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Remarkable Wavelength-Dependent Photoreactions of the Bis(diazo) Ketone Having Inequivalent Diazo Groups: Studies in Fluid Solutions and in Low-Temperature Matrixes

Shigeru Murata,* Junko Kobayashi,† Chiharu Kongou,† Mamoru Miyata,†
Takeshi Matsushita,† and Hideo Tomioka*,†

Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Meguro, Tokyo 153-8902, Japan, and Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan

cmura@mail.ecc.u-tokyo.ac.jp

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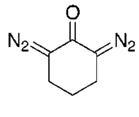
The photoreactions of the bis(diazo) ketone **11**, which has two inequivalent diazo groups, have been investigated in solutions at room temperature and in matrixes at 12 K. Irradiation of **11** in benzene containing methanol gave a mixture of the spironorcaradiene **13** and the diazo ketone **17** as primary isolable photoproducts. The former **13** originated from the diazo ketene **20**, which was formed from the initial extrusion of N_2 from the 2-position of **11**, while the latter product **17** was derived from the diazo ketene **24** which was generated by the initial decomposition of the diazo group at the 4-position of **11**. The product distribution was remarkably dependent upon the excitation wavelength: **13** was predominantly obtained in the photolysis with light of >350 nm, while the irradiation with long-wavelength light (>420 nm) exclusively gave **17**. The consistent wavelength effects were observed in photoreactions in an Ar matrix at 12 K. The irradiation of **11** matrix-isolated in Ar with light of >350 nm afforded **20** in preference to the isomer **24** as the first-formed intermediates, while **24** was mainly obtained in the long-wavelength irradiation (>420 nm). On the basis of these experimental data, we conclude that the short-wavelength irradiation of **11** causes a preferential cleavage of the diazo group at the 2-position and that the selective extrusion of N_2 from the 4-position is practically achieved by the irradiation with long-wavelength light. The reason for the selective cleavage of the two inequivalent diazo groups of **11** is discussed on the basis of theoretical calculations with the PM3 CI method.

The photodecomposition processes of 1,3-bis(diazo) ketones are of interest because the formation of new reactive intermediates derived from an intramolecular interaction between the two reaction sites can be expected. Moreover, 1,3-bis(diazo) ketones have been proved to be useful precursors of various attractive molecules, such as cyclopropenones and strained alkynes. In 1974, Trost and Whitman presented the first mechanistic studies of the photodecomposition processes of 2,6-bis(diazo)cyclohexanone (**1**) and 1,3-bis(diazo)-1,3-diphenyl-2-propanone (**2**) in solutions.[1] Chapman and co-workers reported the photochemistry of **1** in an Ar matrix at cryogenic temperatures and succeeded in the synthesis of acenaphthyne using 1,3-bis(diazo)-1,2-dihydrophenalen-2-one (**3**) as a precursor.[2] Moreover, Maier and co-workers prepared new carbon oxides (C_nO_m) by the irradiation of cyclic bis(diazo) polyketones, such as 3,5-bis(diazo)-1,2,4-cyclopentanetrione (**4**), in matrixes.[3] Recently, we synthesized the two new bis(diazo) ketones, 1,3-bis(diazo)-indan-2-one (**5**)[4] and 5,7-bis(diazo)-1,2,3,4-dibenzocyclohepta-1,3-dien-6-one (**6**),[5] and studied their photodecomposition processes, not only by the characterization of reaction products in solutions but also by the direct observation of reactive intermediates in matrixes at cryogenic temperatures. It was revealed that the two diazo groups of the bis(diazo) ketone **5** incorporated into a five-membered ring are cleaved consecutively and that a Wolff rearrangement is suppressed in the photolytic decomposition of the first diazo group.[4] On the other hand, in the photolysis of the bis(diazo) ketone **6** incorporated into a seven-membered ring, the sequential



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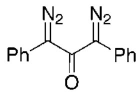

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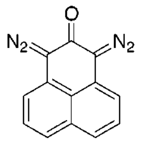

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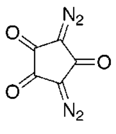

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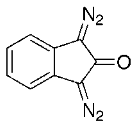

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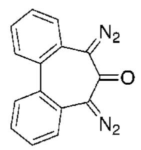

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* To whom correspondence should be addressed.

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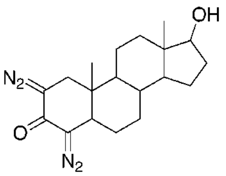
decomposition of the two diazo groups in solutions and the formal simultaneous elimination of two nitrogen molecules in matrixes have been observed.[5] Thus, the photodecomposition processes of bis(diazo) ketones have been found to vary markedly with their structure.

In the course of our studies of the photochemistry of bis(diazo) ketones, we have raised the question whether one diazo group can be selectively cleaved when the diazo functions of a bis(diazo) ketone are inequivalent. As shown above, all the bis(diazo) ketones employed in the recent studies have two equivalent diazo groups. To our knowledge, only two bis(diazo) ketones with two inequivalent diazo groups have been reported so far: 2,4-bis(diazo)androstan-17*β*-ol-3-one (**7**)[6] and 1,3-bis(diazo)decahydronaphthalen-2-one (**8**).[7] The former steroidal bis(diazo) ketone **7** was synthesized by Cava and coworkers in 1966, but its reactivities were not investigated in detail.[6] On the other hand, Borch and Fields reported the selective cleavage of the two inequivalent diazo groups in Ag_2O-catalyzed decomposition of **8**. On refluxing **8** with Ag_2O in methanol, two isomeric esters, **9** and **10**, were obtained in 44 and 16% yield, respectively. They explained that the preferential formation of **9** implied the preferential loss of N_2 at the 1-position of **8**, which would be due to the stabilization of the positive character at the 1-position by the inductive effect of the alkyl group attached to this position.[7] Though the photochemistry of these bis(diazo) ketones was of special interest, the authors preliminarily reported that the photolysis of **8**, as well as of **7**, in solutions afforded a complex mixture from which nothing could be identified.



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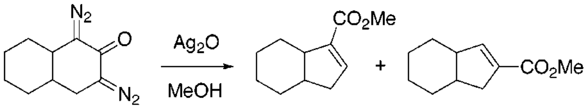
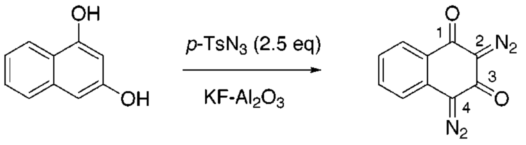


8 **9**, 44% **10**, 16%

Thus, to answer the above question, we decided to design new bis(diazo) ketones with inequivalent diazo groups. After several unsuccessful attempts to prepare new bis(diazo) ketones, we were able to obtain 2,4-bis(diazo)-1,2,3,4-tetrahydronaphthalene-1,3-dione (**11**). One diazo group at the 2-position of **11** is interposed between two keto groups, while the other one at the 4-position is conjugated with both an aromatic ring and a keto group. In this paper, we report our detailed studies of the photochemistry of **11** in solutions and in matrixes, where the first example of selective photodecomposition of one of the two inequivalent diazo groups could be demonstrated.[8]

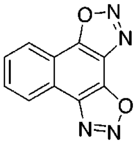


11

Results and Discussion

Preparation and Characterization of 11. We were able to obtain **11** by direct diazo transfer to readily available 1,3-naphthalenediol.[9,10] After chromatographic purification, followed by recrystallization from hexane−dichloromethane, **11** was obtained as orange granules, which decomposed at 188−190 °C.

In the ^{13}C NMR spectrum of **11**, two signals assigned to the carbonyl carbons appeared at δ 173.7 and 176.6, and two weak peaks assigned to the diazo carbons appeared at δ 72.0 and 84.2. The IR spectrum, measured in a KBr disk, showed two diazo-stretching absorptions at 2144 and 2112 cm^{-1} and two carbonyl-stretching bands at 1640 and 1600 cm^{-1}. All of these spectroscopic features are consistent with the bis(diazo) diketo structure of **11**, excluding the contribution of the bis(1,2,3-oxadiazolo)naphthalene structure depicted in **12**.



