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Photolysis of Organic Azides. VI.[1] 1,4-Diacetoxy-2,3-diazidonaphthalene. Formation of Isoquinoline Structure from *α,α'*-Dicyano-*o*-xylylene

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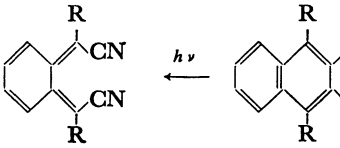
Transient absorbing in the 400—450 nm range was observed in the photolysis of 1,4-diacetoxy-2,3-diazidonaphthalene in rigid matrices at 77 K. The transient was assigned as α,α'-diacetoxy-α,α'-dicyano-*o*-xylylene by comparison with the low-temperature photolysis of the other precursors, 1,2-diacetoxy-1,2-dicyano-1,2-dihydrobenzocyclobutenes. The three *o*-xylylene stereoisomers showed differences in the longest-wavelength absorption maxima. Continued irradiation of the *o*-xylylenes converted them to 2-acetoxy-2-methyl[1,3]dioxolo[4,5-*c*]isoquinoline-5-carbonitrile as the result of the reaction of a cyano group with the *o*-xylylene system and the migration of an acetoxyl group. The rate of formation of the isoquinoline in rigid matrices depends on the viscosity of glassy solvents and the configuration of the intermediate *o*-xylylenes. The room-temperature photolysis of the diazide gave 2,3-diacetamido-1,4-naphthoquinone as the main product and compounds *via* the *o*-xylylene as minor products. A mechanism involving two competitive reactions is discussed.

There has been considerable interest in the structures and properties of *o*-xylylene (*o*-quinodimethane: 5,6-dimethylene-1,3-cyclohexadiene) and its various derivatives.[2—4] In a previous paper we reported the formation of α,α'-dicyano-*o*-xylylenes (**1**) by the photolysis of 2,3-diazidonaphthalenes (**2**).[5] Among the three derivatives,

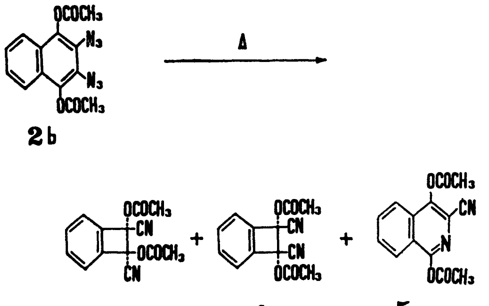


1 **2**

a: R = H
b: R = $OCOCH_3$
c: R = OCH_3

2b gave efficiently an unknown photoproduct *via* **1b** by prolonged irradiation at low temperature in rigid medium, while continued irradiation of the others, **1a** or **1c**, resulted in almost no reaction. We now report a new photochemical reaction of the *o*-xylylene system at low temperature in rigid medium.

In addition, the room-temperature photolysis of **2b** was investigated in connection with the low-temperature photolysis. Pearce *et al.*[6] found the formation of *cis*- and *trans*-1,2-diacetoxy-1,2-dicyano-1,2-dihydrobenzocyclobutenes (**3** and **4**, respectively) and 1,4-diacetoxy-3-isoquinoline (**5**) by the thermal decomposition of **2b**.



2b

3 **4** **5**

(23%) (<3%) (39%)

On the other hand, the room-temperature photolysis of **2b** was quite complicated and considerably different from the thermolysis or the low-temperature photolysis. A new reaction involving the migration of acyl groups to nitreno groups has been found in addition to the formation of **3** *via* **1b**, while **5** has not been produced. The mechanism of the room-temperature *vs.* low-temperature photolysis will be discussed, and a characterization of the photoproducts will be given.

