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Photolysis of Organic Azides. II.[1] The Photolysis of 2,2′-Diazidobiphenyl in Rigid Matrices at Low Temperatures

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The direct, triplet-sensitized, and low-temperature photolyses of 2,2′-diazidobiphenyl have been studied. The direct irradiation afforded 4-azidocarbazole, and the triplet sensitization resulted in the predominant formation of the azo dimer, accompanied by a low yield of benzo[*c*]cinnoline. The photolysis in a rigid matrix at 77 K afforded benzo[*c*]cinnoline quantitatively. The mechanism for its preferential formation in low-temperature matrix photolysis is discussed, and we propose a biphotonic process involving a dinitrene *via* a mononitrene.

The photolysis of 2-azidobiphenyl has received considerable attention in recent years. It has been well established by Swenton and his co-workers[2] that the direct photolysis results in the predominant formation of carbazole and that the triplet sensitization leads to the predominant formation of the azo dimer (2,2′-diphenylazobenzene). In connection with studies of 2-azidobiphenyl, it became of interest to examine the photolytic reaction of 2,2′-diazidobiphenyl (I) and to determine whether the intramolecular azo compound benzo[*c*]cinnoline (II) is given by the triplet-sensitized photolysis.

In our preliminary study[1] of the photolysis of I, we found that, although the sensitized photolysis fell short of our expectations, the low-temperature photolysis in a rigid matrix led to the quantitative formation of II, suppressing other competitive reactions. The preferential intramolecular-azo-bond formation of vicinal diazido compounds under these conditions may provide a useful method for the preparation of cyclo-azo compounds. In this paper, the direct and sensitized photolyses of I and 2,2′-diazido-6,6′-dimethylbiphenyl (VII) at room temperature are examined by comparison with those of 2-azidobiphenyl. Moreover, the low-temperature photolyses in rigid matrices are studied, and we propose a mechanistic scheme involving a dinitrene, which accounts for the exclusive formation of II, on the basis of the absorption spectra at 77 K.

Results

Direct Irradiation of I. It has previously been reported[3] that the direct irradiation of I in heptane affords 4-azidocarbazole (III) in a 50% yield, together with trace amounts of II. We reinvestigated it briefly for a mechanistic study in connection with the sensitized and low-temperature photolyses. In addition to III (55—65%) as the major product, II and the bimolecular product IV were identified in trace amounts (<1%) (Table 1). In the case of I, the photochemical reaction is not simple compared with the photolysis of 2-azidobiphenyl because III and IV still have one more reactive azido group. With the increase in the irradiation time, most of the photoproducts become intractable polymeric materials. Hence, the yields of these compounds (also VI, which will be described later) are subject to experimental indefiniteness. Therefore, the following product yields were determined in an earlier stage which could be analyzed. Unless otherwise stated, the product analysis was carried out within about 20% of conversion at most. Among the final products, the azo dimer (V) of III was not detected, although the irradiation of isolated III seemed to afford the azo dimer, which was characterized by an absorption spectrum with a broad peak between 350 and 400 nm. The yield of III is rather insensitive to solvents, as is shown in Table 2.

Table 1. Products from the irradiation of I

Reactants	Solvent	Temperature	Products
I(4×10^{-4} M)a)	Hexane	Room temp	III (65%), II & VI (trace)
I(10^{-2} M)a)	Hexane	Room temp	III (55%), II & VI (trace)
I(10^{-2} M), Acetophenone (1.8 M)b)	Benzene	Room temp	VI (45%), II (<5%), IV (trace)
I(10^{-2} M), Benzophenone (0.5 M)b)	Benzene	Room temp	VI (40%), II (<5%), IV (trace)
I(6×10^{-4} M)a)	EPA	77 K	II (98%)
I(6×10^{-4} M)a)	3MP	77 K	II (98%)
I(5×10^{-4} M)a)	Glycerol	201 K	II (55%), III (10%)

a) Irradiation with a 6W low-pressure mercury lamp. b) Irradiation with a 100W high-pressure mercury lamp through a filter solution of 0.13 wt% naphthalene in ethyl alcohol.