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The absorption spectrum of **11**, recorded in benzene, is exhibited in Figure 1. The spectrum shows a transition with maximum at 307 nm and a shoulder around 372 nm ($\log \epsilon = 4.14$ and 3.28, respectively). The wavelengths of maximal absorption of both of these transitions are slightly blue-shifted in methanol. The spectrum also shows a weak tailing to ca. 500 nm, so that **11** can be photolyzed with the light filtered by an optical glass filter that cuts the wavelength to shorter than 420 nm, as mentioned in the following sections.

Photoreactions of 11 in Solutions. (1) Photoproducts in a Benzene−Methanol Binary Solvent. In the earlier studies, the photoreactions of 1,3-bis(diazo) ketones were mainly investigated in alcoholic solvents.[1,11] Irradiation of **11** in methanol, however, gave a very complicated mixture, from which methyl 3-oxoindan-1-carboxylate[12] was obtained in ca. 10% yield as a sole isolable photoproduct. After examination of various solvents employed for the irradiation of **11**, we found that the photolysis of **11** in benzene containing a small amount of methanol (1−10%) gave a satisfactory result, where the total yield of the isolated photoproducts amounted to ca. 40%. The success of this binary solvent system is probably due to the following two known

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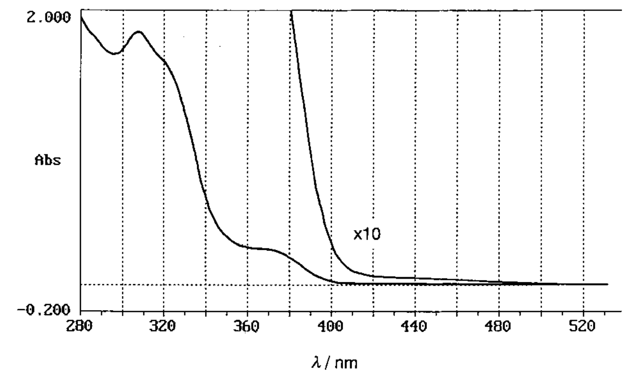
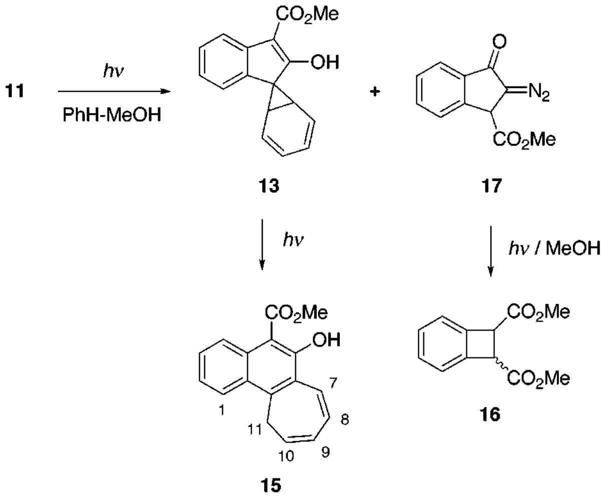


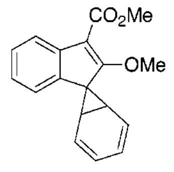
Figure 1. UV–vis spectrum of **11** in benzene: [**11**] = 1.33 × 10^{-4} M.

reactivities of carbenes.[13] First, it has been reported that in the photolysis of some diazo ketones in methanol, the insertion of the ketocarbene into the OH bond of methanol occurs in competition with a Wolff rearrangement. The α-ketoether resulting from the OH insertion photochemically decomposes to the corresponding ketone, which would further complicate the photoreaction.[14] In a lower methanol concentration, however, the rate of the OH insertion is reduced, so that Wolff-rearrangement products are predominantly obtained. Second, benzene is known as an efficient trapping reagent for ketocarbenes reluctant to undergo a Wolff rearrangement,[4,15] as well as for fluorenylidene and related carbenes.[16]

A solution of **11** in benzene containing 1% (v/v) methanol was irradiated with a high-pressure mercury lamp (>300 nm). After the starting material was completely consumed, the reaction mixture was separated by gel permeation liquid chromatography (GPLC) to yield four reaction products (Scheme 1). The main product was identified as the spironorcaradiene **13** (16%), although it could not be completely purified, owing to its instability. However, by treatment of the reaction mixture obtained after the irradiation of **11** with excess diazomethane, **13** was converted to the methyl ether **14**, which could be isolated by GPLC and fully characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of **14** showed three sets of multiplets centered at δ 3.86, 6.10, and 6.39, which are characteristic of norcaradiene structures.[4,17] The similar signals at δ 3.61/3.24, 6.13, and 6.51, which were observed in the photoreaction mixture and disappeared on treatment with diazomethane, could be assigned to the norcaradiene protons of **13**. It should be noted that the protons attached to a three-membered ring, as well as to the methoxy protons, of **13** were observed as two sets of signals in a 1.5:1 ratio, which probably implied that this photoproduct existed in a keto–enol equilibrium mixture in solutions, as depicted in **13** and **13a**.

Scheme 1





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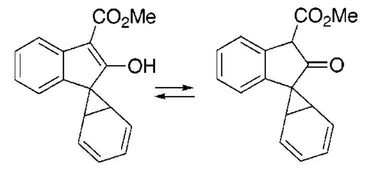

13 **13a**

The second photoproduct was identified as cyclohepta[*a*]naphthalenol **15** (6%), the ^{1}H NMR spectrum of which showed a set of signals due to the partial structure $-CH_2-CH{=}CH-CH{=}CH-$. The position of the methylene group was determined to be the 11-position, because the nuclear Overhauser effect was detected between the methylene protons and the aromatic proton at the 1-position. It was revealed that **15** was photochemically derived from **13**, because an independent irradiation of **13** in benzene containing 1% (v/v) methanol using a high-pressure mercury lamp exclusively gave **15**. This reaction can be explained in terms of the photochemical [1,2]-carbonyl migration of **13a**, followed by enolization and a hydrogen shift. The analogous photorearrangement has been already reported.[4,18]

The third photoproduct, which was obtained as a mixture of two isomers in a 2:1 ratio, was assigned to the *cis* and *trans* isomers of dimethyl benzocyclobutene-1,2-dicarboxylate (**16**, 7%). The structure of **16** was confirmed by the agreement of its ^{1}H NMR spectrum with that of the diester obtained by the acid-catalyzed hydrolysis of 1,2-dicyanobenzocyclobutene,[19] followed by the esterification with diazomethane. According to the assignment of the geometry of 1,2-dicyanobenzocyclobutene reported by Storr and co-workers, the major isomer obtained in the photoreaction of **11** was the *cis* isomer.

The fourth photoproduct was identified as methyl 3-oxo-2-diazoindan-1-carboxylate (**17**, 6%), the IR spectrum of which showed an intense diazo-stretching band at 2180 cm^{-1} and stretching absorptions of the carbonyl

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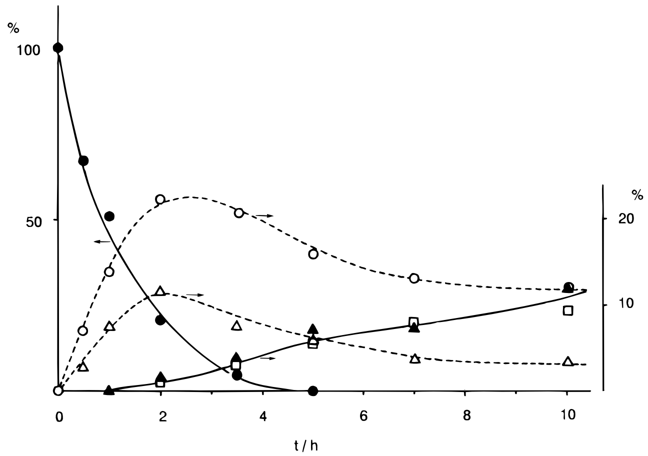
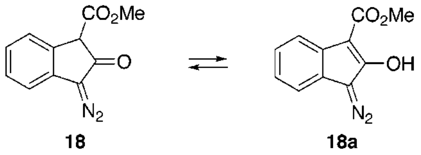


Figure 2. Change in the concentration of the material **11** (●) and the photoproducts **13** (○), **15** (□), **16** (▲), and **17** (△) in benzene containing 1% (v/v) methanol vs irradiation time.

groups at 1735 and 1670 cm^{-1}. In its ^{1}H NMR spectrum, the methine proton appeared at δ 5.10 as a sharp singlet. An independent irradiation of **17** in benzene containing 1% (v/v) methanol using a high-pressure mercury lamp exclusively afforded a mixture of *cis* and *trans* isomers of **16**. It is well-known that benzocyclobutene derivatives are obtained by the photochemical ring contraction of diazoindanones.[13] We ruled out 2-oxo-3-diazoindan-1-carboxylate (**18**) as a possible structure for the fourth photoproduct, because, as is the case with **13**, it would be reasonable to assume that the enol tautomer **18a** largely contributes to the 2-oxoindan-1-carboxylate **18**, while we had no evidence for the contribution of the enol tautomer in this photoproduct.