Results and Discussion

Low-temperature Photolysis. A rigid glassy solution of **2b** in EPA (diethyl ether/isopentane/ethanol, 5 : 5 : 2) was irradiated at 77 K with a 500-W super high-pressure mercury lamp through a 300 nm cutoff filter. Figure 1 shows the photochemical process followed by absorption spectroscopy. The absorbance in the range of 424—450 nm increased in the early stage of irradiation. At this stage, warming of the glassy solution to room temperature resulted in disappearance of the absorption. This transient absorbing in the 400—450 nm range was tentatively identified as the α,α'-dicyano-*o*-xylylene (**1b**) in the previous paper,[5] by analogy to the low-temperature photolysis of the parent 2,3-diazidonaphthalene. Continued irradiation resulted in the disappearance of the absorption in the 400—450 nm range and in the appearance of a new absorption in the 355—380 nm range. In the cases of the other diazidonaphthalenes, **2a** and **2c**, the conversion from the *o*-xylylenes, **1a** and **1c**, proceeded even after prolonged irradiation. The secondary photoproduct having absorption bands at 355—380 nm was stable at room temperature. By a separate irradiation of **2b** on a preparative scale, a product with two fewer nitrogen molecules than the starting material was isolated in an almost quantitative yield. Although the product was presumed to be an isoquinoline derivative, on the basis of the IR, ^{1}H-NMR, and ^{13}C-NMR spectra, its final identification was difficult because its UV absorption spectrum (longest-wavelength: λ_{max} 376, 368, 358, 355 sh nm) was considerably different from that (λ_{max} 304 nm) of the isoquinoline (**5**) given by the thermal treatment. Therefore, an X-ray crystal structure analysis was made of a single-crystal grown from dichloromethane–ethanol. The structure was established as 2-acetoxy-

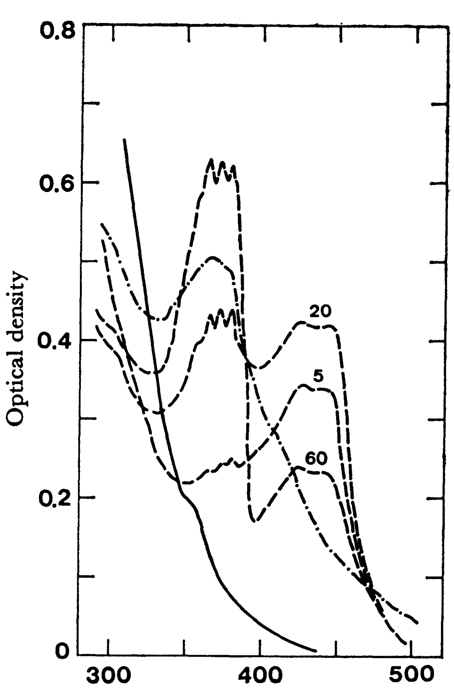
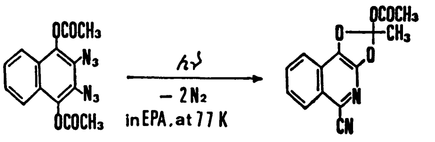


Fig. 1. Absorption spectra of **2b** in EPA at 77 K before (——) and after (----) irradiation. Numbers refer to irradiation times in min. Absorption spectrum (—·—) of **2b** recorded at room temperature after irradiation for 60 min.

2-methyl[1, 3]dioxolo[4, 5-*c*]isoquinoline-5-carbonitrile (**6**).[7] The formation of such an isoquinoline derivative by the photolysis in a rigid matrix was quite unexpected.



2b **6**

In addition, it is interesting that the electronic absorption spectra of isoquinoline derivatives depend highly on the position of the cyano group and on the presence of the dioxolane ring fused with the isoquinoline nucleus.

Irradiation of **2b** at 77 K was carried out in various media. The reaction proceeded as in the case of EPA. Figure 2 shows the relation between the irradiation time and the yield of the secondary photoproduct **6**, which was measured by monitoring the peak height of the 362 nm UV absorption due to **6** during stepwise photolysis. From a consideration of the viscosity of media as given in Table 1, it was found that the rate of formation decreased with the increase of the viscosity in a series of mixed solvents of isopentane and 3-methylpentane. In the case of EPA, the highly efficient formation, compared with other nonpolar media, may be attributed to solvent polarity.

Low-temperature photolyses of *trans*- and *cis*-1,2-diacetoxy-1,2-dicyano-1,2-dihydrobenzocyclobutenes (**3** and **4**, respectively) were carried out in order to confirm the intermediate and to study the mechanism of low-temperature photolysis of **2b**. Figures 3 and 4 show the photochemical processes of **3** and **4**, respectively, in EPA at 77 K. As in the case of **2b**, the longer-wavelength transient absorptions appear in the range of 400—450 nm in the early stage of irradiation, and a new absorption in the range of 355—380 nm begins to appear with the increase of irradiation time. Moreover, the prolonged irradiation with longer-wavelength light (>300 nm) results in the increase of that absorption, together with the decrease of the 400—450 nm absorption. The absorption peaks in the 355—380 nm range are completely consistent with those of **6**. However, the peaks of the transients generated from **3** and **4** are shifted to slightly shorter wavelengths than those of the intermediate generated from **2b**. This spectral shift could be explained in terms of the different configurations of the *o*-xylylenes. The intermediate generated

