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Low-temperature Photolysis of *ortho*-Substituted Azidobiphenyls. Formation of Phenazines from 2,2′-Diazidobiphenyls[1)]

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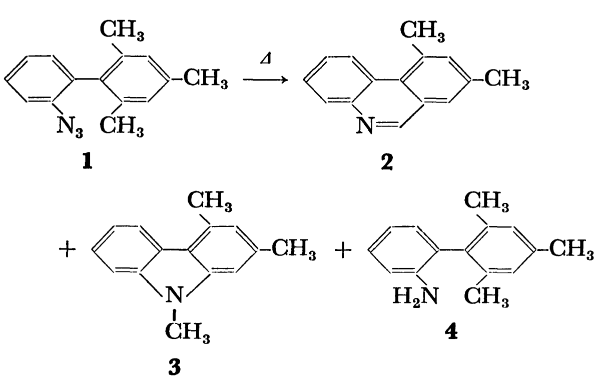
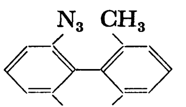
It was found that the unexpected phenazines were formed as minor products by the low-temperature photolysis of 2,2′-diazidobiphenyls in a rigid matrix. The phenazine formation results from the 1,1′-C–C bond fission of the biphenyl nucleus and suggests the aziridine intermediates. The low-temperature photolysis of 2-azido-2′-methylbiphenyl and 2-azido-2′,4′,6′-trimethylbiphenyl leads to the triplet-derived phenanthridine derivatives as major products.

It has been reported that 2-azido-2′,4′,6′-trimethylbiphenyl (**1**) gives the phenanthridine **2** (48%), as well as the carbazole **3** (5%) and the hydrogen abstraction product **4** (29%), on thermolysis.[2)] When, on the other hand, the related 2,2′-diazido-6,6′-dimethylbiphenyl (**5**) was heated alone or in a number of solvents, tar rather than expected 4,9-diazapyrene (**6**) or *N*,*N*′-dimethylpyrrolo[2,3,4,5-*def*]carbazole (**7**) was obtained.[3)] However, it was found, in the course of work on the low-temperature photochemistry of 2,2′-diazidobiphenyl,[4)] that the photolysis of **5** in EPA at 77 K gave 1,10-dimethylbenzo[*c*]cinnoline (**8**) in a 60% yield. The present author has now reinvestigated the possibility of forming the compound **6** or **7** as a minor product. The present paper reports that the unexpected 1,6-dimethylphenazine instead of the expected **6** and **7** was formed, together with the major product, **8**, by the low-temperature photolysis of **5** in glassy matrices. The phenazine formation involving the unusual 1,1′-C–C bond fission of the biphenyl nucleus will be discussed in terms of the interesting intermediate aziridine in nitrene chemistry. Moreover, the low-temperature photolysis of 2-azido-2′,4′,6′-trimethylbiphenyl will briefly be reported.





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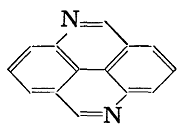

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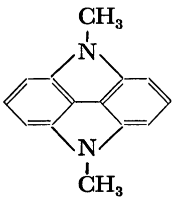

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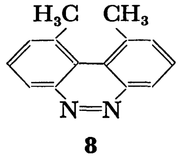

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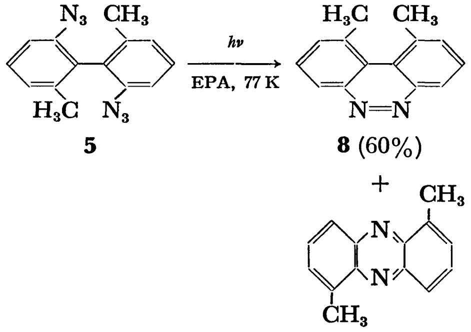
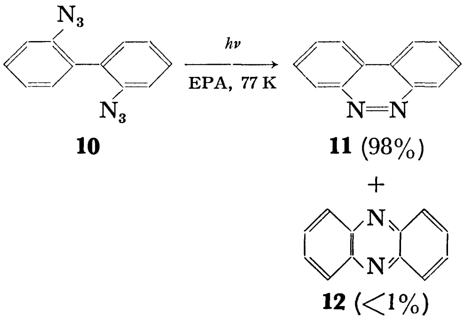
Results and Discussion