The concentration profile of the products with increasing irradiation time is shown in Figure 2. Judging from the ^{1}H NMR spectrum of the reaction mixture obtained at the early stages of the photoreaction, where the conversion of **11** was ca. 30%, no products other than **13** and **17** were formed in an appreciable yield, and the total yield of these two products amounted to 30−40%, based on the reacted starting material. Thus, we concluded that **13** and **17** were the primary isolable photoproducts of **11** in benzene containing methanol. The mechanism for the formation of both products is discussed in the following section.

(2) Mechanism for the Formation of 13 and 17. Both of the photoproducts, **13** and **17**, have an indanone skeleton, which could be formed through a Wolff-type ring contraction of the ketocarbenes photolytically generated from **11**. There are two possible pathways from **11** to **13**, as shown in Scheme 2. The first pathway is initiated by the photochemical extrusion of N_2 from the 2-position of **11** to yield the ketocarbene **19**.[20] The bond linking the carbonyl group at the 1-position with the aromatic ring migrates to the carbenic center to yield the diazo ketene **20**, which is captured by methanol to afford the diazo ketone **18**. The decomposition of the diazo group of **18**, followed by reaction with benzene, yields the final product **13** (path A). In the second pathway, the diazo group at the 4-position of **11** initially decomposes to yield the ketocarbene **21**, which is trapped by benzene to yield the diazo norcaradiene **22**. The decomposition of the diazo group of **22**, followed by a Wolff rearrangement, yields the keto ketene **23**, which is captured by methanol to afford **13** (path B). We would prefer path A for the formation of **13** for the following two reasons, based on the known reactivities of carbenes with benzene:[13]

First, the reaction of **21** with benzene to yield **22** shown in path B is quite unlikely. In general, the photolysis of diazo ketones in benzene yields a complex mixture, because the rate of a Wolff rearrangement of the photolytically generated ketocarbene is much faster than that of reaction with benzene, and the ketene resulting from the rearrangement cannot be captured with benzene but polymerizes to yield tarry products. Only when a Wolff rearrangement is suppressed for steric reasons is a ketocarbene trapped with benzene to afford a norcaradiene or a phenyl-substituted product.[15] It is reasonable to think that the ketocarbene incorporated into a six-membered ring can smoothly undergo a rearrangement, because the strain in the transition state for a ring contraction is not so severe. In fact, there has been no example of trapping of the ketocarbene incorporated into a six-membered ring with benzene. Second, in contrast, the reaction of the carbene from **18** with benzene, shown in path A, is understandable. If path A is a correct mechanism for the formation of **13**, the diazo ketone **18** should be a primary photoproduct of **11**. However, we could not detect any intermediate products to **13** in the reaction mixture. We propose that the diazo ketone **18** is produced but decomposes quickly to afford **13**, because, as discussed in the previous section, it is reasonable to think that **18** largely exists in the enol form **18a**, where the resonance between the carbonyl and diazo groups is completely lost, so that the thermal stability of **18** would be much reduced compared with the normal diazo ketones. Assuming the large contribution of the enol form **18a**, we could expect the reactivity of **18** to be similar to that of diazoindene rather than that of 1-diazoindan-2-one. The reactivity of the carbene generated from **18a** with benzene to yield **13** is not inconsistent with that of indenylidene, which has been reported to add to benzene, forming a spironorcaradiene derivative.[16a,c]

On the other hand, the mechanism for the formation of **17** can be readily explained, as illustrated by Scheme 3. The carbene **21**,[20] generated by the extrusion of N_2 from the 4-position of **11**, undergoes a Wolff rearrangement, forming the diazo ketene **24**, which is trapped by methanol to yield **17**. A higher thermal stability of **17**, compared with **18**, is not surprising, because **17** contains a normal $CO-CN_2$ group, which is capable of resonance.

Thus, we can propose the reasonable mechanism for the formation of both primary isolable photoproducts obtained in the irradiation of **11** in a benzene−methanol binary solvent. We should emphasize that **13** and **17** are the products derived from the carbenes generated by the initial decomposition of the diazo group at the 2-position

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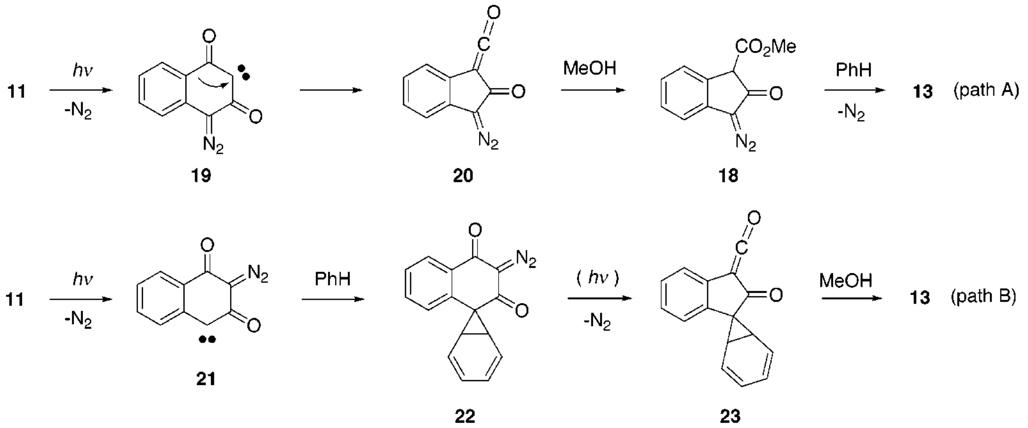
(20) It is the hot issue whether the Wolff rearrangement of an α-diazoketone to ketene in solutions proceeds through a ketocarbene intermediate or whether a ketene is directly formed from an α-diazoketone in its excited state. In this paper, we tentatively describe the ketocarbenes **19** and **21** as the intermediates of the Wolff rearrangement. It seems likely that the extrusion of N_2 and the bond migration occur in a concerted manner to yield the ketenes **20** and **24** directly from the excited state of **11**.

