Photolysis and Thermolysis of Some 2-Azido-2′-arylazobiphenyls

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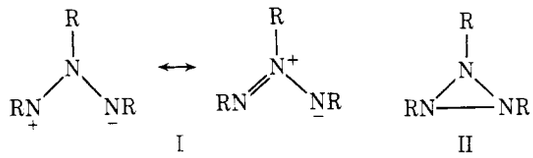
A series of four 2-azido-2′-arylazobiphenyls has been prepared and their photolytic and thermal decomposition investigated in order to throw light on the question whether aryl azides are actually capable of adding to azo compounds by a nonconcerted "nitrene" mechanism and to explore the possible synthetic utility of such additions as a route to benzo[*c*]cinnoline *N*-arylimides. All four azides exhibit formation of benzo[*c*]cinnoline *N*-arylimides and 4-arylazocarbazoles as major isolable products on photolysis; the same products are apparently formed on thermolysis but removal of the initially formed *N*-arylimides occurs leading to benzo[*c*]cinnoline, thus producing no substantial yields of isolable *N*-arylimides. The reaction products are discussed in terms of a possible nitrene mechanism.

Nitrenes are reactive organic intermediates which can attack multiple bonds and nonbonding electron pairs according to their polar character, giving a great variety of products.[1]

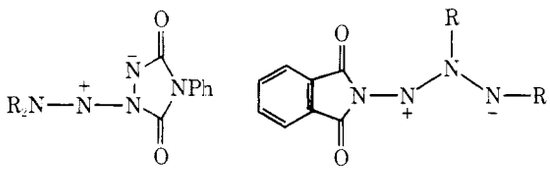
Addition of nitrenes to azo compounds could be in principle the simplest route to azimines (I), the open 1,3-dipolar valence isomers of the unknown triaziridines (II); however, formation



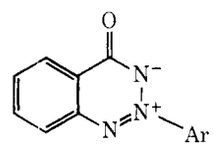
I II

of azimines by reaction of nitrenes (or nitrene precursors) with azo compounds has been positively established only in a few cases.

A number of nucleophilic aminonitrenes have in fact been shown to add smoothly to azoalkanes and azoarenes, giving *N*-aminoazimines (III–IV, R = alkyl or aryl),[2] but photolysis



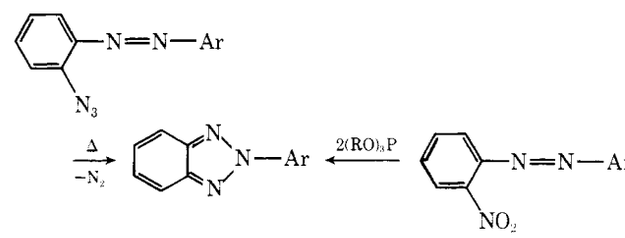
III IV



V

of ethyl azidoformate in the presence of diethyl azodicarboxylate[3] and thermolysis of the same azide in the presence of azobenzene[4] failed to give any isolable azimine, which was postulated as an intermediate to account for the reaction products. Moreover, the cyclic azimine (V, Ar = 4-$NMe_2C_6H_4$) has been reported in very low yield (3%) by reaction of 2-(4′-dimethylaminophenylazo)benzhydrazide with nitrous acid.[4]

So far no clear-cut report on azimine formation by addition of arylnitrenes or their precursors to azo compounds is available in the literature and the question whether arylnitrenes are actually capable of adding to azo compounds is still open. Thermal decomposition of 2-azidoazobenzenes[5] and deoxygenation of 2-nitroazobenzenes by triethyl phosphite[6] are formal intramolecular addition examples of arylnitrenes to azobenzenes.