Table 2. Effect of solvents on the direct irradiation of Ia)

Solvent	Yield of III
Hexane	50—55%
Ether	48—54%
Benzene	45—52%
2-Propanol	46—52%

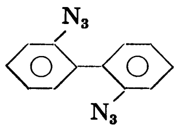
a) 10^{-2} M solution of I; irradiation with a 6W low-pressure mercury lamp through a UV-D25 filter.

Sensitized Photolysis of I. In connection with the photolysis of 2-azidobiphenyl, where the triplet sensitizer led to the predominant formation of the azo compound, we could expect that triplet sensitizers would increase the yield of II in the photolysis of I. With this expectation, we used acetophenone and benzophenone, which are good triplet sensitizers in the case of 2-azidobiphenyl. Both sensitizations afforded the intermolecular azo compound (VI), instead of the expected II, as the major product, although the yield of II increased relatively (<*ca.* 5%) (Table 1).

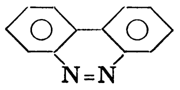
Low-temperature Photolysis of I in a Rigid Matrix. Photolyses of azido compounds at low temperatures in rigid matrices have been studied with considerable attention from the spectroscopic point of view of the nitrenes resulting from them. It is well-known that the irradiations of many aromatic azides in organic matrices at the temperature of liquid nitrogen afforded indefinitely stable intermediate nitrenes.[4] However, no study of the low-temperature photolysis of vicinal diazido compounds has been reported. It is thus of interest to examine whether both mononitrenes and dinitrenes are trapped or converted to some final products under these conditions.

We found that the intramolecular azo compound II was formed effectively with a short irradiation of I in a rigid matrix at low temperatures. The irradiation of I in EPA (5: 5: 2), 3-methylpentane (3 MP), or methylcyclohexane–isopentane (1: 3) at 77 K resulted in an almost quantitative formation of II. The photolysis of I in a glycerol matrix at −72 °C gave 55% of II and about 10% of III. At 77 K the dependence of the yield of II on the solvents was not observed, and there were no reactions with solvents.

Photolysis of VII. In order to study the steric effects on the reactivity of the vicinal two azido groups, the photolysis of VII was briefly examined. The first attempt at the pyrolysis and photolysis of VII by Coffin and Robbins[5] resulted in amorphous materials which could not be characterized. Our attempts to obtain the intramolecular azo compound (1,10-dimethylbenzo[*c*]-cinnoline: VIII) by the triplet-sensitized photolysis of a 10^{-3} M solution of VII in benzene with acetophenone or benzophenone gave only unidentified polymeric materials, like the direct irradiation. However, the irradiation of a 5×10^{-4} M solution of VII in EPA at 77 K afforded expected VIII in a 60% yield.



I



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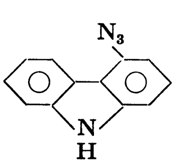

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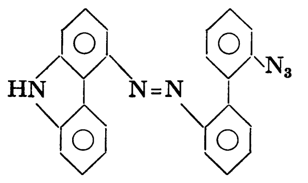

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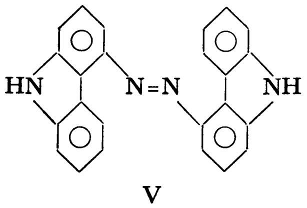

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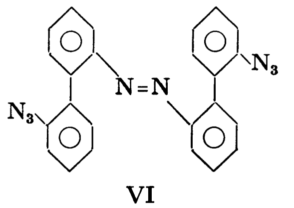

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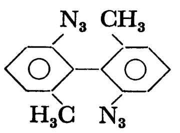
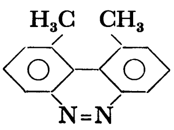