Scheme 2



Scheme 3

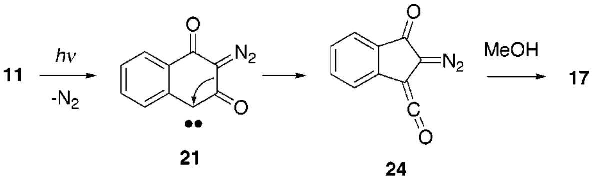


Table 1. Wavelength Dependence of the Photoproducts of 11 in Benzene Containing 1% (v/v) Methanol

conditions[a]		yield (%)[b]		
source (lamp)	filter (nm)	**13**	**17**	[**13**]:[**17**]
high-press. Hg	Pyrex (>300)	21	9	2.4
Xe-arc	UV-35 (>350)	26	11	2.4
Xe-arc	L-39 (>390)	19	9	2.1
Xe-arc	L-42 (>420)	2	32	0.06

[a] [**11**] = 7×10^{-3} M. Conversion of **11** was 20–30%. [b] Determined by the integration of ^{1}H NMR spectra.

and at the 4-position, respectively. This observation reveals that the photodecomposition of the two inequivalent diazo groups of **11** is not selective under the photoreaction conditions described in the previous section. Furthermore, although the main photoproduct isolated was **13**, we cannot insist on the preferential cleavage of the diazo group at the 2-position in the photolysis of **11** at this stage, because the mechanism cannot be identified for the formation of tarry products, the yield of which amounted to ca. 60%.[21]

(3) Wavelength Effect on the Photolysis in Solutions. The effect of wavelength on the photolysis of **11** in benzene containing methanol was examined. The wavelength employed in the irradiation was regulated by the use of a xenon-arc lamp and various optical-cutoff glass filters. The wavelength dependence of the distributions of the primary photoproducts **13** and **17** is summarized in Table 1. The ratio of the products obtained in the photolysis with the light through the filter that cut wavelengths to <350 nm was identical to that obtained with the Pyrex-filtered light (>300 nm). A similar product distribution was obtained when **11** was irradiated using the cutoff filter at 390 nm. However, the product distribution was dramatically changed in the irradiation with the light of wavelength >420 nm, where the yield of the diazo ketone **17** increased and that of the spironorcaradiene **13** considerably decreased. No new photoproducts were detected in the ^{1}H NMR spectrum of the reaction mixture obtained for the irradiation using light of >420 nm. Unfortunately, **11** could not be practically photolyzed with a longer-wavelength light (>450 nm), which was probably due to a small absorptivity in the wavelength range.

Thus, we have found that the product distribution obtained in the photolysis of **11** is remarkably dependent upon the wavelength employed in the irradiation. These results imply that the irradiation with the long-wavelength light (>420 nm) can yield **17** but not **13**. Taking into account that **13** and **17** are derived from the carbenes generated by the initial decomposition of the diazo groups at the 2- and 4-positions, respectively, these observations strongly suggest that the photolysis with the long-wavelength light (>420 nm) can initiate the decomposition of the diazo group at the 4-position but fails to cause the extrusion of N_2 from the 2-position of the bis(diazo) ketone **11**.

Photoreactions of 11 in an Ar Matrix at 12 K. (1) Direct Observations of Reactive Intermediates by IR Spectroscopy. By the characterization of the products yielded in the photolysis of **11** in solutions, we obtained results suggestive of the selective decomposition of the diazo group at the 4-position in the long-wavelength irradiation (>420 nm). To gain further evidence for the selective decomposition, we examined the photochemistry of **11** in an Ar matrix at 12 K.

The bis(diazo) ketone **11** matrix-isolated in Ar showed two intense diazo-stretching bands at 2150 and 2094 cm^{-1} and two carbonyl-stretching bands having medium intensities at 1654 and 1636 cm^{-1}. These bands were assigned to the stretching vibrations of the diazo groups at the 2- and 4-positions and of the carbonyl groups at the 1- and 3-positions, respectively, with the aid of theoretical calculations using the PM3 method. Some vibrational frequencies with relatively large intensities calculated for the PM3-optimized geometry of **11** are shown in Table 2 and are in fair agreement with the experimental data. Irradiation (>350 nm) of **11** at 12 K resulted in a simultaneous decrease in the intensities of the two diazo-stretching bands, as well as those of the two carbonyl-stretching bands. New peaks appeared at 2142, 2088, 1690, and 1381 cm^{-1}, which revealed the formation of products having a cumulenic double bond and a carbonyl group (designated as **A**). On further

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(21) The tarry products were obtained by GPLC from a fraction of the higher molecular weight. The ^{1}H NMR spectrum of the tarry products showed many methoxy signals at δ 3.5–4 and broad signals in the region of aromatic protons, from which we could gain no information about the selectivity of the cleavage of the two inequivalent diazo groups.

Scheme 4

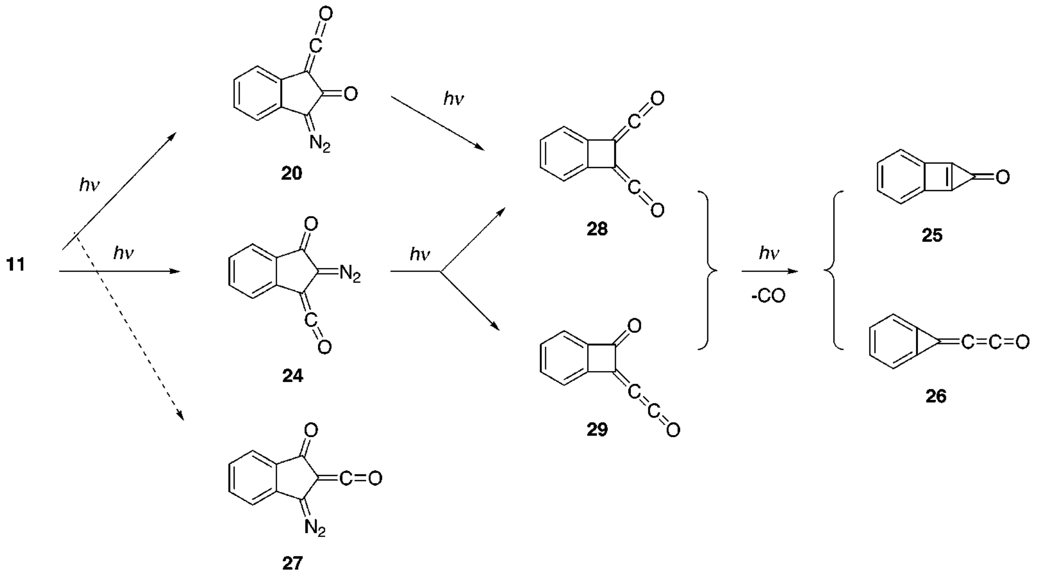

Table 2. IR Spectroscopic Data of 11, Matrix-Isolated in Ar at 12 K and Calculated Using the PM3 Method

exptl[a] ν (cm^{-1})	calcd[b] ν (cm^{-1})	assignment
2150m	2160 (56)	C_2=N=N str
2094s	2121 (100)	C_4=N=N str
1654m	1659 (17)	C_1=O str
1636m	1626 (29)	C_3=O str
	1561 (5)	Ar-ring ip
	1545 (3)	Ar-ring ip
1463w	1425 (7)	Ar, 6-ring ip
1349m	1380 (9)	Ar, 6-ring ip
1326s	1313 (51)	6-ring ip
1310w	1303 (6)	6-ring ip, C_4=N str
1272m	1276 (8)	6-ring ip, C_2=N str
950w		
890w		
756w	725 (2)	CH oop

[a] Measured in Ar at 12 K: s, strong; m, medium; w, weak. [b] Calculated frequencies are multiplied by 0.87. Relative intensities are designated in parentheses. Frequencies with relative intensities greater than 2% are given in the table.

irradiation (>350 nm) of the matrix containing the product **A**, the IR peaks due to **A** started to decrease, and new peaks appeared at 2152, 2116, 1780, and 1422 cm^{-1}. Thus, the first-formed products **A** were photolytically converted to the alternative products having a cumulenic structure and a carbonyl function (designated as **B**). The products **B** were unreactive under irradiation with the Pyrex-filtered light (>300 nm), while short-wavelength irradiation (>200 nm) resulted in a decrease in the intensities of the IR peaks due to **B**, and the formation of new photoproducts with IR bands at 2102, 1811, 1798, and 1362 cm^{-1} (designated as **C**). Interestingly, the products **C** were identical with the final photoproducts formed by the irradiation of 1,3-bis(diazo)-indan-2-one (**5**) matrix-isolated in Ar at 10 K, which have been tentatively assigned to a mixture of the cyclopropenone **25** and the propadienone **26** in the literature (Scheme 4).[4]

Thus, it was found that the bis(diazo) ketone **11** which was matrix-isolated in Ar is photolytically decomposed in the successive three steps. For the following three reasons, we propose that the initial two steps correspond to the consecutive extrusion of the two N_2 molecules, followed by a Wolff rearrangement to afford a corresponding ring-contracted ketene and that the final step corresponds to the decomposition with the extrusion of carbon monoxide. First, neither intermediary product **A** nor **B** can be identified as a triplet ketocarbene, such as **19** and **21**, because products, **A** and **B**, when generated in the Ar matrix doped with 1% O_2, remained unchanged when the matrix was warmed to 35 K.[22] Second, an increase in the wavenumber of the carbonyl-stretching band, when going from the starting material **11** (1654 and 1636 cm^{-1}) to the first-formed intermediates **A** (1690 cm^{-1}) and further to the second intermediates **B** (1780 cm^{-1}), can be reasonably explained in terms of an increase in the steric constraint of the carbonyl function with the progress of the photoreaction. This interpretation is consistent with the successive ring contraction induced by a photochemical Wolff rearrangement. Finally, there have been many precedents for the extrusion of carbon monoxide by UV irradiation of benzocyclobutenones and ketenes which are matrix-isolated at cryogenic temperatures.[22a,23] Consequently, the first-formed intermediates **A** are reasonably assigned to the group of diazo ketenes having an indanone skeleton, for which three possible structures (**20**, **24**, and **27**) are feasible. Furthermore, the diketene **28** and the propadienone **29**, having a benzocyclobutene skeleton, are reasonable candidates for the intermediates **B**. The total scheme proposed for the photoreaction of **11** in an Ar matrix at 12 K is summarized in Scheme 4.