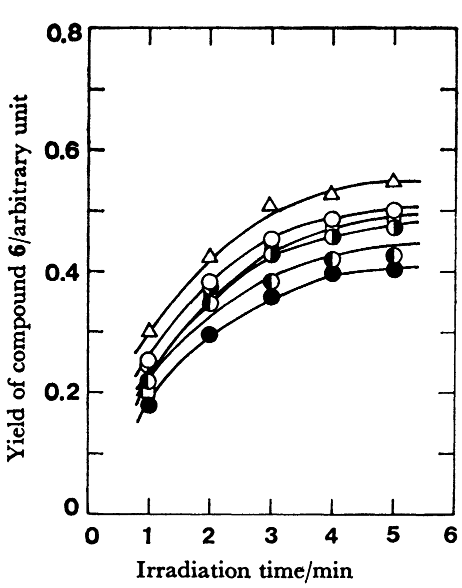


Fig. 2. Relation between the irradiation time and the yield of **6** by the photolysis of **2b** (0.1 mol m^{-3}) at 77 K in various solvents (shown in Table 1). Runs 1 (○), 2 (◑), 3 (◐), 4 (●), 5 (□), and 6 (△). The yields of the compound **6** correspond to the absorbances (λ 362 nm) due to **6**.

TABLE 1. VISCOSITY OF THE MEDIA IN THE PHOTOLYSIS OF **2b** AT 77 K

Run	Solvent (Composition in parts by volume)	Viscosity / Pa s	Ref.
1	Isopentane, 3-methylpentane (97 : 3)	8.9×10^{4}	a)
2	Isopentane, 3-methylpentane (3 : 2)	1.8×10^{7}	a)
3	Isopentane, 3-methylpentane (1 : 9)	2.4×10^{10}	a)
4	3-Methylpentane	9.4×10^{10}	a)
5	Methylcyclohexane, isopentane (1 : 3)	1.0×10^{7}	b)
6	Ether, isopentane, ethanol (5 : 5 : 2)	8.0×10^{7}	b)

a) J. R. Lombardi, J. Raymonda, and A. C. Albrecht, *J. Chem. Phys.*, **40**, 1148 (1964). b) Estimated from Fig. 2 in the literature: H. Greenspan and E. Fischer, *J. Phys. Chem.*, **69**, 2466 (1965).

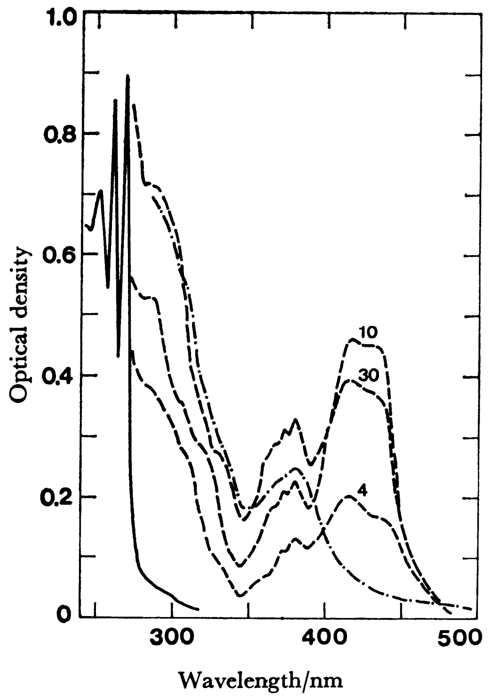


Fig. 3. Absorption spectra of **3** in EPA at 77 K before (——) and after (----) irradiation. Numbers 4 and 10 mean irradiation times (min) with a low-pressure mercury lamp, and 30 means irradiation time with a high-pressure mercury lamp (20 min) in addition to the 10 min irradiation. Absorption spectrum (—•—) recorded at room temperature after 30 min irradiation.

