_a are the moles

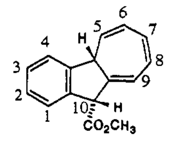
$$k_{\mathrm{ins}}/k_{\mathrm{add}} = (p_i/p_a) \times (I_a/I_i) \tag{1}$$

of the products derived from **24** and **30**, and I_i and I_a are the initial moles of methanol and benzene, respectively. The value p_i/p_a can be regarded as the ratio of **22** to the sum of **29**, **30**, and X, which is obtained from Table I. Thus, we obtain the insertion–addition selectivity of **25** as $k_{\mathrm{ins}}/k_{\mathrm{add}} = 0.7$ for a 95:5 binary solvent ($I_a/I_i = 8.7$), which agrees fairly with the value of 0.9 for a 50:50 binary solvent ($I_a/I_i = 0.46$).[18] This agreement between the values obtained from the two different binary solvents appears to justify the reaction mechanism shown in Scheme IV.

Photoreaction of the Diazo Ketonorcaradiene 30 in Methanol. In order to identify the products expressed as X in the previous section, irradiation of **30** in methanol was carried out on a preparative scale. A solution of **30** in methanol was irradiated with a high-pressure mercury lamp. After separation by chromatography, a number of products, which could be classified into three categories on the basis of their structures, were obtained. The first photoproduct was identified as methoxy ketonorcaradiene **32**. The ^{1}H NMR spectrum of **32** showed the methoxy and methine protons at δ 3.59 and 4.88, respectively, together with three sets of multiplets, which are characteristic of norcaradiene structures, and a shielded aromatic proton at δ 6.81. The formation of **32** is rationalized by the insertion of the ketocarbene **31** photolytically generated from **30** into the OH bond of methanol (Scheme V).

The photoproducts in the second category were assigned to the cyclohepta[*a*]naphthalen-6-ols, the ^{1}H NMR spectrum of which showed the presence of two isomers, **33** and **34**, in a 2.7:1 ratio (Scheme VI). In the ^{1}H NMR spectrum, each isomer exhibited a set of signals due to the partial structure —CH$_2$CH═CHCH═CH—. The methylene protons for the major and minor isomer appeared at δ 3.19 and 3.31, respectively, and the terminal olefinic proton for the major and minor isomer appeared at δ 7.89 and 7.64, respectively. Taking into account the magnetic anisotropy of the adjacent aromatic ring, we tentatively assigned the major isomer to 7*H*-isomer **33** and the minor to 11*H*-isomer **34**. It was revealed that **33** and **34** were derived from the ketonorcaradiene **32**, because an independent irradiation of **32** in methanol with a high-pressure mercury lamp afforded a mixture of **33** and **34**. The formation of **33** and **34** is possibly explained in terms of the photochemical [1,2]-carbonyl migration, followed by enolization and a hydrogen shift to form a naphthalene ring (Scheme VI).[19] We could not detect the possible intermediate **35** involved in the proposed reaction scheme. This result was not surprising because the isomerization of **35** to **33** and **34** would proceed smoothly to gain an aromatization energy.

The third category of the photoproducts contained four compounds, three of which were identified as the dihydrobenz[*a*]azulene isomers **36**–**38**. The ^{1}H NMR spectrum of **36** resembled that of **37** very closely, except that **36** showed the broad methine proton at the 4b-position and the olefinic proton at the 5-position split into a doublet of doublets at δ 3.48 and 5.23, respectively, while **37** showed these protons at δ 3.73 and 5.61, respectively. Thus, we assigned **36** and **37** to the epimers of methyl 4b,10-dihydrobenz[*a*]azulene-10-carboxylate, and **36** was tentatively assigned as the cis isomer by considering the effect of magnetic anisotropy of the methoxycarbonyl group at the 10-position on the chemical shift of the 4b-proton. The isomer **38** was identified as methyl 9,10-dihydrobenz[*a*]azulene-10-carboxylate, the ^{1}H NMR of which showed the methylene doublet at the 9-position and the terminal olefinic proton at the 5-position split into a doublet at δ 2.90 and 7.02, respectively. The formation of **36**–**38** is possibly interpreted as shown in Scheme VII. Photolysis of **30** in methanol gives **39** through a Wolff rearrangement and the subsequent capture of the resulting ketene with methanol. The norcaradiene **39** isomerizes to the cycloheptatriene **40**, which affords the *o*-quinodimethane derivative **41**. The ring closure to **42**, followed by the photochemical hydrogen migration, gives the final products **36**–**38**.[20] The fourth compound in this category, which had a deep blue color, was assigned to methyl benz[*a*]azulene-10-carboxylate (**43**)[21] (Scheme VIII), the formation of which was rationalized in terms of dehydrogenation of **36**–**38** by air in the course of photoreaction and separation.



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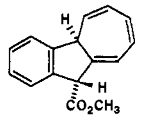

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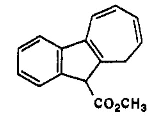

38

The total scheme of the photoreaction of **30** in methanol is summarized in Scheme VIII, and the product distribution is shown in Table II. We should point out that the products **32**–**34** originated from the insertion of the ketocarbene **31** photolytically generated from **30** into the OH bond of methanol, while the products **36**–**38** and **43** were formed via a Wolff rearrangement. Thus, we can roughly estimate OH insertion–Wolff rearrangement

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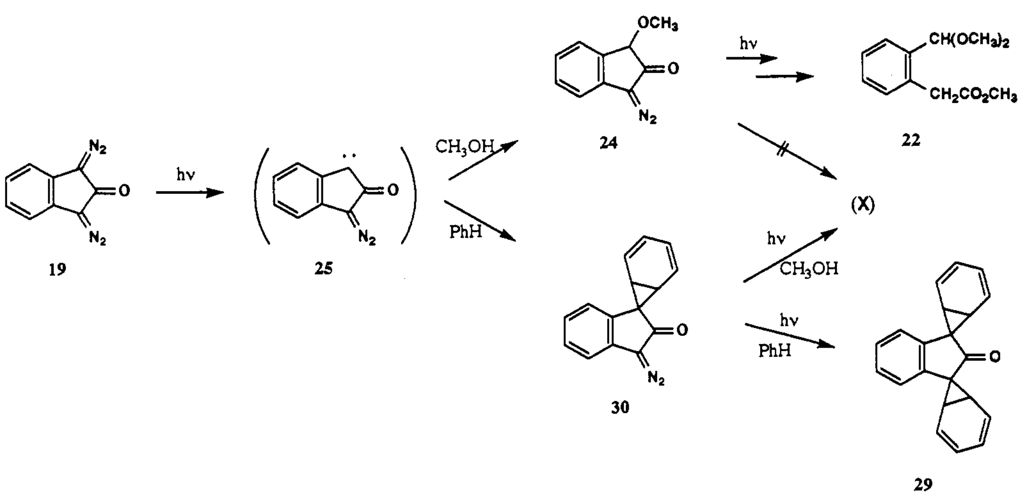
[18] Methanol OH insertion–benzene addition selectivity of the carbene generated from methyl (*p*-nitrophenyl)diazoacetate was reported to be $k_{\mathrm{ins}}/k_{\mathrm{add}} = 13$. Reference 17b.