The previous paper reported that 2,2′-diazidobiphenyl afforded benzo[*c*]cinnoline (98%) almost quantitatively upon irradiation in glassy matrices at 77 K, and that, in the case of **5**, the yield of **8** was decreased to 60% by the steric effects.[4)] The 3.18×10^{-4} mol dm^{-3} EPA (5: 5: 2) solution of **5** was irradiated at 77 K with a low-pressure mercury lamp. The residue remaining after the removal of solvents from the irradiated solution was examined by thin-layer chromatography. Initial TLC (silica gel) results using ether–hexane eluants indicated the unchanged starting material, **5**, as the first elute, and **8** as the second elute, plus a chromatographically nonmobile material, as described in the previous paper. However, the TLC results using the eluent benzene indicated a new fraction as the second elute, and bright yellow crystals were isolated in an 8% yield. It was identified as 1,6-dimethylphenazine (**9**) on the basis of the microanalysis and spectral properties. The chromatographically nonmobile material is, from the intermediate, presumed to be a polymeric product, because the existence of another remaining azido group was ascertained from the IR absorption spectrum (2120 cm^{-1}).



Similarly, the irradiation of 2,2′-diazidobiphenyl (**10**) in EPA at 77 K and the separation by TLC were reexamined in order to confirm that the phenazine formation was a general reaction of 2,2′-diazidobiphenyls. The parent phenazine (**12**) was detected in the second fraction, along with the major product, benzo-

[*c*]cinnoline (**11**), in the third fraction. The yield, which was determined by absorption spectroscopy, consisted of trace amounts (less than 1%).



The photochemical reaction with the increase in the irradiation time was followed by absorption spectroscopy. From the spectra shown in Fig. 1, it becomes apparent that 1,6-dimethylphenazine (**9**) is formed not by the thermal reaction of some photoproducts from **5**, but by the irradiation of **5** in a rigid matrix. The absorption maximum at 308 nm that is observed in the early stages is a transient absorption which disappears on warming to room temperature. It is tentatively identified as the nitrene, **13**, based on its similarity to other nitrenobiphenyls.[5] With the increase in the irradiation time the absorption maximum of the transient is obscured by the appearance of the absorption in the 320—330 nm range; this shows the formation of the major photoproduct, **8**. In addition, a small absorption at 362 nm is also observed on the tail of the large absorption of **8**. That is, the absorption (λ_{max} 362 nm) which is attributed to phenazine appears, together with that of **8**, as a secondary product from the nitrene, **13**.

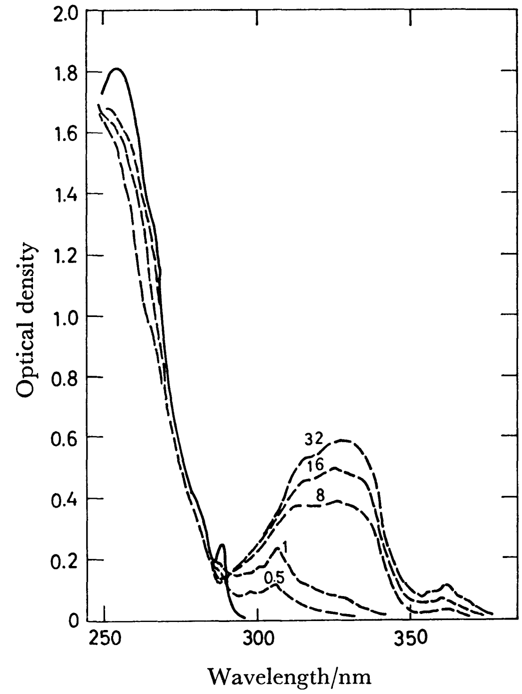


Fig. 1. Absorption spectra of 2,2′-diazido-6,6′-dimethylbiphenyl prior to (——) and after (– – –) photolysis in EPA at 77 K. Numbers refer to irradiation time in minute.