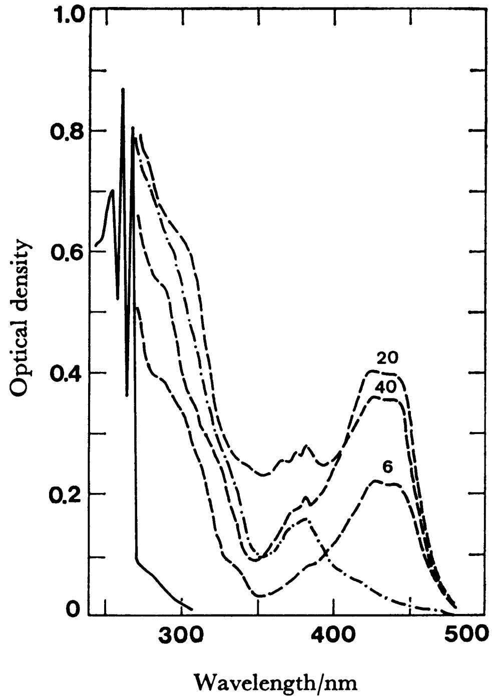
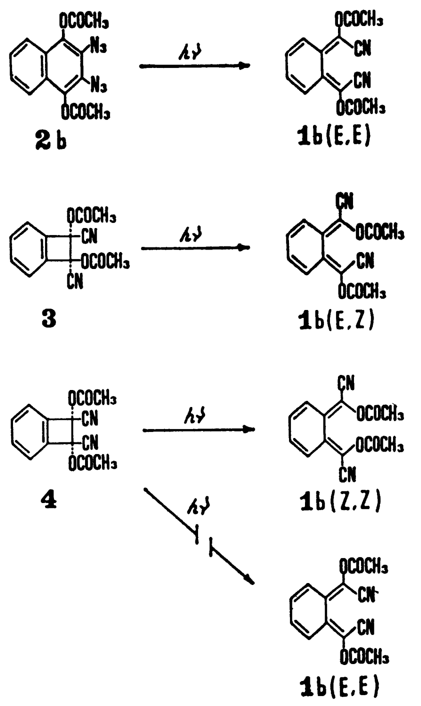


Fig. 4. Absorption spectra of **4** in EPA at 77 K before (——) and after (----) irradiation. Numbers 6 and 20 mean irradiation times (min) with a low-pressure mercury lamp, and 40 means irradiation time with a high-pressure mercury lamp (20 min) in addition to the 20 min irradiation. Absorption spectrum (—•—) recorded at room temperature after 40 min irradiation.

from **2b** must be the *E*,*E*-form stereoisomer (**1b**(*E*,*E*)) of α,α′-diacetoxy-α,α′-dicyano-*o*-xylylenes, as described in the previous paper[5] by analogy to the case of 1,2-diazidobenzene. The intermediates generated from **3** and **4** are presumed the *E*,*Z*-form **1b**(*E*,*Z*), and the *Z*,*Z*-form **1b**(*Z*,*Z*) or *E*,*E*-form **1b**(*E*,*E*), respectively, from a consideration of the orbital symmetry rule. In the case of **4**, the intermediate structure must be **1b**(*Z*,*Z*)', because the absorption peaks generated from **4** are not identical with those generated from **2b**. The spectral shifts of these stereoisomers are consistent with those of the *o*-xylylene derivatives. The absorbing peaks of the *o*-xylylene stereoisomers are summarized in Table 2.

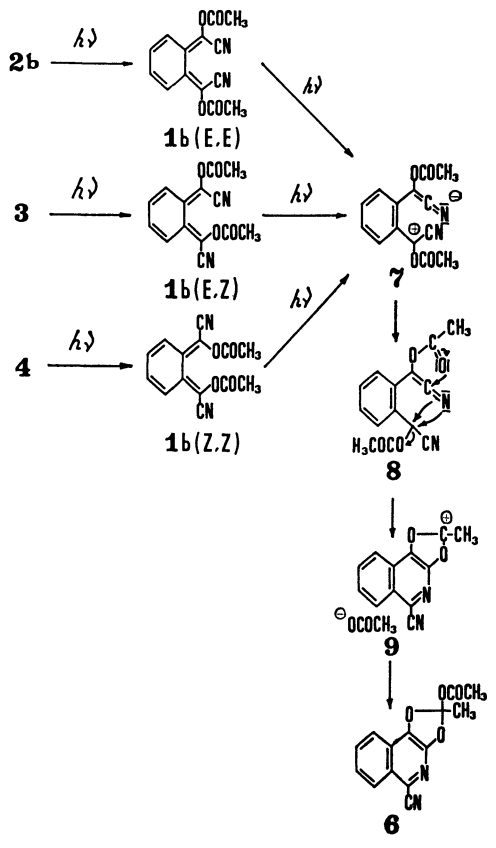


The secondary photoproduct from **3** or **4** is identified as **6** on the basis of the spectral properties of the crystals isolated from a separate irradiation on a preparative scale. The results of this photochemical reaction show that final product **6** is formed by a similar mechanism from the different stereoisomers of **1b**. A plausible mechanism which accounts for the formation of the isoquinoline (**6**) is depicted in Scheme 1.