[19] The analogous photorearrangement of a spironorcaradiene–spirocycloheptatriene equilibrium mixture to a bicyclo[5.4.0]undecapentaene has been reported: (a) Pauly, K.-H.; Dürr, H. *Tetrahedron Lett.* **1976**, 3649. (b) Dürr, H.; Pauly, K.-H.; Fischer, K. *Chem. Ber.* **1983**, *116*, 2855.

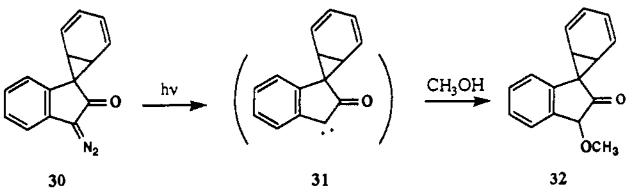
[20] The analogous rearrangement has been reported in the spirocycloheptatriene formed by the thermal decomposition of the sodium salts of benzocyclobutenone tosylhydrazone in benzene. It was also reported that the rearrangement of the 2-methyl derivative occurred more readily than that of the parent molecule and that the resulting 9a,10-dihydrobenz[*a*]azulene was quite photolabile to undergo [1,7]-proton migration: (a) O'Leary, M. A.; Wege, D. *Tetrahedron Lett.* **1978**, 2811. (b) O'Leary, M. A.; Richardson, G. W.; Wege, D. *Tetrahedron* **1981**, *31*, 813.

[21] Nozoe, T.; Yang, P. W.; Wu, C. P.; Huang, T. S.; Lee, T. H.; Okai, H.; Wakabayashi, H.; Ishikawa, S. *Heterocycles* **1989**, *29*, 1225.

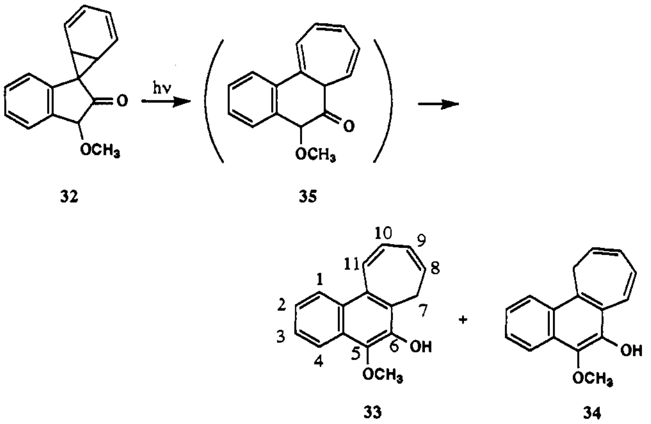
Scheme IV



Scheme V



Scheme VI

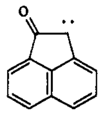


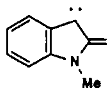
selectivity (k_i/k_r) in the photoreaction of **30** in methanol, which can be regarded as the ratio of **32**–**34** to **36**–**38** and **43**. From Table II, the insertion–rearrangement selectivity obtained is $k_i/k_r = 0.9$. As indicated in the photoreaction of **19** in benzene (Scheme III), the ketocarbene **31**, as well as diazo ketocarbene **25**, is reluctant to undergo a Wolff rearrangement. However, the photoreaction of the diazo ketone **30** in methanol has revealed that on irradiation of **30**, a Wolff rearrangement takes place actually in competition with the OH insertion of the generated ketocarbene **31**.

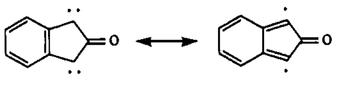
Photochemistry of 1,3-Bis(diazo)indan-2-one (19) at Cryogenic Temperatures. Few reports on the direct observation of α-ketocarbene have been presented.[17b,22] Chapman and his co-workers reported the thorough spectroscopic characterization of α-ketocarbenes generated photolytically from 2-diazoacenaphthen-1-one and its derivatives,[23] which have been known to fail to undergo a Wolff rearrangement photochemically in solution.[15]

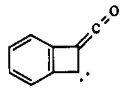
If a Wolff rearrangement is suppressed in the photoreaction of 1,3-bis(diazo)indan-2-one (**19**), as predicted in the preceding sections, it will be possible for the first-formed diazo ketocarbene **25** to be observed spectroscopically in matrices at cryogenic temperatures. Thus, we tried to identify the diazo ketocarbene **25** directly by the use of ESR, IR, and UV–vis spectroscopy.

(1) Detection of Triplet Diazo Ketocarbene 25 by ESR Spectroscopy. A solution of **19** in a 2-methyltetrahydrofuran glass was irradiated with a high-pressure mercury lamp through a Pyrex filter at 18 K. The signals at 50.2, 446.0, 533.3, and 720.2 mT were observed in the X-band ESR spectrum (microwave frequency = 9.314 GHz) together with an intense signal at 333.0 mT, which was due to doublet radicals probably formed from chemical reactions of the carbene with matrices. The former four signals are assigned to H_z, H_x, H_y, and H_z transitions of a triplet species, the zero-field splitting (zfs) parameters of which are calculated to be $D = 0.3631$ cm^{-1} and $E = 0.0225$ cm^{-1}. We identified this triplet species as the diazo ketocarbene **25** for the three following reasons. First, the zfs parameters of the observed triplet species are in fair agreement with the reported values of triplet ketocarbenes with a 5-membered ring, e.g., **44** ($D = 0.406$ cm^{-1}, $E = 0.0264$ cm^{-1})[23] and **45** ($D = 0.38$ cm^{-1}).[24] Second, the triplet species appeared immediately after irradiation of **19**. The formation of **25** from **19** requires the extrusion of only one dinitrogen, while the extrusion of two nitrogen molecules should be involved in the generation of the other possible structures, e.g., dicarbene **46** and ketene carbene **47**. Finally, even if the extrusion of dinitrogen to generate the species **46** or **47** occurred in a one-photon process, the observed ESR spectrum differs from what would be expected for these species. The dicarbene **46** is better described as having the localized 1,3-diradical structure, **46a**, because of the conjugation of two π-electrons at the carbenic centers. The zfs parameters of localized triplet 1,3-diradicals