The irradiations of **5** in different solvents, at different temperatures, and more different light intensities were carried out in order to find the factors governing the phenazine formation. The results in Table 1 seem to show that the nature of the solvent plays no substantial role. The difference in the room-temperature *vs.* low-temperature photolysis is represented by the rigidity of the reaction medium together with the reaction temperature. In a series of photolyses in IP-3MP matrices whose viscosities are varied in the range of five orders, the ratios of the yields of **8** and **9** are very similar, within the range of experimental error. However, the formations of both **8** and **9** are subject to suppression in more viscous media. The rise in the temperature, although the reaction medium is still highly rigid, changed the photolytic reaction, which could not be characterized. The formation of **8** and **9** was no longer detectable. In conclusion, the reaction is found to be highly sensitive to the reaction temperature rather than the rigidity. Table 2 shows the dependency of the product yields on the light intensity in the photolysis at 77 K in EPA. It is of interest that the yield of

Table 1. Irradiations of 2,2′-diazido-6,6′-dimethylbiphenyl (5) at low temperatures in rigid matrices

Run	Solvent[a] (Composition in parts by volume)	T/K	Viscosity[b] / Pa s	Yield/% Cinnoline **8**	: Phenazine **9**
1	EPA (5: 5: 2)	77	(8×10^{7})	60	8
2	MCH, IP (1: 3)	77	(1×10^{7})	60	8
3	IP, 3MP (97: 3)	77	8.9×10^{4}	60	7.5
4	IP, 3MP (3: 2)	77	1.8×10^{7}	56	7.5
5	IP, 3MP (3: 7)	77	1.4×10^{9}	55	7
6	IP, 3MP (1: 9)	77	2.4×10^{10}	50	6.5
7	EtOH, MeOH (1: 1)	77	($>1\times10^{13}$)	55	7
8	3MP	93.5	7.7×10^{4}	—	—[c]
9	EtOH, MeOH (1: 1)	115	2×10^{11}	—	—[c]
10	Glycerol, MeOH (10: 1)	201	1×10^{12}	—	—[c]

a) EPA (diethyl ether, isopentane, ethanol), MCH (methylcyclohexane), IP (isopentane), 3MP (3-methylpentane). b) Cited from Ref. 6. The values in parentheses are estimated from the figures cited in the literature. c) Not detectable, or negligible even if formed.

Table 2. Dependence of product distributions on the light intensity
(Irradiations of **5** at 77 K in EPA)

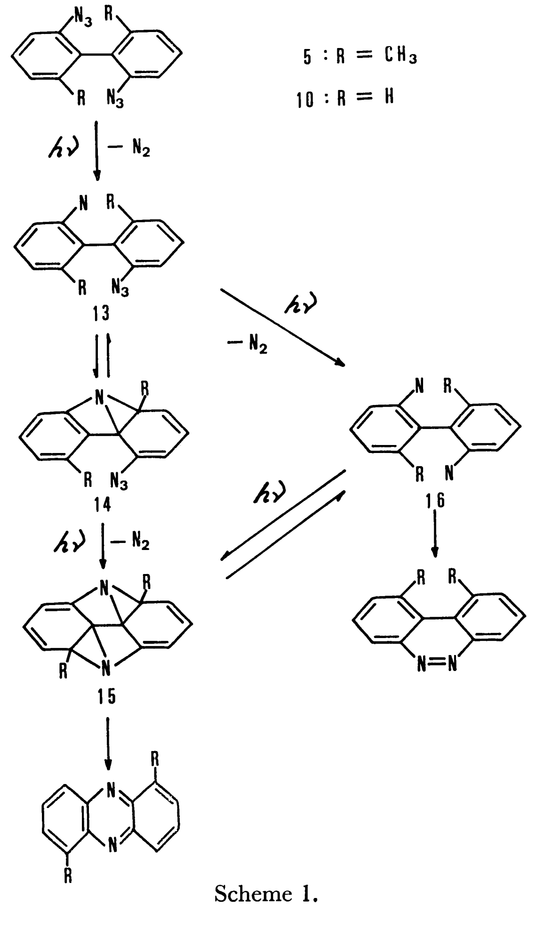
Run	Light[a]	Yield/% Cinnoline **8** :	Phenazine **9**
1	L-P(100%)	60	8
2	L-P(50%)	62	3
3	L-P(12.5%)	58	*ca.* 1
4	L-P(100%) H-P	55	14