Although the formation of **6** *via* **1b** from **2b** proceeds efficiently with the irradiation of a high-pressure mercury lamp, the rate of formation of **6** from **3** or **4** is very slow during irradiation of a low-pressure mercury lamp. In particular, the formation of **6** in the case of **4** occurs in a lower yield, compared with the case of **3**, after 10 min irradiation, as shown in Figs. 3 and 4. When the concentration of the intermediate **1b** was increased appropriately after 10 min irradiation, prolonged irradiation was carried out with a high-pressure mercury lamp (>300 nm). However, the rate of formation of **6** from **4** was much lower than that of **6** from **3** or, particularly, from **2b**. In the isoquinoline

Table 2. Absorbing peaks of *o*-xylylene stereoisomers (Absorption above 350 nm, at 77 K)

Substituents	Solvent	Absorbing peaks / nm		
		(*E*, *E*)	(*Z*, *Z*)	(*E*, *Z*)
α,α′-Diphenyl-[3e]	Methylcyclohexane	465		455
α,α′-Dicyano-[5]	EPA		432 458	432 454
α,α′-Diacetoxy-α,α′-dicyano-	EPA	424 448	423 444	415 435

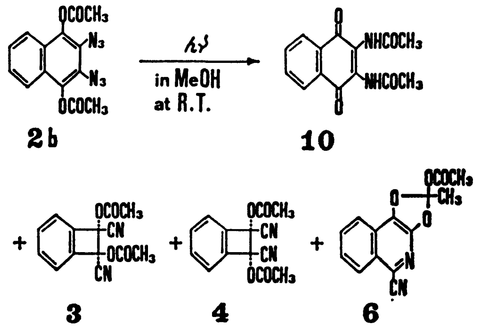


Scheme 1.

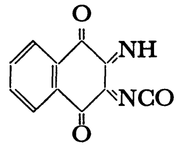
formation, the *o*-xylylene derivatives **1b**(*E*,*E*) and **1b**(*E*,*Z*) would have more favorable configurations than **1b**(*Z*,*Z*). The rigid medium at low temperature would control large rotational motions in each stereoisomer. The rigidity effects of glassy solvents have also been observed in the photolysis of **2b**, as shown in Fig. 2 and Table 1. The π-electrons of the *o*-xylylene system are delocalized by the substitution of the two cyano groups, and consequently the aromatization is liable to occur. The deactivation of the *o*-xylylene system by the cyano groups is consistent with the fact that the attempt to trap **1b** with dienophiles, such as *N*-phenylmaleimide or maleic anhydride, has failed. The formation of the isoquinoline structure is accomplished *via* the dipolar intermediate **7**, as shown in Scheme 1. The formation of the dioxolane ring is accompanied by the formation of the C–N bond, and the cleavage of the acetoxyl group follows. Finally, the migration of the acetate anion to the positive carbon atom of the dioxolane ring proceeds in the cage of rigid medium.

Although various photochemical and thermal reactions of *o*-xylylenes have been reported, it is interesting that the cyano groups conjugated with *o*-xylylene system participate in the reaction of *o*-xylylene structure. Moreover, it should be noted that the reactions involving a large rotational motion and a migration of the large acetoxyl group proceed readily in the rigid matrices at low temperature.[8]

Room-temperature Photolysis. A methanol solution of **2b** (0.52 mol m^{-3}) was irradiated at room temperature with a 400-W high-pressure mercury lamp through Pyrex. The photoproducts showed very complicated spots on a thin layer chromatogram of silica gel. As a major product, 2,3-diacetamido-1,4-naphthoquinone (**10**) was isolated in a 46% yield, together with the dihydrobenzocyclobutene **3** (25%) and the compound **6** (8%). Interestingly, the yield of the dihydrobenzocyclobutene **4** was only less than 1%, and 1,4-diacetoxy-3-cyanoisoquinoline (**5**), the main product in the case of the thermal decomposition of **2b**, was not detected.



Irradiation of **2b** in hexane gave a new compound instead of **10** as a main product, together with **6** as a minor product. Its structure was identified as 2,3-dihydro-2-imino-3-acetylimino-1,4-naphthoquinone (**11**) based on the spectral properties.