44


45


46 46a


47

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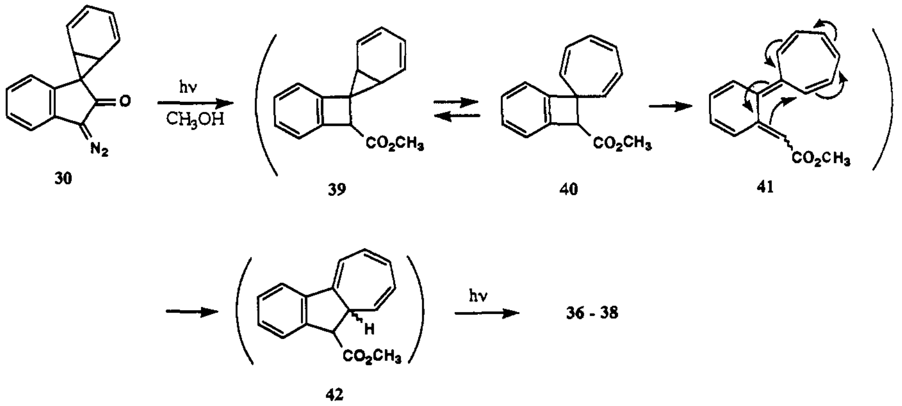
(22) Murai, H.; Safarik, I.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 1025.

(23) (a) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1983**, *105*, 7786. (b) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.

(24) Moriconi, E. J.; Murray, J. J. *J. Org. Chem.* **1964**, *29*, 3577.

Scheme VII



Scheme VIII

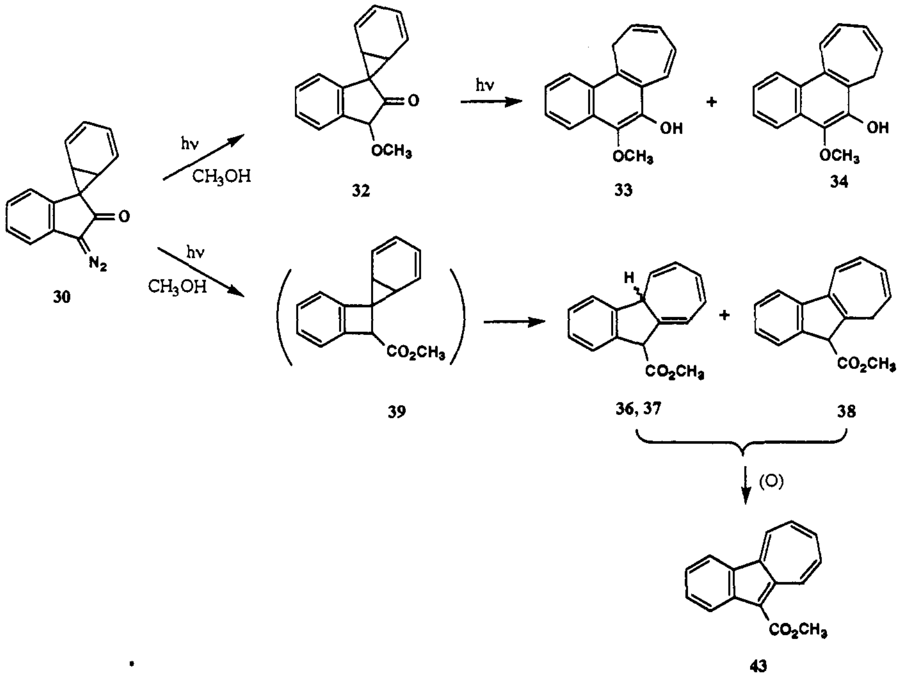


Table II. Photoproducts of **30** in Methanol

	32	**33**	**34**	**36**	**37**	**38**	**43**
yield (%)[a]	27	11	4	15	13	10	8

[a] Determined by the integration of ^{1}H NMR in the reaction mixture.

have been reported to be $D = 0.04–0.11$ cm^{-1},[25] which are much smaller than the observed value. Though the zfs parameters of triplet benzocyclobutenylidene have not been reported, it would be predicted that the zfs parameters of **47** would be quite different from those of **44** or **45**. Conjugation of the carbenic center with the ketene function in **47** would be less effective than in the 5-membered-ring ketocarbenes, which would result in a rather large D value. Further, the smaller angle of the divalent carbon in **47** as compared to those of the 5-membered-ring ketocarbenes would cause a larger E value. However, zfs parameters of the observed triplet species are not consistent with these predictions.

Thus, we could observe directly the diazo ketocarbene **25** by ESR spectroscopy. This carbene is likely to have a triplet ground state, since the intensities of its ESR signals decreased linearly with the reciprocal of the temperature in the range of 18–30 K. The signal intensities decreased irreversibly above 30 K, probably due to chemical reactions of the triplet carbene with matrices or of a thermally populated singlet state. The thermal stability of **25** in a 2-methyltetrahydrofuran glass is comparable to that of the ketocarbene generated from methyl (p-nitrophenyl)diazoacetate.[17b]

(2) Photoreactions of 19 in an Ar Matrix at 10 K. 1,3-Bis(diazo)indan-2-one (**19**) matrix-isolated in Ar at 10 K showed intense diazo stretching bands at 2096 and 2084 cm^{-1} and a carbonyl stretching band with a medium intensity at 1692 cm^{-1}.[26] Irradiation (350 ± 20 nm) of **19** at 10 K resulted in a decrease in the intensity of the peak of carbonyl stretching, as well as that of the diazo stretching bands. Two kinds of new carbonyl bands appeared (Figure 5). One of the first-formed carbonyl compounds with the C=O stretch at 1647 cm^{-1} was assigned to the diazo ketocarbene **25** for the two following reasons. First, Chapman and his co-workers reported that the carbonyl absorptions of the ketocarbene shifted to lower frequencies than those of the starting diazo ketones.[23] Second, when the Ar matrix was doped with 1% O_2, warming the matrix containing **25** to 35 K caused the complete disappearance of **25** and the generation of a new species having IR bands at 970 and 945 cm^{-1}, which was reasonably assigned

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(25) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753.

(26) The carbonyl stretching band was shifted to higher frequency when **19** was isolated in an Ar matrix at 10 K than when isolated in a KBr disk at room temperature. The analogous shift has been reported in the carbonyl stretching band of 2-diazoacenaphthylen-1-one, 1680 cm^{-1} in KBr and 1702 cm^{-1} in Ar: ref 23b.