a) L-P (a 15 W low-pressure mercury lamp); H-P (a 500-W high-pressure mercury lamp through a UV-31 filter). The light intensity of the low-pressure mercury lamp was regulated with slits (transmittances of 50 and 12.5%).

phenazine **9** rises to 14% when the sample is simultaneously irradiated with strong long-wavelength light (λ>310 nm) in addition to the usual source of 254 nm light.

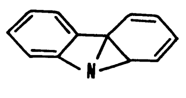
The phenazine formation by the decomposition of 2,2′-diazidobiphenyls is quite unexpected and unusual, involving the 1,1′-C–C bond fission of the biphenyl structure. A plausible mechanism to account for the phenazine formation is depicted in Scheme 1.

As the intermediate, **13**, is stable indefinitely at 77 K in rigid medium, the **13**→**14** conversion is a photochemical process. It is well-known that the ground states of arylnitrenes are triplet.[7] Although **13** is once populated from the ground state to the excited triplet state (T*) by light absorption, the excited singlet state may also be efficiently populated *via* T*. Therefore, the multiplicity of the nitrene leading to the aziridine intermediate can not be concluded easily without the direct observation of the excited state. In rigid matrices at 77 K the **13**→**14** process must be less effective, much like the carbazole formation from 2-nitrenobiphenyl,[5] than the process to benzo[*c*]cinnoline *via* **16**. The dependence on the light intensity obtained from Table 2 is revealed in the two competitive processes: the **13**→**14** conversion and the decomposition of the second azido group. The strong long-wavelength light appreciably facilitates the less effective process, **13**→**14**. Moreover, the light-intensity dependency may mean that the **16**→**15** conversion occurs by light absorption, while the reverse conversions, **14**→**13** and **15**→**16**, occur spontaneously as nonphotonic processes. In the competitive processes from **13**, the steric effects by the 6,6′-dimethyl substitution, which suppresses the coupling of nitrenes to lead to the cinnoline, contribute to the difference in the yields between **8** and **12**. As the **14** structure is highly strained, the 1,1′-C–C bond must be bent. Therefore, the **14**→**15** process may be relatively facile compared with the **13**→**14** process, although the **15** structure must be much more strained than **14**. Once the intermediate, **15**, is formed, the phenazine formation will follow to stabilize it by aromatization. The finding that **8** and **9** are formed only at a restricted low temperature is ascribable to facile side reactions from the reactive intermediates, **13**—**16**, although the details of the mechanism remain unknown.



Scheme 1.

The mechanism of the phenazine formation contains two aziridine intermediates, **14** and **15**. The structure of **14** is similar to that (**17**) proposed in the carbazole formation from 2-azidobiphenyl.[8b)] However, Sundberg and his co-workers[8)] proposed another aziridine, **18**, rather than **17**, as a result of their estimation that **17** is about 10 kcal/mol less stable than **18**. The aziridine intermediate **17** has not been well-confirmed in the carbazole formation from azidobiphenyls. The phenazine formation, however, results from the attack of the nitrene on 1′-C and the 1,1′-C–C bond fission of the biphenyl nucleus; consequently, the **14** and **15** structures may be suggested as appropriate intermediates. These intermediates are of great interest in nitrene chemistry, although the direct evidence for them and further mechanistic aspects remain to be elucidated.