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The product distributions were sensitive to the solvent used. The results for the room-temperature photolysis of **2b** in various solvents are summarized in Table 3. An unknown photoproduct having UV absorption bands at 362 and 285—325 nm was observed in the case of hexane, and was the main product in the case of benzene. This was not characterized, although it is

Table 3. Room-temperature photolysis of 1,4-diacetoxy-2,3-diazidonaphthalene (**2b**)

Solvent	Concn/mol m^{-3}	Irrad time/min	Yield/%				
			3	**4**	**6**	**10**	**11**
Methanol	0.52	120	25	1	8	46	
2-Propanol	0.52	120	18	trace	6	45	
Diethyl ether	0.52	90	15		8	40	
Benzene	0.52	120	6		10	5	6
Hexane	0.26	30	3		12	3	48

presumed to be 1,2,3,4-naphthalenetetrone derivative (IR absorption bands at 1798, 1725, and 1690 cm^{-1}). It is certain that the products **3**, **4**, and **6** were given *via* the *o*-xylyelene **1b**, and **10** and **11** were formed by a different mechanism. Furthermore, in these room-temperature photolyses, the dihydrobenzocyclobutene, the product *via* the *o*-xylylene **1b**(*E*,*E*), was exclusively the *trans*-isomer (**3**). A consideration of the orbital symmetry rule shows that the cyclization of the *o*-xylylene is not a photoinduced but a thermal reaction.

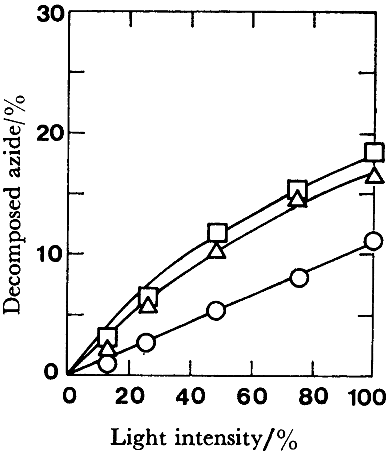
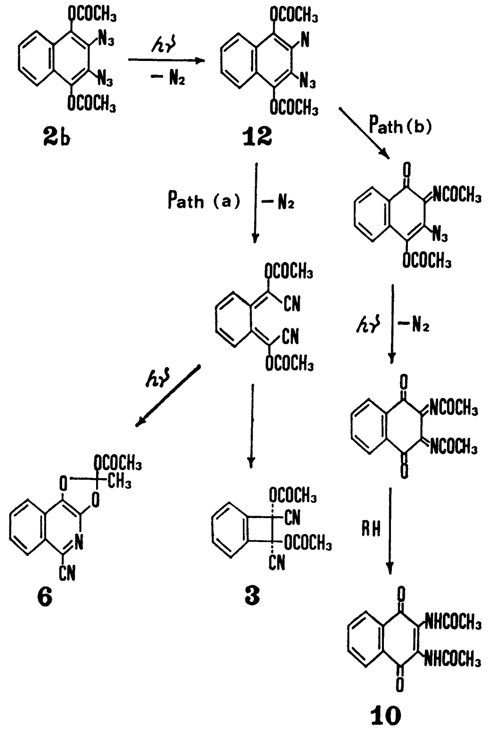


Fig. 5. Relation between the decomposed azide **2b** and light intensity. Photolyses (○) in EPA at 77 K, (△) in methanol at room temp, and (□) in hexane at room temp.

The dependence of the rate of decomposition of **2b** on the light intensity was examined. The amounts (%) of the decomposed azide were calculated on the basis of the measurement of the decrease in absorbance after 10 s irradiation. The results involving the low-temperature photolysis are shown in Fig. 5. In the previous paper,[5] it was found that the formation of **1a** or **1c** from **2a** or **2c**, respectively, was a monophotonic process. Similarly, the decomposition of **2b** in a rigid matrix at 77 K would lead quantitatively to the *o*-xylylene **1b**. Therefore, the relationship between the rate and the light intensity shows good linearity, suggesting a monophotonic reaction. On the other hand, the relationship deviates from linearity and displays downward curvature in the cases of the photolyses in methanol and in hexane. This indicates the participation of a biphotonic process. Therefore, the formation of **10** and **11** would be interpreted by the mechanism involving the stepwise decomposition of the two azido groups. Thus, there are two competitive reactions (Paths (a) and (b)) after the first azido group was decomposed. The process of the room-temperature photolysis is depicted in Scheme 2.



Scheme 2.