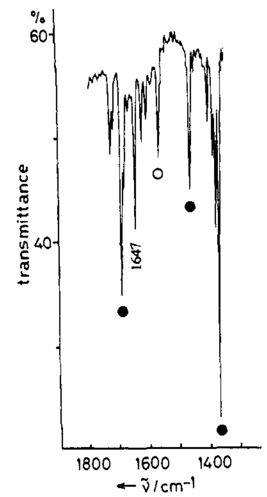


Figure 5. IR spectrum obtained by irradiation (350 ± 20 nm; 2 h) of **19** matrix-isolated in Ar at 10 K. The peak at 1647 cm^{-1} is assigned to the carbonyl stretching band due to the diazo ketocarbene **25**. The peaks marked with ● and ○ are assigned to the bands due to **19** and **49**, respectively.

to the corresponding carbonyl oxide **48**.[27] Thus we could characterize the diazo ketocarbene **25** by IR spectroscopy. The other carbonyl absorptions appeared at 1728 and 1718 cm^{-1}. These peaks were tentatively assigned to the C=O stretches in a ketodiazirine structure, since the carbonyl bands of ketodiazirines were reported to shift to higher frequencies than those of their corresponding diazo ketones.[28]

Unfortunately, the diazo ketocarbene **25** could not be identified by UV–vis spectroscopy, though it was reported that ketocarbenes showed weak $\pi \rightarrow \pi^*$ transitions with fine vibrational structures in the region of 560–620 nm.[23] It would probably be due to the low concentration of **25** and the overlapping with the intense absorptions of photoproducts formed from **25**.

Continued irradiation (350 ± 20 nm) resulted in the total disappearance of the IR bands of **19** and the first-formed carbonyl compounds and produced the diazo ketene **49** having an intense IR peak at 2106 cm^{-1} and weak peaks at 1569, 1066, and 542 cm^{-1}. The matrix took on a red color, and its UV–vis spectrum showed a broad absorption with a maximum at 507 nm. The formation of the diazo ketene **49** is explained by a photochemical Wolff rearrangement of the diazo ketocarbene **25**. The stepwise Wolff rearrangement in matrix, which proceeds through an α-ketocarbene, has been reported in the irradiation of diazo ketone, which fails to undergo a Wolff rearrangement in solution.[23]

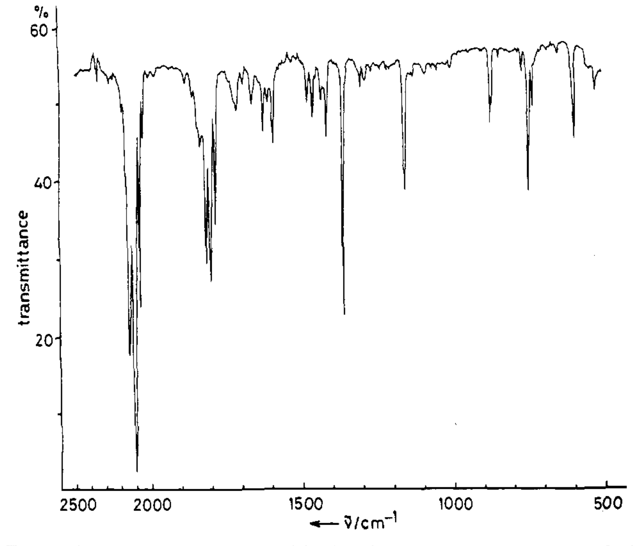
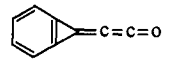


Figure 6. IR spectrum obtained by irradiation (>350 nm; 34 h) of **19** matrix-isolated in Ar at 10 K.

Further irradiation (>350 nm) of **49** caused a decrease in intensities of the IR peaks due to **49**. Simultaneously, characteristic bands at 1813, 1800, and 1783 cm^{-1} appeared. However, the intense 2106-cm^{-1} band decreased to the extent of ca. 80% of the maximum intensity and increased slightly on further irradiation (Figure 6). In the UV–vis spectrum, irradiation (>350 nm) of the red matrix containing the diazo ketene **49** resulted in the appearance of very intense absorptions with fine vibrational structures in the region of 320–370 nm. Thus, irradiation of **49** produced a mixture of a ketone with a strained carbonyl function and a compound with a cumulenic structure. The ketone having characteristic IR bands at 1813, 1800, and 1783 cm^{-1} is assigned to the cyclopropenone **20**. However, **20** is better described as having the dimethylenecyclopropanone structure **20a**, since the center of the carbonyl stretching bands is much lower than that of the reported cyclopropenones.[7,29] The observed UV absorptions could be assigned to the $\pi \rightarrow \pi^*$ transitions of the *o*-xylylene structure of **20a**, since the fine vibrational structure of *o*-xylylene has been reported.[30] The product with the 2106-cm^{-1} band is tentatively assigned to the propadienone **50**, which could be formed by a Wolff-type rearrangement of the ketene carbene **47** generated from **49**.[31]



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The photoproducts of **49** were unreactive under short-wavelength irradiation (>200 nm). Thus we could not synthesize benzocyclobutenyne (**21**) by an approach starting with **19**. The failure in the photodecarbonylation of **20** might be attributed to the fact that the photostationary state between **20** and **21** with carbon monoxide largely favors the former, since the photochemical addition of carbon monoxide to 3,3,6,6-tetramethylcyclohexyne matrix-isolated in Ar was reported.[32]

The change in intensity of the characteristic peaks with irradiation time is shown in Figure 7. The curves indicate that the species are formed sequentially. The total scheme of the photoreaction of **19** in an Ar matrix at 10 K is summarized in Scheme IX. It should be emphasized that the two diazo groups of **19** decompose stepwise and that the first-formed diazo ketocarbene **25**, which undergoes a Wolff rearrangement photochemically, is characterized by IR, as well as ESR, spectroscopy.[33]

Finally, we have to refer to the reactivity of the diazo ketocarbene **25** with molecular oxygen in an Ar matrix. When the matrix was doped with a large amount of oxygen, the photoreaction of **19** proceeded by a mechanism different from that displayed in Scheme IX. Irradiation (350 ± 20 nm) of **19**

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(27) The formation and spectroscopic identification of carbonyl oxide has been reviewed: Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. See also: Murata, S.; Tomioka, H.; Kawase, T.; Oda, M. *J. Org. Chem.* **1990**, *55*, 4502.

(28) (a) Franich, R. A.; Lowe, G.; Parker, J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2034. (b) Voigt, E.; Meier, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 103. (c) Voigt, E.; Meier, H. *Chem. Ber.* **1975**, *108*, 3326. (d) Miyashi, T.; Nakajo, T.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1978**, 422. (e) Laganis, E. D.; Janik, D. S.; Curphey, T. J.; Lemal, D. M. *J. Am. Chem. Soc.* **1983**, *105*, 7457.

(29) Krebs, A.; Cholcha, W.; Müller, M.; Eicher, T.; Pielartzik, H.; Schnöckel, H. *Tetrahedron Lett.* **1984**, *25*, 5027.

(30) (a) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400. (b) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840. (c) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683.