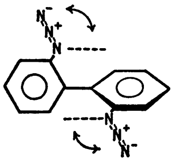
VII



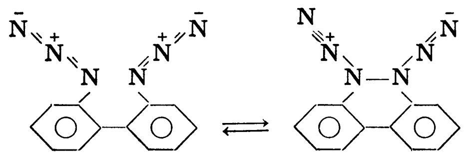
VIII

Discussion

The results of the photolysis at room temperature indicate that the reaction mechanism is rather similar to that for 2-azidobiphenyl. The direct irradiation led exclusively to the inserted compound (III) in the *o*′-position of biphenyl, and the azo compound formation is almost negligible. The lower yield of III, compared with the yield of carbazole in the case of 2-azidobiphenyl, must be due to some subsequent reactions by one more azido group, resulting in polymeric materials. Also, the triplet sensitization was similar to that of 2-azidobiphenyl. The predominant formation of the intermolecular azo compound rather than the intramolecular one could be explained in terms of a structural factor of *o*,*o*′-disubstituted biphenyls. Although it is difficult to deduce exactly the structure of the excited triplet I, which is presumed to be the precursor for the azo bond formation,[6] the two azido groups must be situated in positions which are far apart from each other, as is shown in Ia. In view of the spectroscopic study of hindered biphenyl compounds, the twisting about the central (1,1′)bond (the angle θ between the two benzene rings) seemed to be similar to that of 2,2′-dimethylbiphenyl ($\theta=70°$), since the effective radius of an azido group is 2.04 Å,[7] compared to 2.0 Å of a methyl group. Moreover, the close similarity of the absorption spectra of 2-azidobiphenyl, I, and VII indicates that such interaction between two "vicinal" azido groups, as represented by the structures of Ib and Ic, is negligible. Thus, the bulky two azido groups are partly free to rotate about the C–N bond at room temperature, as is shown in Ia, and they must prefer the intermolecular one.



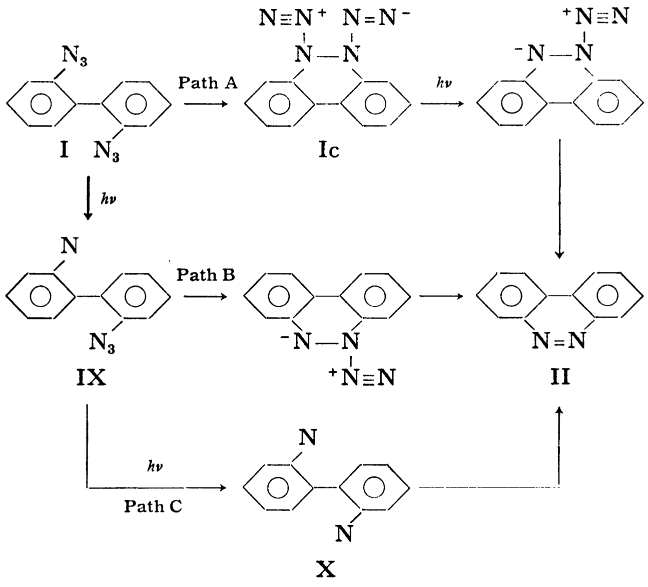
Ia



Ib Ic

The photolysis of I in a rigid matrix at 77 K gave a clear-cut product different from that obtained at room temperature. There is no doubt that the matrix rigidity suppresses a bimolecular reaction. The intramolecular insertion in the *o*′-position, however, could be a possible reaction like the carbazole formation by the irradiation of 2-azidobiphenyl in a rigid matrix at 77 K.[8a)] In what follows, we wish to discuss the low-temperature photolysis. The possible mechanisms leading to II from I may be depicted as follows.

Path A involves the azido-azido intramolecular-interacting structure Ic; Path B, the attack on an



intramolecular azido group by the nitreno group (IX); and Path C, the intramolecular recombination of the nitreno groups (2,2′-dinitrenobiphenyl: X) *via* IX. Although the Ic structure in Path A was excluded in the case of photolysis at room temperature, it must be considered a little possible in low-temperature photolysis because the rotation about the C–N bond may be locked in the plane of the ring at 77 K.[8b)] If the two azido groups are locked in a rather non-hindered state, the activation energy for the rotation of benzene rings must be lowered to only a few kcal/mol. However, the observed absorption spectrum at 77 K does not shift from that at room temperature. Therefore, the twisting about the central (1,1′) bond seems to be similar to that at room temperature. Thus, Path A may be ruled out, although the mechanisms involving Ic in an excited state still remain as possibilities.