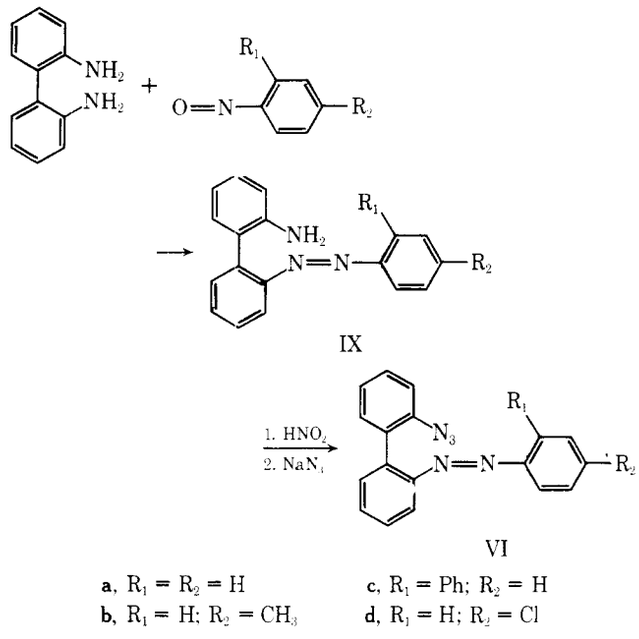
These reactions always result in cyclization to give 2-substituted benzotriazoles, most probably without the actual intermediacy of nitrenes. Cyclization by a concerted process appears in fact much more plausible to account for the low reaction temperatures and the absence of other products expected from nitrene intermediates.[7] On the other hand, isolation of azobenzenes in good yields from reactions producing arylnitrenes would suggest that the reactivity of these nitrenes toward azobenzenes cannot be high.[8] In order to throw light on the reactivity of arylnitrenes (or azides) toward azo compounds and to explore the potential synthetic utility of these reactions as a route to azimines we have investigated the photolytic and thermal decomposition of a number of 2-azido-2′-arylazobiphenyls (VI). In the 2-azido-2′-arylazobiphenyls (VI) the nitrenes that would be derived from the azido group would have the choice of inserting into the C–H bond in the ortho′ position, giving rise to 4-arylazocarbazoles (VII), or adding to the azo group in the other ortho′ position, producing presumably isolable azimines, i.e., benzo[*c*]cinnoline *N*-arylimides (VIII), a number of which have recently been reported and shown to fairly stable.[9]

Since it is generally accepted that carbazole produced in high yield by either photolysis or thermolysis of 2-azidobiphenyl proceeds from the intermediate 2-nitrenobiphenyl,[10] formation of carbazoles (VII) together with azimines (VIII) (if formed at all) could be construed as diagnostic evidence for the intermediacy of 2-nitreno-2′-arylazobiphenyls (XI) in the decomposition of VI and thus possibly in the formation of *N*-arylimides (VIII).

All starting azides (VI) were most readily prepared from the corresponding amines (IX) by diazotization followed by treatment with sodium azide. Amines (IX) were in turn obtained by condensation of 2,2′-diaminobiphenyl with the appropriate nitrosobenzene derivative. The general procedure is outlined in Scheme I.

Photolysis of azides (VIa–d) with a 100-W high-pressure mercury lamp in benzene solution for ca. 24 h (until TLC showed complete decomposition of starting material) led to the isolation of benzo[*c*]cinnoline *N*-arylimides (VIIIa–d) (35–40%), 4-arylazocarbazoles (VIIa–d) (10–15%), 2-amino-2′-arylazobiphenyls (IXa–d) (1–2%), and benzo[*c*]cinnoline (X) (2–4%) as the only identifiable products after column chromatography of the reaction mixtures.

Scheme I



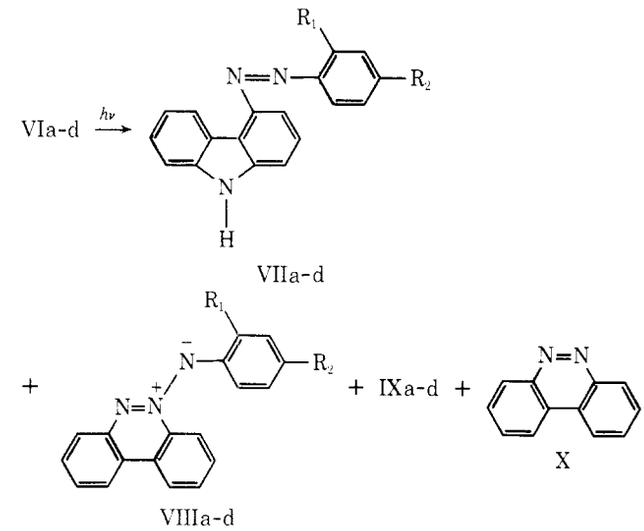
IX

VI

a, $R_1 = R_2 = H$ c, $R_1 = Ph$; $R_2 = H$
b, $R_1 = H$; $R_2 = CH_3$ d, $R_1 = H$; $R_2 = Cl$