In Path (b), the attack of the nitreno groups upon the neighboring acetoxyl groups has been observed in the thermal decomposition of 1,4-diacetoxy-2-azidobenzenes.[6] The migration of acyl groups proceeded in a high yield (45—89%) for the reported compounds, although **5** was given as a main product and **10** was not given completely in the thermal decomposition of **2b**. In the room-temperature photolysis of **2b**, the migration of the acyl groups (Path (b)) has become the main process, taking the place of the formation of the *o*-xylylene (Path (a)) or **5**. Along Path (a), the cyclization to the dihydrobenzocyclobutene has become the main process, as a typical reaction of *o*-xylylene system.

The room-temperature photolysis of **2b** in the presence of some additives was carried out in order to study the factors governing the two competitive processes and the spin state of the nitrene **12**. The results are summarized in Table 4. The presence of dichloromethane (known to enhance singlet processes[9]) or iodomethane (heavy atom effect) gave nearly the same product distribution as in the case of the direct irradiation (Runs 1 and 2). However, the addition of pyrene (a triplet quencher and singlet promoter[10]) in methanol raised the yield of **10** to 58%, while the yields of **3** and **6** were decreased (Run 3). The addition of benzophenone or acetophenone (triplet sensitizers[10]) seemed to show no remarkable effects (Runs 4 and 5). Based on the results of Run 3, one could predict that Paths (a) and (b) were divided into triplet-derived and singlet-derived processes, respectively. That is to say, the spin state of the nitrene (**12**) which attacks the neighboring acetoxyl group is singlet, whereas the nitrene (**12**) which attacks the remaining azido group is in the triplet state. The direct observations of actual precursors and quenching rates are lacking, so this conclusion cannot be confirmed yet.

TABLE 4. ROOM-TEMPERATURE PHOTOLYSIS OF **2b** IN THE PRESENCE OF ADDITIVES

Run	Conditions[a)]	Yield / %		
		3	**6**	**10**
1	MeOH/CH_2Cl_2 (50%)	25	8	46
2	MeOH/CH_3I (10%)	25	6	42
3	MeOH/Pyrene (8.2 mol m^{-3})	3	<1	58
4	Benzene/Acetophenone (10%)	5	8	5
5	Benzene/Benzophenone (9.2 mol m^{-3})	6	15	<1

a) Concentration of **2b**: 0.52 mol m^{-3}. Irradiation time: 120 min.

Some differences in the low-temperature *vs.* room-temperature photolysis have been found in the processes of the attack by a nitreno group upon an acetoxyl group and the cyclization of the *o*-xylylene to the benzocyclobutene. The suppression of these processes in the low-temperature photolysis could be ascribed to a rigidity-controlled and activation-energy-controlled field.

Experimental

Measurements. The melting point is uncorrected. The IR and UV/VIS spectra were recorded on Hitachi Model 260-30 and Shimadzu Model UV-300 spectrophotometers respectively. The ^{1}H NMR and ^{13}C-NMR spectra were recorded on Varian Model XL-100-12 (100 MHz) and JEOL Model FX-100 (25 MHz) spectrometers respectively using TMS as an internal standard. The mass spectra were recorded on a Hitachi Model RMU-6M spectrometer. The microanalysis was performed at the Institute of Physical and Chemical Research.

Materials. 1,4-Diacetoxy-2,3-diazidonaphthalene (**2b**), and *cis*- and *trans*-1,2-diacetoxy-1,2-dicyano-1,2-dihydrobenzocyclobutenes were prepared according to the literature.[6]