Both Paths B and C involve 2-azido-2′-nitrenobiphenyl (IX) as an intermediate, whereas Path A does not require a discrete intermediate. It seemed first that II was produced directly without being trapped as the nitrene or dinitrene intermediate upon the direct irradiation of I. However, the results from the absorption spectra which are followed with a faint irradiation indicate at least a two-step process (Fig. 1). The absorption peaks of I at 232 and 252 nm decreased slightly upon a faint irradiation. Then, with the increase in irradiation the strong peaks belonging to II appeared rapidly in the same region. When the cell which was immersed in liquid nitrogen was taken up outside at room temperature after a faint irradiation at 77 K, and after this procedure had been repeated over and over again, III was obtained, whereas it was never detected after complete irradiation at 77 K within the limits of our analytical method. These results indicate that IX is trapped as an intermediate in the initial stage of photolysis. In Fig. 1, the decrease in absorbance at about 250 nm after a faint irradiation means that only a small fraction of I is converted to IX in preference to the formation of II. The extinction coefficient of II (33000 at 250 nm) is larger than that (18400 at 252 nm) of I; consequently, that of IX near 250 nm is estimated to be less than that of I. When the cell with the decrease in absorbance at 250 nm was kept in the dark at 77 K, the absorbance increased very slightly (about 2—3%) for periods as long as 4 h. Although this increase in absorbance may indicate the formation of II from IX along Path B, the rate is almost negligible compared with that of the formation upon further irradiation.

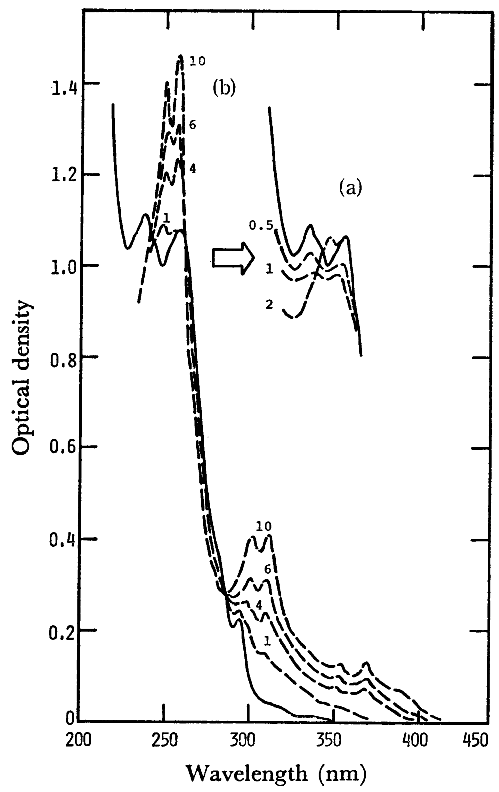


Fig. 1. Absorption spectra of I in EPA at 77 K, —: before irradiation, ---: (a) in the region at ᴅ50 nm after irradiation through the 1/2 slit, (b) after irradiation through the open slit. Numbers refer to irradiation time in minutes.

Another clue to elucidating whether the mechanism is Path B or C is the dependence of the formation rate of the final product, II, on the incident-light intensity. Path C is a biphotonic process, whereas Path B is monophotonic. The yields of II *vs.* the irradiation time

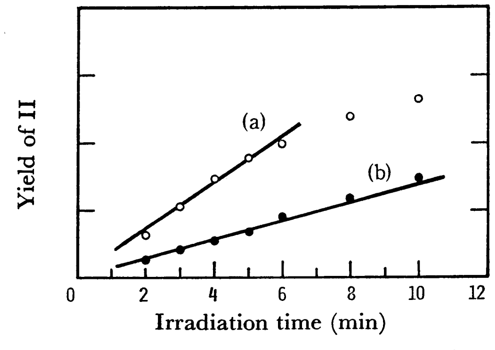


Fig. 2. Dependence of the formation rate of II from I in EPA at 77 K on the light intensity, (a) ○: I_0, (b) ●: $I_0/2$. The ratio of the formation rate is 1: 1/3.4, which is calculated from the slopes of (a) and (b).