Benzo[*c*]cinnoline *N*-phenylimide (VIIIa) has been previously described.[9] Spectral properties of the new *N*-arylimides (VIIIb–d) were very similar to those of VIIIa. They all show a mass spectral base peak at *m/e* 180 and a low-field one-proton multiplet near δ 8.5–9 in the NMR spectrum, characteristic of the unsubstituted benzo[*c*]cinnoline *N*-imide[9a] and the isoelectronic benzo[*c*]cinnoline *N*-oxide.[9a]

Scheme II



VIIa-d

VIIIa-d

The 4-arylazocarbazoles (VIIa–d) were identified on the basis of the elemental analysis and spectroscopic data. In particular they all show the expected sharp N–H stretching absorption at ca. 3460 cm^{-1} in the IR spectrum and a mass spectral base peak at *m/e* 166 corresponding to loss of the arylazo fragment from the parent ion. In the case of VIIc chemical confirmation of the structure was also obtained through hydrogenation of the azo compound to 4-aminocarbazole[11] and 2-aminobiphenyl.

The photolysis products (VII–IX) could be rationalized by postulating the intermediacy of the 2-nitreno-2′-arylazobiphenyls (XI) which undergo intramolecular addition to the azo group to give *N*-arylimides (VIII), intramolecular insertion into the aromatic C–H bond to give carbazoles (VII), and hydrogen abstraction to give amines (IX). Formation of benzo[*c*]cinnoline (X) can be attributed to photolytic fragmentation of *N*-arylimides (VIII), a general trend encountered with all benzo[*c*]cinnoline *N*-imides previously reported.[9a] Control experiments showed the *N*-arylmides (VIII) to fragment rather slowly, no more than 10% fragmentation to benzo[*c*]cinnoline (X) occurring after the same irradiation time employed to bring about complete decomposition of azides (VI). As far as photochemical fragmentation of benzo[*c*]cinnoline *N*-imides is concerned, a plausible route to benzo[*c*]cinnoline (X) would be the N–N bond cleavage leading to X and a formal nitrene fragment. Indeed the nitrene fragment has been intercepted in photolysis of the *N*-ethoxycarbonylimide (VIII, $R_1R_2C_6H_3 = CO_2Et$)[9a] but it has never been detected with other *N*-imides examined and in particular no trace of benzofurazan *N*-oxide has been observed in photolysis of the *N*-2,4-dinitrophenylimide (VIII, $R_1 = R_2 = NO_2$).[9a] In our hands the *N*-arylimides (VIIIa–d) proved to fragment to benzo[*c*]cinnoline and tars, but no evidence of products deriving from nitrene fragments was found. In particular neither carbazole nor azo-2-biphenyl was observed in the photolysis of VIIIc and the nature of the nitrene fragment remains uncertain in these cases.