(2) Wavelength Effect on the Photolysis in the Matrixes. Analogously to the irradiation with light of >350 nm, irradiation of **11** in an Ar matrix at 12 K with light of wavelength >420 nm caused a simultaneous decrease in the intensities of the two diazo-stretching bands. However, new peaks appeared at 2136, 2070, 1695, and 1468 cm^{-1} which were slightly but significantly different from the positions of the peaks which were observed in the irradiation with light of >350 nm, described in the previous section. Figure 3 illustrates the

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(22) For reviews of reactivities of carbenes in matrixes at cyogenic temperatures, see: (a) Sheridan, R. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1986; Vol. 8, p 159. (b) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344.

(23) (a) Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8940. (b) Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1990**, *112*, 4046. (c) Leung-Toung R.; Wentrup, C. *J. Org. Chem.* **1992**, *57*, 4850.

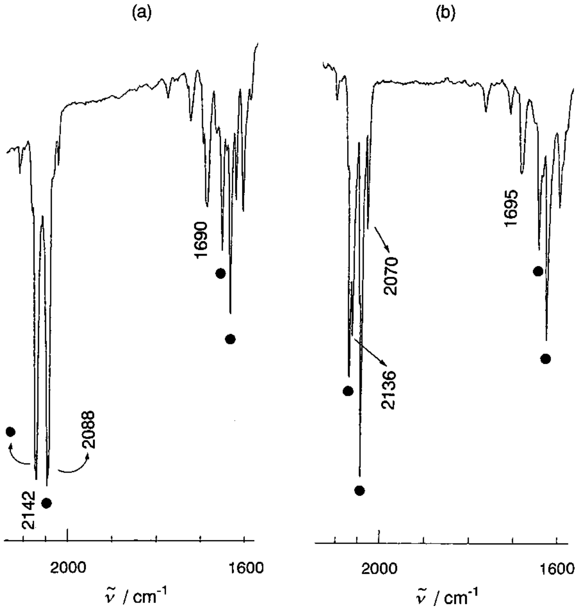
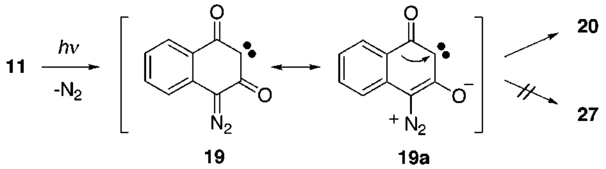


Figure 3. (a) IR spectrum obtained after irradiation of **11** in Ar at 12 K for 0.5 h with light of >350 nm. (b) IR spectrum obtained after irradiation of **11** in Ar at 12 K for 4 h with light of >420 nm. The peaks marked with ● are assigned to the bands due to **11**.

IR spectrum obtained in the irradiation of **11** with light of >420 nm (Figure 3b), compared with that obtained with light of > 350 nm (Figure 3a). Under irradiation with the long-wavelength light (>420 nm), the photochemical conversion of **11** was considerably slower, and the first-formed intermediates (designated as **A′**) were unreactive. When the matrix containing **A′** was irradiated with light of >350 nm, however, the intensities of the peaks due to **A′** decreased rapidly, and new peaks started to grow at 2096, 1808, 1778, and 1346 cm^{-1}, showing the conversion of **A′** into new products having a cumulenic double bond and a carbonyl function (designated as **B′**). Further irradiation of the matrix containing the second intermediates **B′** using the shorter-wavelength light (>200 nm) resulted in the formation of the final photoproducts **C**.

By comparison of the IR spectrum of the second intermediates **B′**, which were obtained in the irradiation of **11** with light of >420 nm and followed by the irradiation of the resulting matrix with light of >350 nm, with that of **B** obtained in the continuous irradiation of **11** with light of >350 nm, the following two findings should be pointed out. First, the IR spectrum of the intermediates **B′** in the region of carbonyl stretching was practically identical to that of **B**, which showed a peak around 1780 cm^{-1} with a medium intensity and a weak peak around 1810 cm^{-1}. However, these carbonyl-stretching bands were observed to be much more intense in **B′** than in **B**. Second, the intermediates **B** showed two intense bands at 2152 and 2116 cm^{-1} in the cumulenic-stretching region, while in the spectrum of **B′**, a single intense peak at 2096 cm^{-1} was observed which had two weak bands practically identical to those of **B**. These differences observed in the spectra of the intermediates **B** and **B′**, which were formed by the further irradiation of the first-formed intermediates **A** and **A′**, respectively, in the matrixes, could be reasonably interpreted in terms of the different ratios of the diketene **28** to the propadienone **29** (Scheme 4). Taking into account that the species with the carbonyl stretching bands is assigned to the propadienone **29**, it seems reasonable to think that the intermediates **B** consist predominantly of the diketene **28** containing a small amount of the propadienone **29**, while the propadienone **29** is present in a manner comparable to the diketene **28** in the intermediates **B′**.

Scheme 5



These observations concerning the second intermediates **B** and **B′**, as well as the different peak positions between the first-formed intermediates **A** and **A′**, imply that the composition of the intermediates **A′** formed by the long-wavelength irradiation of **11** (>420 nm) is significantly different from that of the intermediates **A** formed by the irradiation of **11** with light of >350 nm. A detailed discussion on the identification of the first-formed intermediates, **A** and **A′**, is given in the following section.

(3) Identification of the Intermediates A and A′. As shown in Scheme 4, there are three possible structures (**20**, **24**, and **27**) for the intermediates **A** and **A′**. It should be noted that the two diazo ketenes, **20** and **27**, can be formed by the extrusion of N_2 from the 2-position of **11**, while the initial decomposition of the diazo group at the 4-position simply yields the diazo ketene **24**.

First, we propose that the diazo ketene **27** is ruled out as a candidate for the intermediates **A** and **A′** on the basis of the known relative migration tendencies in a Wolff rearrangement.[13] Examination of a Wolff rearrangement of asymmetrically substituted 2-diazo-1,3-dicarbonyl compounds has revealed that a partial double-bonding character, as well as the substitution of an electron-withdrawing group, significantly reduces the migration ability of the bond.[24,25] Moreover, there have been a number of reports on the retardation of a Wolff rearrangement due to a partial double-bonding character in the photochemistry of α-diazo carbonyl compounds.[4,26] As shown in Scheme 5, it is reasonable to assume that in the ketocarbene **19** generated by the initial decomposition of the diazo group at the 2-position of **11**, the canonical structure **19a** contributes significantly to yield a large partial double-bonding character of the C(3)−C(4) bond. Thus, the migration of the bond linking the carbonyl group at the 1-position with the aromatic ring to the carbenic center takes place to yield the diazo ketene **20** in preference to the migration of the C(3)−C(4) bond to yield **27**. This assumption would be supported by the result that in the photochemistry of **11** in solutions, the products derived from **20** were isolated as the spironorcaradiene **13** and the cycloheptanephthalenol **15**, while no products which originated from **27** were detected in the photoreaction mixture.