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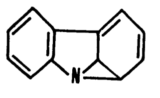

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In the low-temperature photolysis of *ortho*-substituted azidobiphenyls, there has been considerable interest in the possibility of intramolecular arylnitrene insertion into a suitably located methyl group. The intramolecular reaction between the arylnitrene and the methyl group could not occur in the case of **5**, so that neither 4,9-diazapyrene nor phenanthridine derivatives were

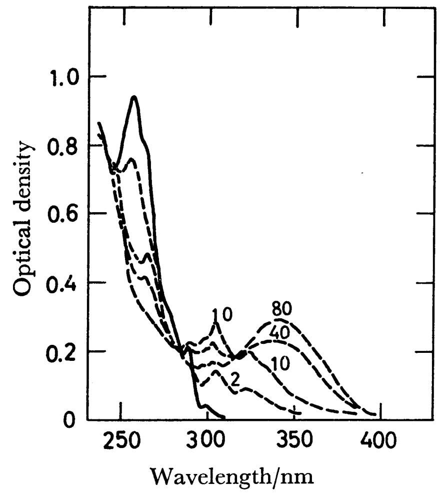


Fig. 2. Absorption spectra of 2-azido-2′-methylbiphenyl prior to (——) and after (----) photolysis in EPA at 77 K. Numbers refer to irradiation time in minute.

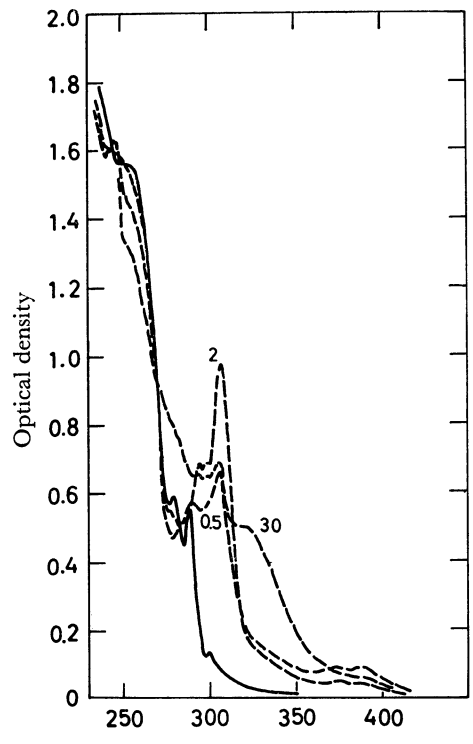
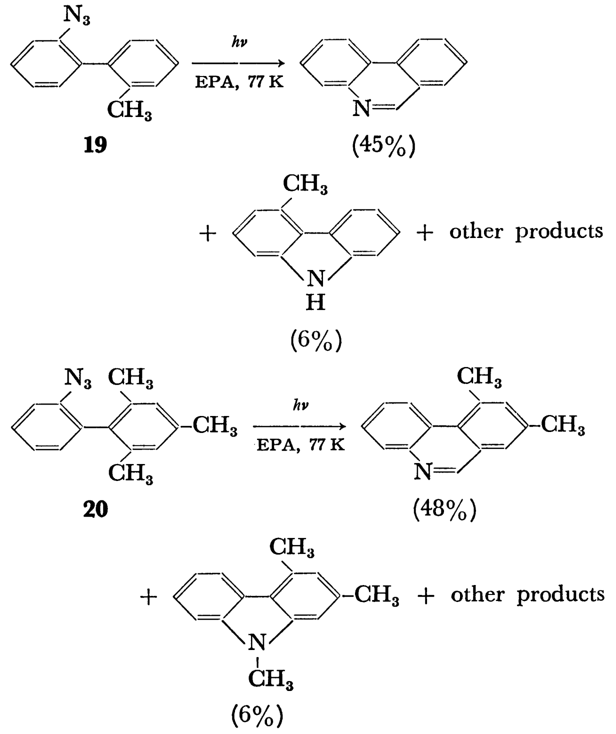