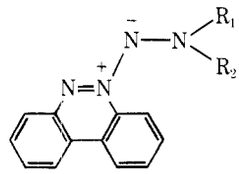
In contrast with photolysis, thermolysis of 2-azido-2′-arylazobiphenyls (VIa–d) in refluxing *o*-dichlorobenzene did not give any isolable benzo[*c*]cinnoline *N*-arylimides (VIIIa–d). In these cases the major reaction products were benzo[*c*]cinnoline (X) (34–43%) and 4-arylazocarbazoles (VIIa–d) (8–10%) together with polymeric material. In thermolysis of the azide VIc 2-aminobiphenyl was also isolated in yield comparable to that of X. The formation of benzo[*c*]cinnoline (X) and the absence of the *N*-arylimides (VIII) could be at first sight most easily explained by thermal fragmentation of the initially formed *N*-arylimides (VIII) incapable of surviving the high-temperature conditions. This "obvious" route to benzo[*c*]cinnoline (X) was promptly ruled out since *N*-arylimides (VIII) were found to fragment to X very slowly in refluxing *o*-dichlorobenzene, being quantitatively recovered after the same pyrolysis time as employed to effect decomposition of the azides (VI) (ca. 1 h). However, when *N*-arylimides (VIII) were refluxed in *o*-dichlorobenzene in the presence of a slight excess of the corresponding azides VI rapid removal of VIII occurred before decomposition of VI was complete. Moreover, the same results [rapid decomposition to benzo[*c*]cinnoline (X)] were obtained when the *N*-arylimides VIII were refluxed in the presence of *p*-chlorophenyl azide. In particular with the *N*-imide (VIIIc) 2-aminobiphenyl and benzo[*c*]cinnoline (X) were obtained in comparable yields. Thus reaction must occur between *N*-arylimides (VIII) and aryl azides (or nitrenes) and this point is under investigation at the present time.

These results would lead to the conclusion that benzo[*c*]cinnoline (X) isolated in the thermolysis of azides VI derives from reaction of the initially formed *N*-arylimide (VIII) with some reactive species present in the reaction mixture. Complete confirmation of this conclusion was found by carrying out thermolysis of azides VI in refluxing bromobenzene. In this solvent the reaction was rather slow and initial formation of the *N*-arylimides (VIII) could be observed by TLC in each case. In the thermolysis of VIc and VId the corresponding *N*-arylimides VIIIc and VIIId were also isolated by column chromatography after ca. 30% azide decomposition had occurred.

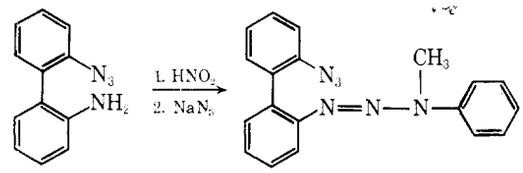
The yields of *N*-arylimides (VIII) were found to decrease rapidly with increasing decomposition of the starting azides (VI). No trace of VIII was left in each case after ca. 50% decomposition of azides VI had occurred.

In order to investigate the possibility of utilizing the intramolecular addition of aryl azides to an azo group as a route to the yet unknown *N*-aminoazimines (XII, R_1 and R_2 = alkyl

or aryl) we prepared the azide XIII. The synthesis of XIII was accomplished by diazotization of the recently reported 2-amino-2′-azidobiphenyl[12] (XIV) and coupling of the diazonium salt with *N*-methylaniline.



XII



XIV XIII

Photolysis of XIII, however, did not furnish any isolable *N*-aminoazimine (XII, R_1 = CH_3; R_2 = Ph), but carbazole (35%) was obtained together with traces of [*c*]cinnoline (X), other minor unidentified products, and much polymeric material. The same results were obtained from thermolysis of azide XIII in refluxing chlorobenzene. Formation of carbazole indicates that cleavage of the diazoamino linkage occurs in these reactions. Moreover, the presence of benzo[*c*]cinnoline (X) only in trace amounts and the absence of *N*-aminoazimine (XII, R_1 = CH_3; R_2 = Ph) would suggest that the cleavage of the diazoamino linkage takes place presumably before decomposition of the azido group.

The results obtained from photolysis and thermolysis of 2-azido-2′-arylazobiphenyls (VI) indicate that, at least in these cases, "azimines" are indeed formed by addition of aryl azides to azo compounds, presumably through the intermediacy of nitrenes, if (a) formation of 4-arylazocarbazoles (VII) [and 2-amino-2′-arylazobiphenyls (IX)], (b) normal decomposition temperatures shown by azides VI (>140 °C), and (c) irreversible formation of *N*-arylimides (VIII) which are not converted thermally or photolytically into VII (and IX) are assumed to provide evidence for the intermediacy of 2-nitreno-2′-arylazobiphenyls (XI) in the decomposition of azides VI and thus in the formation of the *N*-arylimides (VIII). However, the possibility that a nitrene mechanism, leading to VII (and IX), may be in competition with a concerted cyclization mechanism, leading to VIII, in which the azo group provides anchimeric assistance for the elimination of nitrogen, cannot be completely excluded at present and further studies are needed to throw full light on this point as well as on the spin states of nitrenes involved in these cyclizations.