Subsequently, taking into account the different ratios of the diketene **28** to the propadienone **29** between the

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[24] Zeller, K.-P.; Meier, H.; Müller, E. *Tetrahedron* **1972**, *28*, 5831.

[25] (a) Lowe, G.; Ridley, D. D. *J. Chem. Soc., Chem. Commun.* **1973**, 328. (b) Lowe, G.; Ridley, D. D. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2024.

[26] (a) Rando, R. R. *J. Am. Chem. Soc.* **1970**, *92*, 6706. (b) Voigt, E.; Meier, H.; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 103. (c) Voigt, E.; Meier, H. *Chem. Ber.* **1975**, *108*, 3326.

Table 3. IR Spectroscopic Data of the Intermediate A and A′ Generated in Ar at 12 K and of 20 and 24 Calculated Using the PM3 Method

exptl[a] ν (cm^{-1})		calcd[b] ν (cm^{-1})		
A	**A′**	**20**	**24**	assignment
2142s	2136s	2145 (67)	2133 (100)	$C{=}N{=}N$ str
2088s	2070s	2061 (100)	2056 (63)	$C{=}C{=}O$ str
1690m	1695m	1722 (18)	1743 (27)	$C{=}O$ str
		1602 (2)	1600 (7)	Ar-ring ip
1478w	1468m	1472 (7)	1466 (5)	5-ring ip
		1421 (10)	1416 (2)	Ar, 5-ring ip
1381m		1382 (12)	1392 (5)	Ar, 5-ring ip
	1300w		1337 (9)	Ar, 5-ring ip
			1255 (4)	Ar, 5-ring ip
1179w	1152w	1169 (8)	1166 (11)	Ar, 5-ring ip
	1108w	1159 (2)	1143 (2)	Ar, 5-ring ip
1095w	1064w			
869w	880w	955 (2)		CH ip
749w	750w	698 (9)	683 (5)	CH oop
	676w			

[a] Measured in Ar at 12 K: s, strong; m, medium; w, weak. [b] Calculated frequencies are multiplied by 0.88. Relative intensities are designated in parentheses. Frequencies with relative intensities greater than 2% were given in the table.

second intermediates **B** and **B′** photolytically generated from the first-formed intermediates **A** and **A′**, respectively, it can be assumed that the intermediates **A** consist predominantly of the diazo ketene **20**, while the diazo ketene **24** is a principal constituent of the intermediates **A′**. This assumption was based on the reactivities of the two diazo ketenes **20** and **24** (Scheme 4). Extrusion of N_2 from **20,** followed by a Wolff rearrangement, simply yields the diketene **28**, while **24** can possibly afford the propadienone **29**, as well as **28**.

Thus, we could identify the predominant component of the first-formed intermediates **A** and **A′** as the diazo ketene **20** and **24**, respectively. To gain more support for these assignments, PM3 calculations were carried out for these compounds. The calculated vibrational frequencies are shown in Table 3, together with the frequencies observed for the intermediates **A** and **A′**. Though the IR spectrum calculated for **20** was similar to that for **24**, we should point out the following four features of the vibrational frequencies calculated for **20**, compared with those for **24**: (1) the higher wavenumber of the diazo-stretching band at 2130−2150 cm^{-1}, (2) the higher wavenumber of the ketene-stretching band at 2060−2080 cm^{-1}, (3) the lower wavenumber of the carbonyl-stretching band predicted to appear at 1720−1740 cm^{-1}, and (4) the higher wavenumber of the in-plane deformation of the five-membered ring at 1470−1460 cm^{-1}. These bands could be readily assigned in the IR spectrum of the intermediates, **A** and **A′**, because of their relatively high intensities. As shown in Table 3, all of these features are completely consistent with the features of the vibrational frequencies observed for **A**, as compared with those for **A′**. Thus, the assignments of the IR peaks on the basis of the PM3 calculations present a strong piece of evidence supporting the identification based on the experimental observations concerning the second intermediates, **B** and **B′**. Unfortunately, it was difficult to detect the minor species in the IR spectra because of the severe overlapping of the peaks in the cumulenic- and carbonyl-stretching region, as well as very small intensities of the peaks in other regions. Note that a small amount of the diazo ketene **24** should also be present in the intermediate **A** which was obtained from the irradiation with light of >350 nm, because the further irradiation of the matrix afforded the propadienone **29**.

Thus, it can be concluded that the irradiation of **11** with light of >350 nm in an Ar matrix at 12 K yields the diazo ketene **20** in preference to the isomer **24** as the first-formed intermediates, while **24** is mainly obtained in the long-wavelength irradiation (>420 mm). Taking into account that **20** and **24** are formed by the initial decomposition of the diazo groups at the 2- and 4-positions, respectively, these observations imply that the photolysis with the light of >350 nm predominantly yields the product formed by the initial decomposition of the diazo group at the 2-position, together with a small amount of the product derived from the initial extrusion of N_2 from the 4-position, while the latter product is exclusively obtained in the irradiation with the long-wavelength light (>420 nm).

It should be emphasized that these wavelength effects are completely consistent with those observed in solutions at room temperature. Consequently, on the basis of the experimental data obtained not only in solutions, but also in matrixes, we can conclude that the selective photodecomposition of one of the two inequivalent diazo groups, that is, the diazo group at the 4-position, of the bis(diazo) ketone **11** is practically achieved by the irradiation with the light of >420 nm, and that the use of the short-wavelength light (>350 nm) causes a preferential cleavage of the diazo group at the 2-position. To our knowledge, this provides the first example of the reactivity control of a poly(diazo) compound by means of the excitation wavelength.

Discussion on the Wavelength Effect Based on the Theoretical Studies. The remarkable wavelength effect observed in the photochemistry of **11** suggests the participation of higher excited states in the photoreactions. It is known that most photochemical reactions in solutions occur from the lowest excited state, which is due to the fact that a nonradiative internal conversion is usually faster than photochemical reactions from higher excited states.[27] However, photochemical reactions from higher excited states are expected to be observable when the energy gap between a higher excited state and the lowest excited state is large or the overlap of the electronic wave functions of these two states is poor, either of which leads to a significant decrease in the rate of internal conversion.[27] In fact, the wavelength-dependent photoreactions in solutions have been reported in a ketone having another noninteracting chromophore in which a selective excitation of one of the two chromophores can be achieved.[28]

To have a clue to understanding the observed wavelength effect, we carried out molecular orbital (MO) calculations using the PM3 method on **11**. The MOs calculated for the PM3-optimized geometry of **11** are schematically shown in Figure 4. As shown in the figure, both HOMO and LUMO are mainly composed of the π orbitals of the diazo group at the 4-position, while the π orbitals of the diazo group at the 2-position contribute

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(27) For a review of wavelength effect on photoreactions in solutions, see: Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125.

(28) (a) Ullman, E. F.; Singh, B. *J. Am. Chem. Soc.* **1966**, *88*, 1844. (b) Singh, B.; Ullman, E. F. *J. Am. Chem. Soc.* **1967**, *89*, 6911. (c) Pacifici, J. G.; Diebert, C. *J. Am. Chem. Soc.* **1969**, *91*, 4595. (d) Singh, B.; Zewig, A.; Gallivan, J. B. *J. Am. Chem. Soc.* **1972**, *94*, 1199. (e) Erikson, J.; Jespersen, K. K.; Ratner, M. A.; Schuster, D. I. *J. Am. Chem. Soc.* **1975**, *97*, 5596.