were plotted in each case of light intensity, I_0 and $I_0/2$ (Fig. 2). The observed ratio for the formation rate of II is 1: 1/3.4. Since the extinction coefficient of the product (II) at 253.7 nm is high, and since the diffusion rate in a glassy matrix at 77 K is remarkably low, the actual rate in the case of I_0 is deduced to be additional. Hence, the ratio must approach further to 1/4, which is a theoretical value if it is a biphotonic process.

Thus, it may be concluded that the mechanism for the formation of II in low-temperature matrix photolysis involves the dinitrene (X) *via* the mononitrene (IX). This conclusion is supported by the following observation; the formation of II is due both to the low temperature and to the rigidity of matrices. When the irradiation of I in an isopentane–methylcyclohexane (3: 1) matrix, which formed II quantitatively at 77 K, was carried out in a slightly softened matrix at a slightly increased temperature (about 90 K), the yield of II decreased remarkably, presumably to below 10% (the small amounts of the photoproduct prevented accurate yield data). At the temperature of methanol–solid carbon dioxide (−72 °C), the photolysis gave 55% of III, as at room temperature. At the same temperature, on the contrary, the irradiation in a glycerol matrix with high viscosity (about 10^{13} Poise[9]) gave III in a 55% yield, together with about 10% of II, although the yield of II decreased considerably compared with that in a rigid matrix at 77 K. These results agree with the observations in trapping aromatic nitrenes. Reiser and his co-workers[8b] have found that many aromatic nitrenes are indefinitely stable in a rigid matrix at 77 K, and that a small increase in the temperature (from 77 to 90 K) sufficient to soften slightly the matrix invariably causes the nitrenes to disappear. When 2-azidobiphenyl was irradiated in a glycerol matrix at −72 °C, 2-nitrenobiphenyl could no longer be trapped and carbazole was formed directly. At this temperature the formation of carbazole from 2-nitrenobiphenyl proceeded thermally with no photon, although the conversion of trapped 2-nitrenobiphenyl into carbazole at 77 K was a less efficient photolytic process. This activation energy was estimated to be 8 kcal/mol[8b] or 11.46 kcal/mol.[6] This must also be roughly the case for I. In the stage in which IX is generated, the insertion reaction leading to III must be competitive with the decomposition of the second azido group. Although the latter is still efficient, even at low temperatures, the former, which is an activated process, must be highly affected by the reaction temperature. That is, the formation of III from IX, which is a facile thermal reaction at room temperature or even at −72 °C, is greatly suppressed in a rigid matrix at 77 K. Thus, generated IX survives and is converted into the dinitrene (X) upon further irradiation. Although the quantum yield (Φ_2) for the decomposition of the second azido group could not be determined, we can presume it to be as follows. The quantum yields for the decomposition of I and VII at room temperature are 0.44 and 0.42 respectively, and these must be very similar to the quantum yields (Φ_1) for the decomposition of the first azido group at low temperatures. If it is assumed that the ratio of Φ_2/Φ_1 lies between 2.2 and 3.0, which was found for several p,p'-diazido compounds,[8c] then Φ_2 is estimated to be between 0.8 and 1.0. According to Reiser and his co-workers,[8a] in the case of 2-azidobiphenyl, the quantum yield of carbazole formation which is 0.44 at 25 °C lowers greatly to 0.01—0.02 in a rigid matrix at 77 K. In our cases, it is suggested that the insertion must become negligible compared with the highly efficient decomposition.