Finally we wish to point out that photolysis of 2-azido-2′-arylazobiphenyls (VIII) appears to provide a general synthetic route to benzo[*c*]cinnoline *N*-arylimides (VIII) alternative to those previously reported in the literature.[9]

Experimental Section

All melting points are uncorrected. Reaction products such as benzocinnoline and carbazole were always characterized by mixture melting point determination and IR spectral comparison with authentic commercial samples. IR and NMR spectra are for solutions in carbon disulfide unless otherwise stated. Nitrosobenzene and 4-chloronitrosobenzene were commercial products; 2-nitrosobiphenyl[13] and 4-methylnitrosobenzene[14] were prepared as described in the literature.

Preparation of 2-Amino-2′-arylazobiphenyls (IXa–d). The condensation of 2,2′-diaminobiphenyl with nitrosobenzene, 4-methylnitrosobenzene, 2-nitrosobiphenyl, and 4-chloronitrosobenzene was accomplished by means of the following general procedure.

2-Amino-2′-phenylazobiphenyl (IXa). Nitrosobenzene (8.00 g) in dichloromethane (20 ml) was added over 10 min to a solution of 2,2′-diaminobiphenyl (12.20 g) in a 2:1 mixture of acetic acid and dichloromethane (100 ml). The resulting solution was heated on a steam bath for 20 min, then poured into an excess of water and basified with sodium carbonate. Extraction with ether and evaporation of the extracts left an oil residue which was chromatographed on silica gel. Elution with pentane afforded unreacted nitrosobenzene. Elution with 5% ether–pentane afforded the product (IXa) (7.00 g, 40%) as a red, thick oil which after standing for a few days at 0 °C solidified: mp 58–59 °C; IR ν_{max} 3480 and 3400 cm^{-1} (NH_2); mass spectrum *m/e* 273 (M^+), 257, 181, 167.

Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.09; H, 5.53; N, 15.38. Found: C, 78.84; H, 5.65; N, 15.56.

2-Amino-2′-(4-tolylazo)biphenyl (IXb) was obtained in 38% yield: mp 59–61 °C; IR ν_{max} 3470 and 3380 cm^{-1} (NH_2); mass spectrum *m/e* 287 (M^+), 271, 181, 167, 91.

Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41; H, 5.97; N, 14.62. Found: C, 79.00; H, 5.85; N, 14.40.

2-Amino-2′-(2″-biphenylylazo)biphenyl (IXc) was obtained in 35% yield as a red, thick oil which did not solidify: IR ν_{max} 3463 and 3375 cm^{-1} (NH_2); mass spectrum *m/e* 349 (M^+), 333.

Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.49; H, 5.48; N, 12.03. Found: C, 81.75; H, 5.60; H, 11.85.

2-Amino-2′-(4-chlorophenylazo)biphenyl (IXd) was obtained in 45% yield: mp 86–87 °C; IR ν_{max} 3470 and 3380 cm^{-1} (NH_2); mass spectrum *m/e* 307 (M^+), 291, 181, 167.

Anal. Calcd for $C_{18}H_{14}N_3Cl$: C, 70.24; H, 4.59; N, 13.65; Cl, 11.52. Found: C, 71.00; H, 4.49; N, 13.35; Cl, 11.08.

Preparation of 2-Azido-2′-arylazobiphenyls (VIa–d). The following procedure is typical of that used to prepare azides VIa–d.