(31) The analogous rearrangement has been proposed in flash vacuum pyrolysis of phthalic anhydride: Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *J. Am. Chem. Soc.* **1988**, *110*, 1874.

(32) Sander, W.; Chapman, O. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 398.

(33) It does not seem that the wavelength of the incident light affects the reaction scheme, since irradiation of **19** in matrices at cryogenic temperatures with short-wavelength light (>200 nm) also gave **25** and **49**.

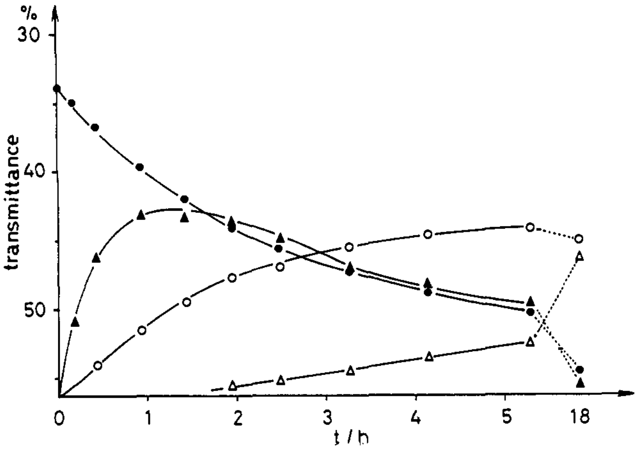


Figure 7. Change in intensity of the characteristic peaks with irradiation time in the photolysis (350 ± 20 nm) of **19** in an Ar matrix at 10 K: **19** (●) 1467; **25** (▲) 1647; **49** (○) 1569; **20** (△) 1800 cm^{-1}.

in an Ar matrix containing 20% O_2 gave 1-diazoindan-2,3-dione (**51**) and ozone (1036 cm^{-1}) as primary photoproducts. The structure of **51** was confirmed by comparison of the IR spectrum with that of the authentic material matrix-isolated in Ar at 10 K.[34] Neither the diazo ketocarbene **25** nor the diazo ketene **49** could be detected. The formation of **51** is explained by the reaction of the triplet diazo ketocarbene **25** with oxygen to give the corresponding carbonyl oxide **48**, followed by the transfer of an oxygen atom from **48** to the other oxygen molecule (Scheme X). It is not surprising that **48** could not be observed by IR spectroscopy, since carbonyl oxides have been reported to be very sensitive to irradiation.[27] Thus, in a matrix doped with 20% O_2, a Wolff rearrangement of the diazo ketocarbene **25** could be completely suppressed.

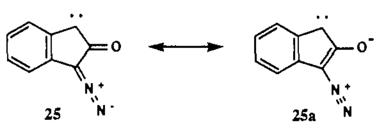
Continued irradiation (>300 nm) of **51** obtained in an oxygen-doped Ar matrix produced the several new carbonyl bands at 1861, 1815, 1787, and 1780 cm^{-1}, and so on, together with an intense peak at 2130 cm^{-1}. The photoproduct having IR bands at 2130 and 1815 cm^{-1} could be identified as the ketoketene **52**, since this product was obtained by the independent irradiation (>300 nm) of **51** in an oxygen-free Ar matrix at 10 K. Further evidence for the assignment of **52** came from the photolysis of 2-diazoindan-1,3-dione (**53**)[12b,d] in an Ar matrix. Irradiation (>300 nm) of **53** matrix-isolated at 10 K gave the same product as obtained from **51** (Scheme XI).

Unfortunately, other photoproducts besides **52** formed by the irradiation of **51** in an oxygen-doped Ar matrix could not be identified. It should be noted, however, that a Wolff rearrangement could not be thoroughly suppressed in the photoreaction of **51** in an Ar matrix containing 20% O_2, while irradiation of **19** under the same conditions gave no Wolff rearrangement products.

Conclusions

The photochemical decomposition processes of 1,3-bis(diazo)-indan-2-one (**19**) have been studied not only by characterization of the photoreaction products but also by direct observation of the reactive intermediates. The three remarkable features of the decomposition process of this bis(diazo) ketone **19** should be emphasized again. First, the two diazo groups of **19** are cleaved stepwise in fluid solutions, as well as in matrices at cryogenic temperatures. It has been reported that the two diazo groups of 1,3-bis(α-diazobenzyl)benzene decompose in benzophenone crystals and in rigid glasses at cryogenic temperatures to produce a quintet dicarbene by the one-photon process, while two photons are required in fluid solutions.[4b] These observations are explained by quenching of the excess energy in the initially-formed monodiazocarbene by collision with solvent molecules. It should be noted that in the case of the bis(diazo) ketone **19**, more than two photons are required for the decomposition of the two diazo groups even in an Ar matrix at 10 K. The consecutive decomposition of the two diazo groups of bis(diazo) compounds in an Ar matrix has been also reported in the photolysis of 2,6-bis(diazo)cyclohexanone (**1**), but this process seems to be quite different from the photolytic process of 1,3-bis(diazo)-1,2-dihydrophenalen-2-one (**17**), where the cyclopropenone **16** was formed immediately upon irradiation.[7] We cannot satisfactorily rationalize these observations at the present stage, though it seems that the number of photons required in the decomposition of bis(diazo) compounds in matrices is dependent on whether or not their structures allow the excess energy gained by the photolytic decomposition of the first diazo group to transfer to the vibrational mode of the second diazo group effectively.[35]

Second, in the photolytic decomposition of the first diazo group of **19**, a Wolff rearrangement does not occur in fluid solutions or in an Ar matrix doped with 20% O_2. The photolysis of **19** results in the extrusion of nitrogen molecules to form the diazo ketocarbene **25** exclusively, which reacts with the solvent or trapping the reagent to give a corresponding 1-diazo-3-substituted-indan-2-one such as **24**, **30**, or **51**. Further, the diazo ketocarbene **25** can be characterized by ESR and IR spectroscopy. In an Ar matrix in the absence of a trapping agent, **25** undergoes a Wolff rearrangement to give the diazo ketene **49** photochemically. These observations are consistent with the features of the diazo ketones, which were reported to fail to undergo a Wolff rearrangement in solution, e.g., 2-diazoacenaphthalen-1-one,[15] 9-diazo-4,5-methylenephenanthren-10-one,[16] and 3-diazoindolin-2-one.[28b,c] How can we explain the suppression of a Wolff rearrangement in the first stage of the photodecomposition of **19**? Though Shechter[15b] and Trost[16] explained failures to undergo Wolff rearrangement in terms of the strain in the transition state for ring contraction, Chapman and his co-workers claimed that stereoelectronic factors were responsible for suppression of the rearrangement.[23] Similarly, in the case of **19**, the strain would considerably increase in the transition state of a Wolff rearrangement, and the rigidity of the 5-membered ring would lessen for the excited bis(diazo) ketone **19*** or the diazo ketocarbene **25** to achieve the ideal configuration for the rearrangement. However, the suppression of the rearrangement in the bis(diazo) ketone **19** cannot be thoroughly explained by only these reasons, since the diazo ketones with an analogous structure, e.g., **51** and **53**, easily undergo a Wolff rearrangement in fluid solutions[12b,d] and in matrices (Scheme XI). We wish to propose that the retardation of the rearrangement in **19** is at least partly due to a partial double-bonding character of the CO–CN_2 bond in the excited bis(diazo) ketone **19*** or the diazo ketocarbene **25**. It has been reported that a partial double-bonding character is responsible for the retardation of a Wolff rearrangement in the photochemistry of 3-diazoindolin-2-one[28b,c] or *N*,*N*-diethyldiazoacetamide,[36] where the insertion of the photolytically generated carbene in methanol into the OH bond of the solvent predominates the formation of the Wolff rearrangement product. It may be pointed out that a partial double-bonding character of the CO–CN_2 bond in the diazo ketocarbene **25**, that is, a large contribution