Fig. 3. Absorption spectra of 2-azdio-2′,4′,6′-trimethylbiphenyl prior to (——) and after (----) photolysis in EPA at 77 K. Numbers refer to irradiation time in minute.

detected. In this connection, the low-temperature photolysis of 2-azido-2′-methylbiphenyl (**19**) and 2-azido-2′,4′,6′-trimethylbiphenyl (**20**) was briefly studied. Figures 2 and 3 show the spectral changes in **19** and **20** respectively in EPA at 77 K with the increase in the irradiation time. In both cases, the formation of intermediate nitrenes with transient absorptions is observed in the early stages; they become photoproducts with absorption at the longer wavelengths after long irradiation times. By separate experiments with a preparative scale, the photoproducts were isolated as follows.



It should be noted that these products contain thermally reacted products in addition to the photoproducts formed in a rigid matrix, because an appreciable amount of the intermediate nirenes remains when the irradiation is stopped. Although the details of these photolyses can not be discussed in this report, it has become apparent that the phenanthridine formation occurs with a higher selectivity than the thermolysis[2,3] or triplet-sensitized photolyses at room or high temperatures.[9] Consequently, the intramolecular arylnitrene insertion into a methyl group occurs effectively in these compounds in a rigid matrix at a low temperature. It is of interest, therefore, that, in the case of **5**, the phenazine formation occurs instead of the insertion into methyl groups.

Experimental

Measurements. The IR and UV 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 the internal standard. The mass spectrum was recorded on a Hitachi Model RMU-6M spectrometer. The microanalysis was performed at the Institute of Physical and Chemical Research.

Materials. 2,2′-Diazido-6,6′-dimethylbiphenyl (**5**),[3] 2-azido-2′-methylbiphenyl (**19**),[3] and 2-azido-2′,4′,6′-trimethylbiphenyl (**20**)[2] were prepared according to the literature. The crude materials were purified by column chromatography on silica gel.

Irradiation of Azides. Low-temperature irradiations on a preparative scale were carried out in a doughnut-shaped quartz vessel (volume: about 160 ml; thickness: 7 mm) which was immersed in liquid nitrogen with a 30-W low-pressure mercury lamp (Riko UVL-30LA) protected with a transparent quartz Dewar vessel. Irradiations at 77 K for spectroscopy were 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. An Oxford Instruments DN-704 liquid nitrogen cryostat was used for the spectroscopic measurements by the irradiation at low-temperatures over 77 K.

Products Analysis. The separation and the yield determination of the photoproducts were carried out with a preparative thin-layer chromatograph (Merck Silicagel 60 F_{254}), and were followed by UV analysis. The identification of the known compounds were confirmed by comparison with authentic samples. *1,6-Dimethylphenazine (9)* was determined on the basis of the following microanalysis and spectral properties.[10] Found: C, 79.23; H, 5.85; N, 12.74%. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45%. MS, *m/e* 208 (M^+). IR (KBr) 2955, 2880, 1730, 1624, 1538, 1480, 1450, 1375, 1348 cm^{-1}. UV (MeOH) 362 (ε 11700), 254 nm (108000). ^1H-NMR ($CDCl_3$) δ 2.93 (s, 6H), 7.6—7.8 (m, 4H), 8.0—8.2 (m, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ 17.6 (q), 128.0 (d), 129.2 (d), 129.7 (d), 137.7 (s), 142.8 (s), 142.9 (s) ppm.

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