2-Azido-2′-phenylazobiphenyl (VIa). A suspension of 2-amino-2′-phenylazobiphenyl (IXa, 1.8 g) in 10 ml of concentrated hydrochloric acid and 30 ml of water was cooled to 0 °C and diazotized by the dropwise addition of 0.5 g of sodium nitrite in 10 ml of water. After standing for 15 min, the resulting solution was treated with 0.8 g of sodium azide in water (10 ml), stirred for 1 h at 0–5 °C, and then extracted with ether. The extracts were dried (Na_2SO_4) and evaporated to give an oily residue which was chromatographed on silica gel. Elution with pentane afforded 1.5 g (80%) of 2-azido-2′-phenylazobiphenyl: mp 43–45 °C; IR ($CHCl_3$) 2120 and 2080 cm^{-1} (N_3); mass spectrum *m/e* 299 (M^+), 271, 270, 257, 219, 180, 152.

Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.22; H, 4.38; N, 23.40. Found: C, 71.55; H, 4.35; N, 23.10.

2-Azido-2′-(4-tolylazo)biphenyl (VIb) was obtained in 70% yield as red needles: mp 50–52 °C; IR ($CHCl_3$) 2119 and 2085 cm^{-1} (N_3); mass spectrum *m/e* 313 (M^+), 285, 284, 271, 270, 180, 152.

Anal. Calcd for $C_{19}H_{15}N_5$: C, 72.82; H, 4.83; N, 22.35. Found: C, 72.60; H, 4.77; N, 22.46.

2-Azido-2′-(2″-biphenylylazo)biphenyl (VIc). This azide was obtained in 80% yield as orange needles: mp 113–115 °C; IR (CCl_4) 2120 and 2085 cm^{-1} (N_3); mass spectrum *m/e* 375 (M^+), 347, 346, 333.

Anal. Calcd for $C_{24}H_{17}N_5$: C, 76.78; H, 4.56; N, 18.66. Found: C, 76.10; H, 4.62; N, 18.35.

2-Azido-2′-(4-chlorophenylazo)biphenyl (VId). This azide was obtained in 77% yield as orange needles: mp 104–105 °C; IR ($CHCl_3$) 2120 and 2080 cm^{-1} (N_3); mass spectrum *m/e* 333 (M^+), 305, 304, 291, 270, 180, 152.

Anal. Calcd for $C_{18}H_{12}N_5Cl$: C, 64.77; H, 3.63; N, 20.98; Cl, 10.62. Found: C, 64.95; H, 3.52; N, 20.72; Cl, 10.75.

Photolysis of 2-Azido-2′-arylazobiphenyls (VIa–d). General Procedure. Stirred solutions of azides VIa–d (1 g) in 400 ml of benzene were purged with purified nitrogen for 0.5 h and then irradiated at room temperature with a 100-W high-pressure mercury lamp. Progress of the reactions was monitored by TLC and irradiation was stopped after TLC showed absence of starting material (24–36 h). The excess benzene was distilled off and the residue was chromatographed on basic alumina.

Elution was as follows: pentane yielded trace amounts of undecomposed azide; 5% ether–pentane eluted benzo[*c*]cinnoline *N*-arylimides (VIII); 10% ether–pentane eluted 2-amino-2′-arylazobiphenyls (IX); 20% ether–pentane gave 4-arylazocarbazoles (VII); and 40% ether–pentane yielded benzocinnoline. Continued elution with ether or higher polarity solvent mixtures afforded untractable tarry materials.

Photolysis of 2-Azido-2′-phenylazobiphenyl (VIa). Chromatography afforded (1) trace amounts of unreacted azide and (2) benzo[*c*]cinnoline *N*-phenylimide (VIIIa, 35%): mp 130–132 °C (lit.[9a] 129–131 °C), identical in all respects with a sample prepared by the method reported by Rees and co-workers;[9a] IR ν_{max} 1934, 1330, 1265, 1135, 755, 710 cm^{-1}; NMR δ 6.8–8.3 (12 H, m) and 8.7–8.95 ppm (1

H, m); mass spectrum *m/e* 271 (M^+), 270, 241, 219, 180, 152.

Anal. Calcd for $C_{18}H_{13}N_3$: C, 79.6; H, 4.8; N, 15.6. Found: C, 79.28; H, 4.91; N, 15.64.