25 25a

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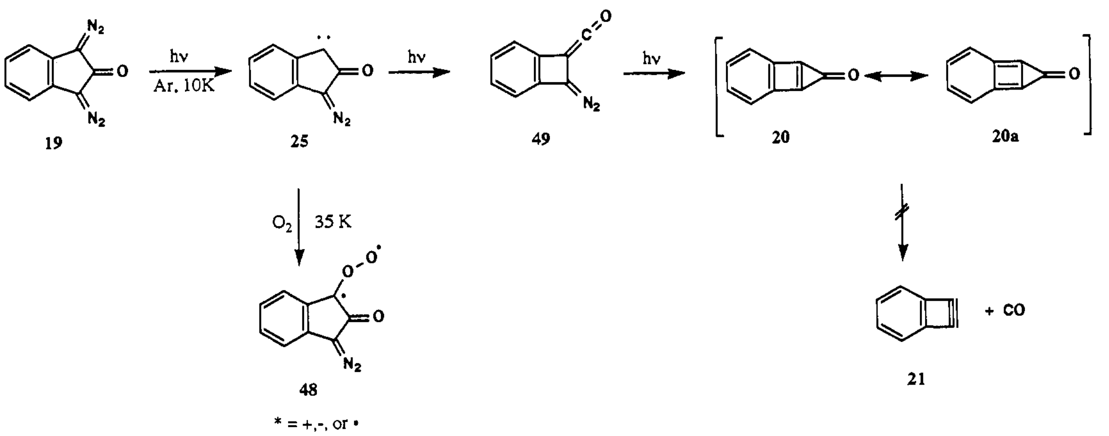
[34] 1-Diazoindan-2,3-dione (**51**) was obtained by singlet oxygen oxygenation of **19**: Murata, S.; Sugiyama, K.; Tomioka, H. *J. Org. Chem.* **1993**, *58*, 1976.

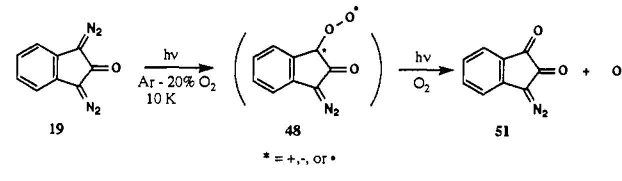
[35] We feel that the transfer of the excess energy would be effective in the bis(diazo) compounds, in which the two diazo functions are incorporated in the same π-conjugated system but not directly conjugated, in other words, from which the generation of quintet dicarbenes could be expected.

[36] Rando, R. R. *J. Am. Chem. Soc.* **1970**, *92*, 6706.

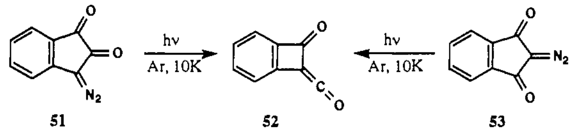
Scheme IX



Scheme X



Scheme XI



of the canonical structure **25a**, is implied by the appearance of the carbonyl absorption band at an extremely lower frequency (1647 cm^{-1}) than the carbonyl absorption bands of the reported ketocarbenes (1658–1678 cm^{-1}).[23]

Finally, the involvement of the cyclopropenone **20** or benzocyclobutenyne (**21**) in the photodecomposition process of **19** in fluid solutions is clearly excluded by the isolation of the intermediate monodiazo ketones **24** and **30**. Though the cyclopropenone **20** could be characterized spectroscopically in an Ar matrix at 10 K, the synthesis of benzocyclobutenyne (**21**) was not successful in an approach starting with 1,3-bis(diazo)indan-2-one (**19**).

At the present stage it is not known whether the photodecomposition scheme of **19** is applicable to the photolytic process of other 1,3-bis(diazo) ketones. Work is in progress to elucidate the general decomposition scheme of 1,3-bis(diazo) ketones.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a JEOL JNM-100 spectrometer and a JEOL JNM-GX-400 spectrometer. IR spectra were recorded on a JASCO A-100 spectrometer and a JASCO IR-700 spectrometer. UV–vis spectra were obtained with a Hitachi 220S spectrophotometer. GC–MS spectra were recorded on a Shimadzu QP-1000 mass spectrometer with a GC column prepared from 5% Silicone OV-17 on Diasolid L (5.0 mm × 1.0 m). ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100-kHz field modulation), equipped with an optical transmission cavity and an Air Products LTD-3-110 liquid helium transfer system, at the Instrument Center of the Institute for Molecular Science in Okazaki. The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column was 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 was carried out on a JASCO HLC-01 high-pressure liquid chromatograph equipped with a Shodex GPC H-2001 column. Thin-layer chromatography was carried out on Merck kieselgel 60 PF$_{254}$, and column chromatography was done on Fuji Davison silica gel BW-127ZH.