Irradiations of 2b in Rigid Media at 77 K. Irradiation on preparative scale was carried out in a doughnut-shaped Pyrex vessel (volume: about 160 ml; thickness: 7 mm) which was immersed in liquid nitrogen with a 400-W high-pressure mercury lamp (Riko UVL-400HA) protected with a transparent quartz Dewar vessel. A solution of **2b** in 160 ml of EPA (0.37 mol m^{-3}) was irradiated for 10 min. Upon warming to room temperature, the solution was condensed on a rotary evaporator. Preparative-TLC (Merck Silica-gel 60 F$_{254}$) analysis of the concentrate gave the starting material (about 40%) and yellow crystals (55%). The crystals were recrystallized from dichloromethane–ethanol. Mp 146 °C (dec). IR (KBr): 2230, 1778, 1598, 1448, 1440, 1388 cm^{-1}. UV (Hexane): 376 (ε 3800), 368 (4500), 358 (4500), 355 sh (4100), 308 (6200), 296 (4600), 233 (19000) nm. ^{1}H-NMR ($CDCl_3$) δ: 2.09 (s, 3H, CH_3), 2.18 (s, 3H, $COCH_3$), 7.5—7.9 (m, 3H, aromatic), 8.20 (s, 1H, aromatic) ppm. ^{13}C-NMR ($CDCl_3$) δ: 21.6 (q), 24.7 (q), 116.0 (s), 119.9 (d), 121.4 (s), 122.0 (s), 125.5 (d), 125.9 (s), 128.2 (d), 129.3 (s), 130.9 (d), 136.0 (s), 150.8 (s), 167.0 (s) ppm. MS: *m/e* 270 (M$^+$), 218, 214, 212, 211, 186. Found: C, 62.33; H, 3.75; N, 10.45%. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37%. The structure of the crystals was determined as *2-acetoxy-2-methyl[1,3]-dioxolo[4,5-c]isoquinoline-5-carbonitrile* based on the spectral properties as described above and finally on the results of X-ray crystallography.

Irradiation for spectroscopy was carried out with a cell (path length: 10 mm) which had been immersed in liquid nitrogen in a quartz Dewar vessel equipped with optical windows on opposite sides. The light source was an Ushio USH-500D 500-W super high-pressure mercury lamp which transimitted through a 300 nm cutoff filter.

Irradiation of 3 or 4 in EPA at 77 K. Irradiation on a preparative scale was performed in the doughnut-shaped quartz vessel which was immersed in liquid nitrogen with a 160-W low-pressure mercury lamp (Riko UVL-160LA) protected with a transparent quartz Dewar vessel. A solution of **3** in 160 ml of EPA (0.44 mol m^{-3}) was irradiated for 2 h. The starting material and yellow crystals were isolated by a similar procedure to that for **2b**. The crystals were identical with those formed by the photolysis of **2b**.

Irradiation of **3** or **4** for spectroscopy was carried out in a manner like that described above for **2b**. The light source was a 15-W low-pressure mercury lamp (Toshiba GL-15).

Irradiation of 2b in Fluid Media at Room Temperature. Irradiation was performed under bubbling of nitrogen in a conventional immersion well-type reactor (volume: about 1200 ml) equipped with a 400-W high-pressure mercury lamp (Riko UVL-400HA) through Pyrex. The separation of the photoproducts was performed by the preparative TLC, and the yield determination was carried out by UV analysis (Tables 3 and 4).

The main photoproduct from the photolysis in methanol was precipitated in condensed solution (46% yield). The crystals were recrystallized from acetone–methanol, yielding yellow needles, mp 249 °C (dec). This product was identified as 2,3-diacetamido-1,4-naphthoquinone (**10**) by comparing the absorption spectrum with that of an authentic sample[11] and by the following spectral data. IR (KBr): 3310 (NH), 1668, and 1650 (quinone CO, acetamido CO) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.3 (s, 6H, CH_3), 7.6—7.9 (m, 2H, aromatic), 8.0—8.2 (m, 2H, aromatic), 8.5 (s, broad, NH) ppm. ^{13}C-NMR ($CDCl_3$) δ: 23.8 (q), 126.9 (d), 128.1 (s), 130.8 (s), 134.3 (d), 167.4 (q) ppm.

The main product from the photolysis in hexane was precipitated in condensed solution (48% yield). The crystals were recrystallized from acetone–dichloromethane. Yellow crystals, mp 180 °C (dec). It was identified as 2,3-dihydro-2-imino-3-acetylimino-1,4-naphthoquinone (**11**) on the basis of the following spectral data. IR (KBr): 1674 and 1640 (quinone CO, acetimino CO) cm^{-1}. MS: *m/e* 228 (M$^+$), 186 (M−ketene), 132. ^{1}H-NMR (DMSO-d_6) δ: 2.45 (s, 3H, CH_3), 7.8—7.9 (m, 2H, aromatic), 8.4—8.6 (m, 2H, aromatic), 12.8 (broad, 1H, NH) ppm. ^{13}C-NMR (DMSO-d_6) δ: 13.1 (q), 120.4 (s), 129.8 (s), 129.9 (s), 132.6 (s), 133.0 (s), 133.4 (s), 136.0 (s), 151.2 (s), 155.0 (s), 162.9 (s), 176.0 (s) ppm.

Preparative TLC (Merck Silica-gel 60 F_{254}) of the filtrates from the condensed solutions gave the photoproducts shown in Table 3.

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