# Photochemistry of 2,4-Bis(diazo)-1,2,3,4-tetrahydro-naphthalene-1,3-dione: Selective Photodecomposition of One of the Two Inequivalent Diazo Groups

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1,3-Bis(diazo) ketones have been of interest as useful precursors of various attractive molecules, such as cyclopropenones, strained alkynes, and new carbon oxides (C_nO_m).[1] In the course of our studies of the photochemistry of bis(diazo) ketones,[2] we have raised the question of whether one diazo group can be selectively cleaved when the diazo functions of a bis(diazo) ketone are inequivalent. To our knowledge, only two bis(diazo) ketones with two inequivalent diazo groups have been reported so far, 2,4-bis(diazo)androstan-17β-ol-3-one[3] and 1,3-bis(diazo)decahydronaphthalen-2-one.[4] Though the photochemistry of these bis(diazo) ketones was of special interest, the authors preliminarily reported that the photolysis of these compounds in solutions afforded a complex mixture from which nothing could be identified. In this paper, we report the photochemistry of a new bis(diazo) ketone with two inequivalent diazo groups, 2,4-bis(diazo)-1,2,3,4-tetrahydronaphthalene-1,3-dione (**1**), where the first example of selective photodecomposition of one of the two inequivalent diazo groups could be demonstrated.
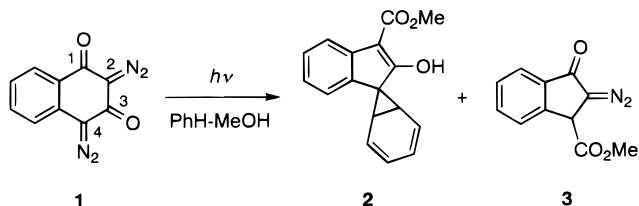
The direct diazo transfer to readily available 1,3-naphthalenediol with *p*-tosyl azide (2.5 equiv) using KF−Al$_2$O$_3$[5] in acetonitrile gave the bis(diazo) ketone **1**[6] in moderate yield. Irradiation of **1** in benzene containing 1% (v/v) methanol with a high-pressure mercury lamp (>300 nm) gave a mixture of the spironorcaradiene **2**[7] (21%) and methyl 3-oxo-2-diazoindan-1-carboxylate (**3**, 9%)[8] as primary isolable photoproducts.[9] The wavelength dependence

of the distributions of the primary photoproducts was examined. The ratio of the products obtained in the photolysis with the light through the filter cutting wavelengths shorter than 350 or 390 nm was similar to that obtained in the photolysis with the Pyrex-filtered light (>300 nm). However, the product distribution was dramatically changed in the irradiation with light of wavelength longer than 420 nm, where the yield of the diazo ketone **3** increased and that of the spironorcaradiene **2** considerably decreased ([**2**]:[**3**] = 0.06).

Both of the photoproducts **2** and **3** have an indanone skeleton, which could be formed through a Wolff-type ring contraction of the ketocarbenes photolytically generated from **1**. We propose that **2** is derived from the diazo ketene **4**, which is formed by the initial decomposition of the diazo group at the 2-position of **1**.[10]
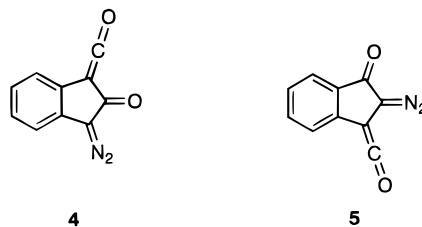
On the other hand, the mechanism for the formation of **3** can be readily explained in terms of the capture of the diazo ketene **5** generated by the extrusion of N_2 from the 4-position of **1** with methanol. Thus, the wavelength effect observed in the photolysis of **1** in benzene containing methanol strongly suggests 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 **1**.

To gain further evidence for the selective decomposition, we examined the photochemistry of **1** in an Ar matrix at 12 K. Irradiation (>350 nm) of **1** matrix-isolated in Ar resulted in a simultaneous decrease in the intensities of the two diazo stretching bands (2150 and 2094 cm^{-1}), as well as those of the two carbonyl stretching bands (1654 and 1636 cm^{-1}). New peaks appeared at 2142, 2088, 1690, and 1381 cm^{-1}, which indicated the formation of products with a cumulenic double bond and a carbonyl group (designated as **A**).[11] Analogously, irradiation of **1** in an Ar matrix with light of wavelength longer than 420 nm caused a simultaneous decrease in the intensities of the two diazo stretching bands. However, peaks of the photoproducts (designated as **A′**) appeared at 2136, 2070, 1695, and 1468 cm^{-1}, which were slightly but significantly different from the positions of the peaks observed in the irradiation with light of >350 nm.