(3) 2-Amino-2′-phenylazobiphenyl (IXa, 2%), identical in all respects with an authentic sample. (4) 4-Phenylazocarbazole (VIIa, 13%), as bright orange needles: mp 190–191 °C; IR ν_{max} 3460 cm^{-1}; mass spectrum *m/e* 271 (M^+), 194, 166, 139, 105, 77.

Anal. Calcd for $C_{18}H_{13}N_3$: C, 79.6; H, 4.8; N, 15.6. Found: C, 78.5; H, 4.8; N, 15.63.

(5) Benzocinnoline (3%).

Photolysis of 2-Azido-2′-(4-tolylazo)biphenyl (VIb). Chromatography afforded (1) trace amounts of unreacted azide and (2) benzo[*c*]cinnoline *N*-(4-tolyl)imide (VIIIb, 36%) as bright orange needles: mp 156–158 °C; IR ν_{max} 1395, 1330, 1265, 1135, 815, 755, 710 cm^{-1}; NMR δ 2.37 (3 H, s), 7–8.3 (11 H, m), and 8.7–8.95 ppm (1 H, m); mass spectrum *m/e* 285 (M^+), 184, 270, 233, 181, 180, 152.

Anal. Calcd for $C_{19}H_{15}N_3$: C, 79.98; H, 5.30; N, 14.72. Found: C, 79.80; H, 5.33; N, 14.74.

(3) 2-Amino-2′-(4-tolylazo)biphenyl (IXb, ca. 1%), IR identical with that of an authentic specimen. (4) 4-(4-Tolylazo)carbazole (VIIb, 14%): orange-red needles, mp 210–212 °C; IR ν_{max} 3460 cm^{-1} (NH); mass spectrum *m/e* 285 (M^+), 194, 166, 139, 119, 91.

Anal. Calcd for $C_{19}H_{15}N_3$: C, 79.98; H, 5.30; N, 14.72. Found: C, 79.84; H, 5.31; N, 14.69.

(5) Benzocinnoline (4%).

Photolysis of 2-Azido-2′-(2″-biphenylylazo)biphenyl (VIc). Chromatography gave (1) trace amounts of unreacted azide and (2) benzo[*c*]cinnoline *N*-(2-biphenylyl)imide (VIIIc, 38%): red plates, mp 119–121 °C; IR ν_{max} 1390, 1330, 1265, 1135, 755, 695 cm^{-1}; NMR δ 6.8–8 (16 H, m) and 8.2–8.5 ppm (1 H, m); mass spectrum *m/e* 347 (M^+), 346, 219, 181, 180, 167, 166, 152, 140, 139.

Anal. Calcd for $C_{24}H_{17}N_3$: C, 82.97; H, 4.93; N, 12.10. Found: C, 82.83; H, 5.04; N, 12.13.

(3) Violet oily product (≤5%) which rapidly decomposed on standing to give more *N*-imide VIIIc. This unidentified product is likely to be an unstable photoisomer of VIIIc since UV irradiation of pure VIIIc leads to partial conversion of VIIIc to the unknown. (4) 2-Amino-2′-(2″-biphenylylazo)biphenyl (<2%), IR identical with that of an authentic specimen. (5) 4-(2-Biphenylylazo)carbazole (VIIc, 11%): red plates, mp 220–222 °C; IR ν_{max} 3460 cm^{-1} (NH); mass spectrum *m/e* 347 (M^+), 346, 181, 166, 153, 152, 139.

Anal. Calcd for $C_{24}H_{17}N_3$: C, 82.97; H, 4.93; N, 12.10. Found: 82.50; H, 4.90; N, 12.03.

(6) Benzocinnoline (2%).

Photolysis of 2-Azido-2′-(4-chlorophenylazo)biphenyl (VId). Chromatography afforded (1) a trace of unreacted azide and (2) benzo[*c*]cinnoline *N*-(4-chlorophenyl)imide (VIIId, 40%): bright orange needles, mp 157–159 °C; IR ν_{max} 1390, 1330, 1268, 1140, 1090, 830, 760, 750, 715 cm^{-1}; NMR δ 6.90–8.00 (11 H, m) and 8.45–8.65 ppm (1 H, m); mass spectrum *m/e* 305 (M^+), 304, 270, 180, 152.