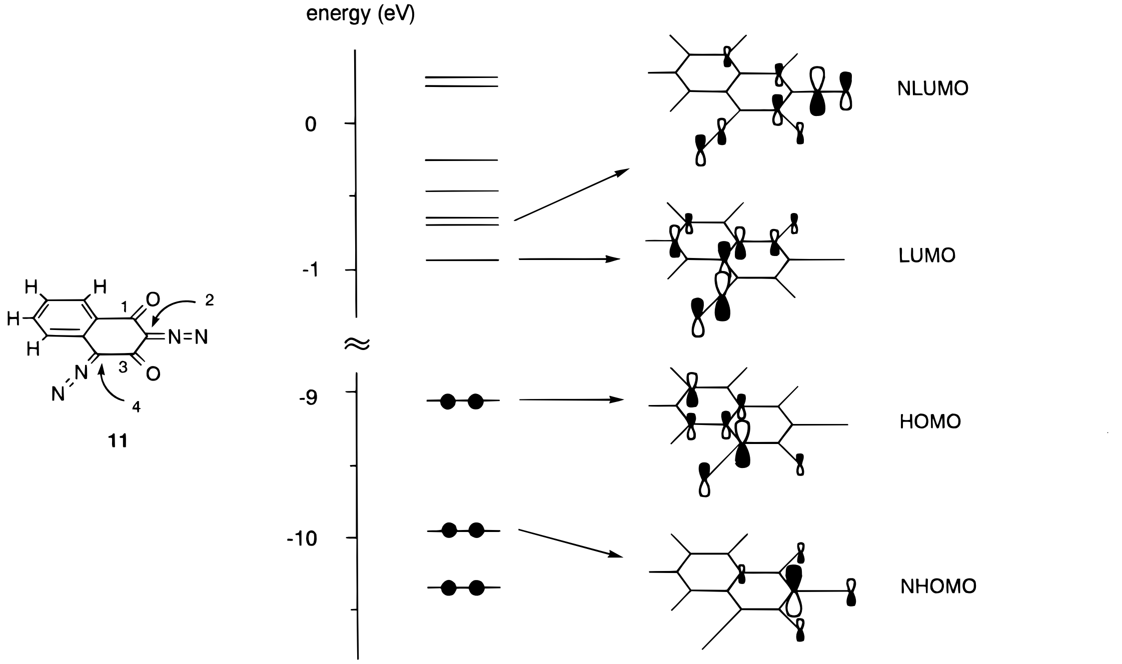

Figure 4. Diagram of molecular orbitals calculated for **11** using the PM3 method.

Table 4. Electronic States of 11 Calculated Using the PM3 CI Method

state	energy (eV)	contribution (%)[a]									
		(2200)	(2110)	(1201)	(2101)	(1210)	(1111)	(2020)	(2011)	(1102)	(0202)
S_0	−0.073	99.1									
T_1	2.865		88.1		10.8						
T_2	3.618			81.2	3.8	13.6					
S_1	3.891		85.1		10.4	0.9		0.7	2.1		
T_3	4.350		10.4	4.5	81.0		1.1		0.5	2.0	
S_2	4.489		10.2	18.8	63.1	1.8	0.8	2.7		1.7	
S_3	4.655		0.8	55.3	17.7	22.9		0.9		0.5	0.9

[a] Calculated from the coefficients of the 4-electron/4-orbital PM3-CI wave functions. Configurations are designated in parentheses as a series of four numbers, each of which is the number of electrons occupying NHOMO, HOMO, LUMO, and NLUMO, respectively. Only configurations with contribution greater than 0.5% are included.

predominantly to NHOMO and NLUMO. Thus, the MO diagram of **11** indicates that the interaction between the two diazo moieties is unexpectedly small, and hence, that a selective cleavage of one of the two diazo groups is not impossible. This prediction is supported by the 4-electron/4-orbital-configuration interaction (CI) calculations using the PM3 MOs, the results of which are summarized in Table 4. At first, we excluded the triplet states from the states responsible for the reactions observed in the photochemistry of **11** for the following two reasons: first, it has been established that photochemical Wolff rearrangements in solutions originate from an excited singlet state of diazo ketones;[13] and second, although it is reported that triplet ketocarbenes which are stable in matrixes at cryogenic temperatures photolytically undergo a Wolff rearrangement,[4,22a,29] we could not detect the triplet ketocarbenes **19** or **21** in an Ar matrix, indicating that a Wolff rearrangement proceeds rapidly to yield the diazo ketenes **20** and **24** within a singlet energy surface. As shown in Table 4, the lowest excited singlet state, S_1, of **11**, which is dominated by a (2110) configuration, can be roughly described as the state in which the HOMO electron is promoted into the LUMO, which leads to a local excitation of the diazo group at the 4-position. On the other hand, the S_2 state is dominated by a (2101) configuration, which is designated as an intramolecular charge-transfer state from the diazo group at the 4-position to that at the 2-position. A (1201) configuration, which implies a local excitation of the diazo group at the 2-position, is found to be a dominant configuration of the S_3 state, having an energy close to that of S_2. On the basis of the PM3 CI calculations, we can have the following three expectations for the photochemical reactivities of **11**: first, the large energy gaps between S_1 and the higher excited-singlet states, as well as the localization of their wave functions on the different moieties of the molecule, give rise to a decrease in the rate of internal conversion from the higher excited-singlet states to S_1; second, the selective excitation into the S_1 state using a long-wavelength light causes the selective cleavage of the 4-position diazo group; third, both S_2 and S_3 contribute to the photoreaction initiated by a short-wavelength light, in which the selective cleavage of the diazo groups cannot be expected, although the diazo group at the 2-position is rather preferentially excited.

It should be noted that the experimentally observed wavelength effects in the photochemistry of **11** mentioned in the previous sections are in accord with the expectations based on the theoretical calculations. Thus, we propose that the selective decomposition of the diazo

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(29) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.

group at the 4-position in the long-wavelength irradiation (>420 nm) is ascribed to the selective excitation into the S_1 state, while the higher excited-singlet states S_2 and S_3 participate in the less selective photoreactions initiated by the short-wavelength light (>350 nm). Unfortunately, the transition frequencies calculated with the PM3 CI method, 313 nm ($S_0 \rightarrow S_1$), 272 nm ($S_0 \rightarrow S_2$), and 262 nm ($S_0 \rightarrow S_3$), are inconsistent with the wavelengths of maximal absorption observed in the UV–vis spectrum of **11** (Figure 1). At the present stage, we assume that, although the absorption observed around 370 nm is assigned to the $S_0 \rightarrow S_1$ transition, the irradiation with light of wavelengths ≤420 nm could cause the excitation not only into S_1, but also into the higher singlet-excited states because of the pronounced tailing of intense transitions with a maximum around 310 nm which are assigned to the $S_0 \rightarrow S_2$ and S_3 transitions. For a more detailed discussion on the wavelength effect observed in the photochemistry of **11**, a calculation with more rigorous methods would be required.

Conclusions

The bis(diazo) ketone **11** has been shown to undergo a remarkable wavelength-dependent photochemical reactions not only in solutions but also in matrixes in which the selective photodecomposition of one of the two inequivalent diazo groups is practically achieved. It has been reported that some wavelength effects in solutions originate from the secondary photolysis of the primary photoproducts.[27] In the case of **11**, however, this possibility is thoroughly ruled out, because the wavelength-dependent formation of the first-formed reactive species **20** and **24** is directly observed in Ar matrixes at 12 K. On the basis of the PM3 CI calculations, we propose that the origin of the wavelength effect can be assigned to the selective excitation into the lowest excited-singlet state in the long-wavelength irradiation, as well as the contribution of the higher excited state in the photoreactions initiated by the short-wavelength light. At the present stage, however, we cannot exclude the possibility that the wavelength effect observed in the photoreaction of **11** originates from the contribution of different vibrational states of the lowest excited-singlet state. Work is in progress to elucidate the excited-state properties of bis(diazo) ketones.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 270 or 500 MHz. ^{13}C NMR spectra were recorded at 126 MHz. 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 a Merck kieselgel 60 PF_{254}. Benzene was distilled from sodium before use, and methanol was purified by distillation from freshly prepared magnesium methoxide.