Materials. 1,3-Bis(diazo)indan-2-one (19). To a solution of 2.0 g (15 mmol) of indan-2-one[37] in 20 mL of ether was added 3 mL of concentrated hydrochloric acid. The reaction mixture was cooled to 5–15 °C, 5.0 mL (37 mmol) of isopentyl nitrite (97%, Aldrich) was added dropwise to the solution, and the mixture was stirred for 1 h at this temperature. After we neutralized the mixture with 3 mL of pyridine, the precipitate was collected by filtration and washed with water to give the crude 1,3-bis(oximino)indan-2-one. The dioxime was added to a mixture of 40 mL of 15 N ammonium hydroxide, 40 mL of 1 N sodium hydroxide, and 40 mL of water. The mixture was cooled to 10–20 °C, and 130 mL of sodium hypochlorite solution (8.5–13.5%, Nacalai Tesque) was added over a period of 1 h, keeping the rate of addition so that the temperature did not exceed 20 °C. The reaction mixture was stirred for 1 h. After additional sodium hypochlorite solution (20 mL) was added, the mixture was stirred for 30 min. The reaction mixture was extracted with chloroform, and the extract was washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was developed on a silica gel column with dichloromethane to give 1.3 g (47%) of **19**. The solid was purified by recrystallization from hexane–ethanol, and further purification was achieved by sublimation under 10^{-6} Torr at 40 °C: orange-red needles; mp 127 °C dec; ^{1}H NMR (CDCl$_3$) δ 7.0–7.2 (4H, br s); IR (KBr) 2100, 2080, 1645, 1365, 1190 cm^{-1}; GC–MS, m/z (rel intensity) 184 (M$^+$, 33), 156 (M$^+$ – N$_2$, 7), 128 (M$^+$ – 2N$_2$, 34), 100 (M$^+$ – 2N$_2$ – CO, 47), 74 (100); HRMS found M$^+$ 184.0399, $C_9H_4N_4O$ requires M$^+$ 184.0385.

Irradiations for Preparative Experiments. A solution (20–30 mL) of the diazo compound (50–100 mg) was placed in a Pyrex tube, purged with argon for 15 min, and irradiated with a 300-W high-pressure mercury lamp at room temperature. The reaction was monitored by GC or TLC. The resulting solution was worked up by the following procedures.

(1) Irradiation of 19 in Methanol. A solution of 50 mg (270 μmol) of **19** in 20 mL of methanol was irradiated for 3 h. The ^{1}H NMR spectrum of the reaction mixture showed the signals due to methyl *o*-(dimethoxymethyl)phenylacetate (**22**) exclusively. The yield of **22** was 69%, which was determined by GC. **22**: oil; ^{1}H NMR (CDCl$_3$) δ 3.30 (6H, s), 3.68 (3H, s), 3.79 (2H, s), 5.46 (1H, s), 7.0–7.6 (4H, m); IR (neat) 1740 cm^{-1}; GC–MS m/z (rel intensity) 209 (M$^+$ – Me, 4), 193 (M$^+$ – OMe, 66), 161 (100), 151 (57). Further characterization of **22** was achieved by hydrolysis with wet silica gel[38] to methyl *o*-formylphenylacetate as follows: the photoreaction mixture was dissolved in dichloromethane (0.5 mL), and the solution was added to a suspension of wet silica gel in dichloromethane, which was prepared by addition of water (0.05 g) to a suspension of silica gel (0.5 g, Fuji Davison BW-127ZH) in dichloromethane (2 mL) with continuous stirring. The reaction mixture was stirred at room temperature for 12 h. The solid was filtered and washed several times with ether. The solvent was removed under reduced pressure, and the residue was separated by the use of GPLC with chloroform eluent to give 15 mg (31%) of methyl *o*-formylphenylacetate: oil; ^{1}H NMR (CDCl$_3$) δ 3.70 (3H, s), 4.08 (2H, s), 7.2–7.6 (3H, m), 7.80 (1H, m), 10.10 (1H, s); GC–MS m/z (rel intensity) 178 (M$^+$, 2), 146 (M$^+$ – MeOH, 96), 119 (M$^+$ – CO$_2$Me, 35), 118 (66), 91 (100); HRMS found M$^+$ 178.0651, $C_{10}H_{10}O_3$ requires M$^+$ 178.0630.

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(37) Horan, J. E.; Schiessler, R. W. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 647.

(38) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.

(2) Isolation of 24 in the Photoreaction of 19 in Methanol. A solution of **19** (80 mg, 430 μmol) in 25 mL of methanol was irradiated for 1 h. After evaporation of the solvent under reduced pressure, the residue was separated by GPLC with chloroform eluent. From the fraction eluted before **19**, ca. 10 mg of the diazo ketone **24** was obtained with small amounts of impurities. No other compounds but **24** or the unchanged starting material could be isolated in this experiment. 1-Diazo-3-methoxyindan-2-one (**24**): orange oil; ^{1}H NMR (CDCl$_3$) δ 3.56 (3H, s), 4.80 (1H, s), 7.11 (1H, d, J = 7.1 Hz), 7.21 (1H, dd, J = 7.1, 7.1 Hz), 7.3–7.5 (2H, m); IR (neat) 2090, 1695 cm^{-1}.

(3) Irradiation of 19 in Benzene. A solution of **19** (100 mg, 540 μmol) in 40 mL of dry benzene was irradiated for 4 h. After evaporation of the solvent, the residue was separated by GPLC with chloroform eluent to give two products together with the unchanged starting material (11%). The yield of products shown in Table I was determined by HPLC on the basis of the reacted material. Dispiro[indan-1,7′-norcara-2′,4′-diene-3,7″-norcara-2″,4″-dien]-2-one (**29**): colorless needles; mp 154–156 °C dec (hexane); ^{1}H NMR (CDCl$_3$) δ 3.20 (4H, m), 6.11 (4H, m), 6.49 (4H, m), 6.79 (2H, m), 7.08 (2H, m); IR (KBr) 1700 cm^{-1}; GC–MS m/z (rel intensity) 284 (M$^+$, 7), 256 (M$^+$ − CO, 60), 178 (M$^+$ − C$_6$H$_6$ − CO, 100). Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.91; H, 5.86. 3-Diazospiro[indan-1,7′-norcara-2′,4′-dien]-2-one (**30**): orange needles; mp 139–143 °C dec (hexane–ethanol); ^{1}H NMR (CDCl$_3$) δ 3.24 (2H, m), 6.11 (2H, m), 6.50 (2H, m), 6.73 (1H, d, J = 7.7 Hz), 7.03 (1H, dd, J = 7.7, 7.7 Hz), 7.17 (1H, d, J = 7.7 Hz), 7.26 (1H, dd, J = 7.7, 7.7 Hz); IR (KBr) 2080, 1680 cm^{-1}; HRMS found M$^+$ 234.0790, $C_{15}H_{10}N_2O$ requires M$^+$ 234.0792.