In general, the dinitrenes resulting from vicinal[10] and geminal[11] diazides have not been trapped even in a rigid matrix at low temperatures (higher than 77 K). The process to II from X must be fast. Thus, the formation of II from I (and of VIII from VII) may be regarded as a consecutive first-order reaction as follows:

$$\mathrm{I} \xrightarrow[k_1]{h\nu} \mathrm{IX} \xrightarrow[k_2]{h\nu} (\mathrm{X}) \xrightarrow[\text{fast}]{} \mathrm{II}$$

The kinetics in the photolysis of the dimethyl derivatives (VII) was obtained conveniently because the absorption peak belonging to the mononitrene was not seriously interfered with that of the final product (VIII). In Fig. 3, the absorption peaks at 308 and 330 nm belong to the intermediate mononitrene and the final product 1,10-dimethylbenzo[*c*]cinnoline (VIII) respectively. On the basis of these spectral data and the independent analysis of the decomposed diazide, the concentration-time relationship shown in Fig. 4 was obtained. Although we withhold all stoichiometric discussion because the plots for the mononitrene may have a fairly large experimental error, there is no doubt that the relationship between these three curves indicates $k_2 > k_1$ at least.

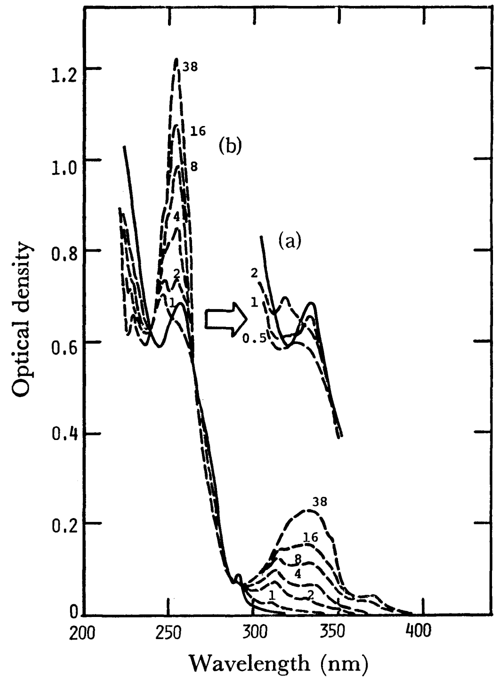


Fig. 3. Absorption spectra of VII in EPA at 77 K, —: before irradiation, ---: (a) in the region at 250 nm after irradiation through the 1/2 slit, (b) after irradiation through the open slit. Numbers refer to irradiation time in minutes.

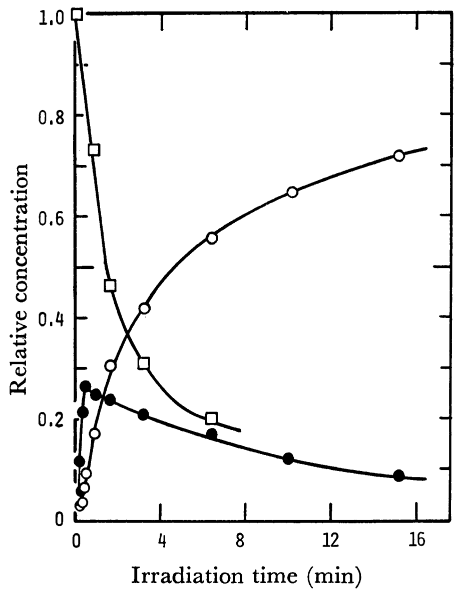


Fig. 4. Kinetics of the photolysis of VII in EPA at 77 K; □: diazide (VII), ●: nitrenoazide, ○: VIII.

Experimental

All the melting points are uncorrected. IR and UV spectra were recorded on JASCO Model IR-S and Shimadzu Model D-40R spectrophotometers respectively. NMR spectra were recorded on a Hitachi Model R-24A spectrometer at 60 MHz using TMS as an internal standard. Mass spectra were recorded on a Hitachi Model RMU-6M spectrometer. The microanalyses were performed at the Institute of Physical and Chemical Research.