2,4-Bis(diazo)-1,2,3,4-tetrahydronaphthalene-1,3-dione (11). To a solution of 100 mg (0.63 mmol) of 1,3-naphthalenediol[9] in 8 mL of anhydrous acetonitrile was added 200 mg of KF–Al_2O_3.[10] The mixture was stirred at 0 °C, and 310 mg (1.56 mmol) of *p*-toluenesulfonyl azide was added dropwise to the solution. The reaction mixture was stirred for 3 h at 0 °C. The mixture was filtered to remove KF–Al_2O_3, and the residue was thoroughly washed with acetonitrile. The filtrate was evaporated under reduced pressure, and the residue was developed on a preparative thin-layer chromatography plate with hexane–dichloromethane (1:1) to yield 61 mg (47%) of **11**. The solid was purified by recrystallization from hexane–dichloromethane: orange granules; mp 188–190 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.16 (1H, d, J = 7.9 Hz), 7.33 (1H, t, J = 7.9 Hz), 7.66 (1H, t, J = 7.9 Hz), 8.24 (1H, d, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 72.0, 84.2, 120.1, 125.6, 125.7, 127.4, 127.8, 134.3, 173.7, 176.6; IR (KBr) 2144, 2112, 1640, 1600, 1324 cm^{-1}; UV–vis (benzene) λ_{max} (log ϵ) 307 (4.14), 319 sh (4.09), 372 sh (3.28) nm; UV–vis (methanol) λ_{max} (log ϵ) 247 (4.65), 302 (4.14), 316 sh (4.10), 368 sh (3.34) nm.

Irradiation of 11 for Preparative Experiments. (1) Isolation of 14. A solution of 20 mg (94 μmol) of **11** in 16 mL of dry benzene containing 1% (v/v) methanol was placed in a Pyrex tube, purged with N_2 for 10 min, and irradiated with a 300-W high-pressure mercury lamp for 45 min at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in 5 mL of ether. The solution was treated with excess diazomethane in ether generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and KOH in the usual manner.[30] The reaction mixture was allowed to stand overnight at room temperature. After evaporation of the solvent, the residue was separated by GPLC with chloroform eluent to yield 5 mg of **14**, together with the unchanged starting material and **17**. Methyl 2-methoxyspiro[indene-1,7′-norcara-2′,4′-diene]-3-carboxylate (**14**): oil; ^{1}H NMR ($CDCl_3$) δ 3.84–3.88 (2H, m), 3.92 (3H, s), 4.17 (3H, s), 6.09–6.12 (2H, m), 6.38–6.40 (2H, m), 7.01–7.02 (2H, m), 7.23–7.25 (1H, m), 7.77 (1H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 49.6, 51.3, 52.2, 62.4, 106.1, 120.8, 122.6, 123.0, 123.5, 125.4, 126.5, 127.4, 128.9, 164.3, 177.0.

(2) Isolation of 15. A degassed solution of **11** (20 mg, 94 μmol) in 16 mL of dry benzene containing 1% (v/v) methanol was irradiated in a Pyrex tube with a 300-W high-pressure mercury lamp for 3 h at room temperature. After evaporation of the solvent under reduced pressure, the residue was separated by GPLC with chloroform eluent to yield 5 mg of **15**. 5-Methoxycarbonyl-11*H*-cyclohepta[*a*]naphthalen-6-ol (**15**): light yellow granules; ^{1}H NMR ($CDCl_3$) δ 3.31 (2H, br s), 4.10 (3H, s), 5.83 (1H, dt, J = 9.2, 7.2 Hz), 6.28 (1H, dd, J = 9.2, 5.1 Hz), 6.84 (1H, dd, J = 11.6, 5.1 Hz), 7.41–7.45 (1H, m), 7.51–7.54 (1H, m), 7.75 (1H, d, J = 11.6 Hz), 8.28 (1H, d, J = 8.2 Hz), 8.73 (1H, d, J = 8.5 Hz), 12.92 (1H, s); ^{13}C NMR ($CDCl_3$) δ 29.6, 52.5, 102.1, 123.9, 124.8, 125.4, 125.6, 125.9, 126.1, 127.2, 127.6, 128.1, 130.5, 132.5, 138.1, 162.3, 173.2.

(3) Isolation of 17. A degassed solution of **11** (13 mg, 61 μmol) in 10 mL of dry benzene containing 1% (v/v) methanol was irradiated in a Pyrex tube with a 500-W xenon-arc lamp through cutoff glass filter (>420 nm) for 5 h at room temperature. After removal of the solvent under reduced pressure, the residue was separated by GPLC with chloroform eluent to yield 3 mg of **17**, together with the unchanged starting material. Methyl 2-diazo-3-oxoindan-1-carboxylate (**17**): yellow oil; ^{1}H NMR ($CDCl_3$) δ 3.84 (3H, s), 5.10 (1H, s), 7.52 (1H, m), 7.64 (1H, m), 7.73 (1H, d, J = 7.9 Hz), 7.81 (1H, d, J = 7.6 Hz); IR (KBr) 2180, 1735, 1670, 1345 cm^{-1}.

***cis*- and *trans*-Dimethyl Benzocyclobutene-1,2-dicarboxylate (16).** To a solution of *cis*-1,2-dicyanobenzocyclobutene[19] (10 mg, 66 μmol) in 2.5 mL of methanol was added 2.5 mL of 16 N H_2SO_4. The reaction mixture was refluxed with stirring for 10 h. The organic material was extracted with ether, and the extract was washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was dissolved in 5 mL of ether. The solution was treated with excess diazomethane in ether.[30] The reaction mixture was allowed to stand overnight at room temperature. After removal of the solvent, the residue was separated by GPLC with chloroform eluent to yield 5 mg of *cis*-**16**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 3.73 (6H, s), 4.60 (2H, s), 7.23 (2H, m), 7.33 (2H, m); ^{13}C NMR ($CDCl_3$) δ 49.5, 52.4, 122.9, 128.7, 141.7, 170.0. In the same manner, *trans*-1,2-dicyanobenzocyclobutene was converted to *trans*-**16**: colorless

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[30] de Boer, Th. J.; Backer, H. J. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. 4, p 250.

oil; ^{1}H NMR (CDCl$_3$) δ 3.77 (6H, s), 4.64 (2H, s), 7.22 (2H, m), 7.30 (2H, m); ^{13}C NMR (CDCl$_3$) δ 49.6, 52.2, 123.0, 128.9, 141.1, 170.6.

Irradiation of 11 for Analytical Experiments. In a typical run, a solution (2 mL) of **11** (3 mg) in dry benzene containing 1% (v/v) methanol was placed in a Pyrex tube, purged with N$_2$ for 10 min, and irradiated with a 300-W high-pressure mercury lamp or with a 500-W xenon-arc lamp at room temperature. The excitation wavelength was regulated by the use of various Toshiba optical-cutoff glass filters, which are shown in Table 1. The consumption of the material and the yield of the photoproducts **13** and **15**−**17** were determined by the integration of ^{1}H NMR in the crude reaction mixture. Identifications of the products **15**−**17** were established by the agreement of their ^{1}H NMR spectra with those of authentic samples, and methyl 2-hydroxyspiro[indene-1,7′-norcara-2′,4′-diene]-3-carboxylate (**13**) was characterized by the three sets of multiplets centered at δ 3.61/3.24, 6.13, and 6.51 assigned to the norcaradiene protons and the methoxy signal at δ 3.97/3.77. (The signals for the minor isomer, which was identified as the keto form **13a**, are indicated after the slant lines.)

Matrix-Isolation Spectroscopy. The apparatus and experimental technique used for matrix-isolation spectroscopy have been described previously.[4,29] The bis(diazo) ketone **11** was vaporized under 10^{-6} Torr at 80 °C. IR data of **11** and the first-formed intermediates, **A** and **A′**, isolated in an Ar matrix at 12 K are shown in Tables 2 and 3, respectively. IR data of the second intermediates, **B** and **B′**, and the final products **C** were as follows. **B**: 2152s, 2116s, 1780m, 1422w, 1131w, 1099w, 901w, 763w, 734w. **B′**: 2133m, 2096s, 1808w, 1778m, 1380w, 1346m, 1131w, 1096w, 900w, 868w, 764w, 744w. **C**: 2132m, 2102s, 2062m, 1811m, 1798m, 1415w, 1362s, 1156m, 749m, 597w.

Calculations. The semiempirical calculations were carried out by the program packages Gaussian 92[31] or Spartan[32] on Sun or SGI workstation computers. The geometry optimizations, as well as the CI calculations, were performed at the PM3 level of theory. Vibrational frequencies and intensities were calculated at the same level of theory.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds **11** and **13**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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