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(6) 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.

(7) The spironorcaradiene **2** 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 protons attached to a three-membered ring, as well as the methoxy protons, were observed as two sets of signals in a 1.5:1 ratio, which was tentatively explained in terms of a keto-enol isomerism of **2**.

(8) 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}.

(9) Prolonged irradiation converted the primary products **2** and **3** into the 5-methoxycarbonyl-11*H*-cyclohepta[*a*]naphthalen-6-ol and dimethyl benzocyclobutene-1,2-dicarboxylate, respectively.

(10) If the diazo ketene **4** is a precursor of **2**, methyl 2-oxo-3-diazoindan-1-carboxylate (**6**) should be a primary photoproduct. We assume that **6** is produced quickly but decomposed to afford **2**, because it is reasonable to think that **6** largely exists in the enol form, reducing its thermal stability owing to loss of the resonance between the carbonyl and diazo groups.

(11) The first-formed products were photolytically converted to the alternative products having IR bands at 2152, 2116, and 1780 cm^{-1}, which are reasonably identified as the diketene and the propadienone with a benzocyclobutene skeleton formed through a Wolff-type ring contraction of the first-formed diazo ketones having an indanone skeleton.

Table 1. IR Spectroscopic Data for the Intermediates **A** and **A′** Generated in Ar at 12 K and for **4** and **5** Calculated with the PM3 Method

experimental[a] ν (cm^{-1})		calculated[b] ν (cm^{-1})		
A	**A′**	**4**	**5**	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

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 in the range above 1300 cm^{-1} with relative intensities greater than 2% are given.

It is reasonable to think that the first-formed intermediates **A** and **A′** are the diazo ketenes with an indanone skeleton, for which two possible structures **4** and **5** are feasible.[12] To identify the structure of the first-formed intermediates, PM3 calculations were carried out for these compounds. The calculated vibrational frequencies are given in Table 1, together with the frequencies observed for the intermediates **A** and **A′**. We should point out the following four features of the vibrational frequencies calculated for **4**, compared with those for **5**: (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 1460–1480 cm^{-1}. As shown in Table 1, all these features are completely consistent with the features of the vibrational frequencies observed for **A**, compared with those for **A′**. Thus, on the basis of the PM3 calculations, we can identify the predominant component of the first-formed intermediates **A** and **A′** as **4** and **5**, respectively. Taking into account that **4** and **5** are formed by the initial decomposition of the diazo group at the 2- and 4-position, respectively, these wavelength effects observed in matrices at 12 K are completely consistent with those observed in solutions at room temperature. Consequently, we can conclude that the selective photodecomposition of one of the two inequivalent diazo groups, i.e., the diazo group at the 4-position, of the bis(diazo) ketone **1** 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.

The remarkable wavelength effect observed in the photochemistry of **1** suggests the participation of higher excited states in the photoreactions.[13] To have a clue to understanding the observed wavelength effect, we carried out molecular orbital (MO) calculations with the PM3 method on **1**. The MO diagram of **1** shows that 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 predominantly to NHOMO and NLUMO, indicating 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 lowest excited singlet state S_1 of **1** can be roughly described as the state where 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 designated as an intramolecular charge-transfer state from the diazo group at the 4-position to the 2-position diazo moiety. A configuration which indicates 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. Thus, on the basis of the PM3 CI calculations, we can expect that selective excitation into the S_1 state using a long-wavelength light causes the selective cleavage of the 4-position diazo group and that both S_2 and S_3 contribute to the photoreaction initiated with a short-wavelength light, where the selective cleavage of the diazo groups cannot be expected, though 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 **1** are in accord with these expectations based on the theoretical calculations.

In conclusion, the bis(diazo) ketone **1** has been shown to undergo a remarkable wavelength-dependent photochemical reactions not only in solutions but also in matrices, where the selective photodecomposition of one of the two inequivalent diazo groups is practically achieved. 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 with the short-wavelength light. To our knowledge, this provides the first example of the reactivity control of a poly(diazo) compound by the excitation wavelength.

Supporting Information Available: Experimental procedures for the synthesis of **1**, spectral data for **1**–**3**, and theoretical calculation results (8 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) There is another possible structure of the diazo ketene with an indanone skeleton, which could be formed by the initial decomposition of the diazo group at the 2-position of **1**, followed by the migration of the C(3)–C(4) bond to the carbenic center. However, we ruled out this structure as a candidate for the intermediate **A** and **A′**, because it is reasonable to think that the migration of the bond linking C(1) with the aromatic ring takes place to give **4** in preference to the C(3)–C(4) bond migration owing to a large partial double-bonding character of the C(3)–C(4) bond.

(13) 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.