(4) Irradiation of 30 in Methanol. A solution of **30** (50 mg, 210 μmol) in 20 mL of methanol was irradiated for 4 h. The mixture was separated into four fractions by GPLC with chloroform eluent. The products in each fraction were identified by ^{1}H NMR. The first-eluted fraction was composed of **32** and **37**, and the second fraction was composed of **36** and **38**. 3-Methoxyspiro[indan-1,7′-norcara-2′,4′-dien]-2-one (**32**): ^{1}H NMR (CDCl$_3$) δ 3.26 (1H, m), 3.34 (1H, m), 3.59 (3H, s), 4.88 (1H, s), 6.15 (2H, m), 6.50 (2H, m), 6.81 (1H, d, J = 7.8 Hz), 7.2–7.4 (3H, m). The dihydrobenz[*a*]azulenes **36–38** could only be identified in the mixture since the chromatographical separation of these isomers was unsuccessful and these compounds were easily dehydrogenated to give **43**. *cis*-Methyl 4b,10-dihydrobenz[*a*]azulene-10-carboxylate (**36**): ^{1}H NMR (CDCl$_3$) δ 3.48 (1H, br s), 3.67 (3H, s), 4.96 (1H, s), 5.23 (1H, dd, J = 10.9, 4.4 Hz), 6.15 (1H, m), 6.49 (1H, m), 6.5–6.7 (2H, m), 7.3–7.5 (4H, m). *trans*-Methyl 4b,10-dihydrobenz[*a*]azulene-10-carboxylate (**37**): ^{1}H NMR (CDCl$_3$) δ 3.73 (1H, br s), 3.80 (3H, s), 4.93 (1H, s), 5.16 (1H, dd, J = 11.6, 5.1 Hz), 6.07 (1H, m), 6.45 (1H, m), 6.5–6.6 (2H, m), 7.2–7.4 (2H, m), 7.45 (1H, d, J = 7.1 Hz), 7.51 (1H, d, J = 7.1 Hz). Methyl 9,10-dihydrobenz[*a*]azulene-10-carboxylate (**38**): ^{1}H NMR (CDCl$_3$) δ 2.90 (2H, d, J = 6.5 Hz), 3.73 (3H, s), 4.47 (1H, s), 5.5–5.6 (1H, m), 6.22 (1H, dd, J = 10.1, 6.5 Hz), 6.7–6.8 (1H, m), 7.02 (1H, d, J = 10.9 Hz), 7.3–7.5 (4H, m). The third fraction obtained by GPLC separation contained **43**[21] alone, and the fourth fraction was composed of **33** and **34**. 5-Methoxy-7*H*-cyclohepta[*a*]naphthalen-6-ol (**33**): ^{1}H NMR (CDCl$_3$) δ 3.19 (1H, d, J = 7.0 Hz), 3.97 (3H, s), 5.90 (1H, td, J = 7.0, 9.4 Hz), 5.96 (1H, br s), 6.20 (1H, dd, J = 9.4, 5.1 Hz), 6.78 (1H, dd, J = 5.1, 11.7 Hz), 7.4–7.5 (2H, m), 7.89 (1H, d, J = 11.7 Hz), 7.93 (1H, d, J = 7.9 Hz), 8.15 (1H, d, J = 8.2 Hz); GC–MS m/z (rel intensity) 238 (M$^+$, 80), 223 (M$^+$ − Me, 100), 195 (M$^+$ − COMe, 62), 165 (75). (The isomers **33** and **34** could not be separated by GC.) 5-Methoxy-11*H*-cyclohepta[*a*]naphthalen-6-ol (**34**): ^{1}H NMR (CDCl$_3$) δ 3.31 (1H, d, J = 7.3 Hz), 3.95 (3H, s), 5.83 (1H, m), 6.09 (1H, br s), 6.23 (1H, m), 6.80 (1H, m), 7.4–7.5 (2H, m), 7.64 (1H, d, J = 11.2 Hz), 7.93 (1H, d, J = 7.9 Hz), 8.27 (1H, d, J = 8.7 Hz).

Irradiation for Analytical Experiments. In a typical run, a solution (1–2 mL) of the diazo compound (2–4 mg) was placed in a Pyrex tube, purged with argon for 5–10 min, and irradiated with a 300-W high-pressure mercury lamp at room temperature. Product identifications were established by GC comparison with authentic samples. For the concentration profile shown in Figures 1 and 4, the consumption of the material and the yield of products were determined by GC or HPLC on the basis of an internal standard (cumene or *m*-terphenyl).

Irradiations at Cryogenic Temperatures. (1) ESR Measurements at 18 K. The bis(diazo) ketone **19** (ca. 3 mg) was dissolved in 2-methyltetrahydrofuran (0.2 mL). The solution was placed in a quartz tube (5 mm o.d.) and degassed by three freeze–thaw cycles. The sample was cooled in a precooled ESR cavity and irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter. The microwave frequency was measured with a Takeda Riken 5201M frequency counter, and the resonance magnetic field values of the signals were read by a Varian E-500 NMR gaussmeter.

(2) Matrix-Isolation Spectroscopy. The matrix-isolation equipment was similar to that described in detail by Chapman and his co-workers.[23b] Cooling was carried out on an Iwatani Cryo-Techno Cryo Mini refrigeration system. For the material of a spectroscopic cold window, CsI for IR experiments or sapphire for UV–vis was used, the temperature of which was regulated by a heater connected to an Iwatani Cryo-Techno Model TCU-1 temperature controller. The high vacuum (less than 10^{-6} Torr) was achieved on a Daia Vacuum Engineering Model DS-412-U high vacuum system. The bis(diazo) ketone **19** was sublimed under 10^{-6} Torr at 40 °C and codeposited with Ar onto a cold window cooled at 20 K. Irradiations were carried out at 10 K with a 250-W high-pressure mercury lamp through either cutoff glass filters or band-pass filters. The matrix isolation in Ar containing O$_2$ was achieved by the codeposition of the sample with Ar mixed with O$_2$ in advance using the gas-handling system having a differential pressure gauge. Spectroscopic data isolated in an Ar matrix at 10 K were as follows. **19**: IR 2096m, 2084vs, 1692m, 1683w, 1467w, 1392w, 1382w, 1371s, 1310w, 1183m, 1096w, 1032w, 881w, 746w; UV λ_{max} 289, 301, 310sh, 349, 368, 374sh nm. **20** with **50**: IR 2134s, 2106vs, 2064m, 1813m, 1800m, 1783w, 1361s, 1159m, 875w, 743m, 597w; UV λ_{max} 332, 340, 348, 353, 362 nm. **25**: IR 1647s, 1408w, 1245w, 1066m. **48**: IR 1718m, 1417w, 1387w, 970m, 945m, 854w. **49**: IR 2106vs, 1569m, 1247m, 1127w, 1089w, 1066m, 1007w, 741m, 542w; UV λ_{max} 507 nm. **51**: IR 2090vs, 1757w, 1721s, 1610m, 1466m, 1387m, 1311w, 1295w, 1186m, 973w, 885w, 751m. **52**: IR 2136vs, 1810s, 1781w, 1595s, 1463w, 1441w, 1424w, 1290m, 896m, 838s, 747m, 715w, 659w. **53**: IR 2120s, 1706s, 1696m, 1356s, 1330m, 1193w, 955w, 879w, 714w.

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