Materials. *2,2′-Diazidobiphenyl (I)* was prepared from 2,2′-diaminobiphenyl by Procedure A of Smith and Brown.[12] The crude material was purified by column chromatography on silica gel and was recrystallized twice from ether–hexane; mp 70—71 °C. IR (KBr): 2180, 2120 (N_3) cm^{-1}. UV (Ether): $\lambda_{max}(\varepsilon)$ 252 (18400), 232 (19000) nm. MS: *m/e* 236 (M^+), 208 (M^+-N_2), 180 (M^+-2N_2). Found: C, 60.81; H, 3.51; N, 36.80%. Calcd for $C_{12}H_8N_6$: C, 61.01; H, 3.41; N, 35.57%.

2,2′-Diazido-6,6′-dimethylbiphenyl (VII) was prepared by the method of Coffin and Robbins.[5] After purification by silica gel column chromatography,it was recrystallized from ethanol; mp 58—59 °C (lit, 56—57 °C[5]). IR(KBr): 3100—2950, 2250 and 2160 (N_3) cm^{-1}. UV (Hexane): 288sh (2500), 254 (19900) nm. NMR ($CDCl_3$): δ 7.5—6.8 (m, 6H), 1.95 (s, 6H). MS: *m/e* 264 (M^+), 236 (M^+-N_2), 208 (M^+-2N_2).

The solvents used in the spectroscopic study and in low-temperature photolysis were dried over sodium wire or a molecular sieve and finally passed through a column of alumina.

Irradiation of Azides. The light source for spectroscopic studies was an Ushio USH-500D 500W high-pressure mercury lamp equipped with a Nikon G-250 monochromator. Irradiations for spectroscopic studies of low-temperature photolysis were carried out with a cell which had been immersed in liquid nitrogen or solid carbon dioxide–ethanol contained in a quartz Dewar vessel equipped with optical windows on opposite sides. Irradiations on preparative scale at room temperature were carried out under nitrogen with a conventional immersion well-type reactor equipped with an Ushio UM-102 100W high-pressure mercury lamp. In a low-temperature photolysis, a cylindrical cell immersed in coolants was irradiated with the low-pressure mercury lamp protected with a transparent quartz Dewar vessel.

Product Analysis. The separation and the yield determination of the photoproducts were carried out with a preparative layer chromatograph (Merck Silicagel 60 F_{254}) and a Hitachi high-speed liquid chromatograph Model 634, followed by UV analysis. The identity of II was confirmed by comparison with an authentic sample. The other products were identified on the basis of the following microanalyses and spectral data.

4-Azidocarbazole (III): mp 118—120 °C. IR (KBr): 3480 (NH), 2170 (N_3) cm^{-1}. UV (Ether): 343 (4020), 328 (3500), 301 (7300), 292 (7300), 250 (23000) nm. MS: *m/e* 208 (M^+), 180 (M^+-N_2). Found: C, 68.99; H, 4.22; N, 26.48%. Calcd for $C_{12}H_8N_4$: C, 69.22; H, 3.87; N, 26.91%.

4-(2′-Azido-2-biphenylylazo)carbazole (IV): mp 122—124 °C. IR (KBr): 3480 (NH), 2170 (N_3) cm^{-1}. UV (Ether): 435 (9900), 306 (9700), 250 (35300) nm. MS: *m/e* 388 (M^+), 360 (M^+-N_2).

2,2′-Bis(o-azidophenyl)azobenzene (VI): mp 144—146 °C. IR (KBr): 2180, 2160 (N_3) cm^{-1}. UV (Ether): 460 (250), 325 (8200) nm. MS:*m/e* 416 (M^+), 388 (M^+-N_2), 360 (M^+-2N_2). Found: C, 69.02; H, 4.14; N, 26.04%. Calcd for $C_{24}H_{16}N_8$: C, 69.22; H, 3.87; N, 26.91%.

1,10-Dimethylbenzo[c]*cinnoline (VIII)*: mp 110—111 °C (lit, 96 °C[5]). IR (KBr): 3080—3000, 1595, 1572, 1460, 1442, 1420, 1385, 1335 cm^{-1}. UV (MeOH): 331 (8900), 252 (36000) nm. NMR ($CDCl_3$): δ 8.7—7.1 (m, 6H), 2.55 (s, 6H). MS: *m/e* 208 (M^+), 180 (M^+-N_2), 179.

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