Anal. Calcd for $C_{18}H_{12}N_3Cl$: C, 70.71; H, 3.96; Cl, 11.59; N, 13.74. Found: C, 70.35; H, 3.80; Cl, 11.62; N, 13.85.

(3) 2-Amino-2′-(4-chlorophenylazo)biphenyl (IXd, 2%), identical with an authentic sample. (4) 4-(4-Chlorophenylazo)carbazole (VIId, 13%; red needles, mp 232–233 °C; IR ν_{max} 3470 cm^{-1} (NH); mass spectrum *m/e* 305 (M^+), 304, 166, 139, 111.

Anal. Calcd for $C_{18}H_{12}N_3Cl$: C, 70.71; H, 3.96; Cl, 11.59; N, 13.74. Found: C, 70.48; H, 3.92; Cl, 11.45; N, 13.92.

(5) Benzocinnoline (4%).

Hydrogenation of 4-(2-Biphenylylazo)carbazole (VIIc). The azo compound (50 mg) was dissolved in 50 ml of methanol and hydrogenated using 50 mg of platinum oxide as catalyst. After removal of the catalyst and the excess solvent the residue was chromatographed on basic alumina. Elution with 10% benzene–petroleum ether afforded 2-aminobiphenyl (10 mg), identical with authentic commercial material. Elution with 50% benzene–petroleum gave 4-aminocarbazole (15 mg), mp 190–192 °C (lit.[11] 188–192 °C), *m/e* 182 (M^+).

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.11; H, 5.50; N, 15.39. Found: C, 78.95; H, 5.35; N, 15.20.

Control Experiments to Determine Photosensitivity of Benzo[*c*]cinnoline *N*-arylimides (VIII). Solutions of *N*-imides VIIIa–d in benzene were irradiated for 36 h, after which time chromatography on basic alumina gave back 90–95% starting material together with benzocinnoline (5–10%). No evidence of products deriving of "nitrene" fragments were found. In particular TLC showed no evidence of carbazole, nor of azo-2-biphenyl or 2-aminobiphenyl from photolysis of the benzocinnoline *N*-(2-biphenylyl)imide (VIIIc).

Thermolysis of 2-Azido-2′-arylazobiphenyls (VIa–d) in *o*-Dichlorobenzene. General Procedure. Solutions of azides VIa–d (1 g) in *o*-dichlorobenzene (40 ml) were refluxed for 1 h, after which time TLC showed that no starting material was left. Dichlorobenzene was distilled off under reduced pressure and the residue was chromatographed on silica gel. Elution was effected with mixtures of ether–pentane as described above for the corresponding photolyses. 2-Azido-2′-phenylazobiphenyl (VIa) gave after thermolysis 4-phenylazocarbazole (VIIa) (9%) and benzocinnoline (34%) as the only identifiable products.

Thermolysis of 2-azido-2′-(4-tolylazo)biphenyl (VIb) afforded 4-(4-tolylazo)carbazole (VIIb, 8%) and benzocinnoline (35%).

Thermolysis of 2-azido-2′-(2″-biphenylylazo)biphenyl (VIc) gave 2-aminobiphenyl (44%), 4-(2-biphenylylazo)carbazole (VIIc, 10%), and benzocinnoline (43%).

From thermolysis of 2-azido-2′-(4-chlorophenylazo)biphenyl (VId), 4-(4-chlorophenylazo)carbazole (VIId, 10%) and benzocinnoline (38%) were isolated.

Control Experiments to Determine Thermal Sensitivity of Benzo[*c*]cinnoline *N*-Arylimides (VIII). The *N*-imides VIIIa–d were quantitatively recovered after refluxing in *o*-dichlorobenzene for 1–2 h. When refluxing was continued for 2–4 days, noticeable formation of benzo[*c*]cinnoline was observed. In one experiment, benzo[*c*]cinnoline *N*-(2-biphenylyl)imide (VIIIc, 50 mg) was heated under reflux for 4 days, yielding after chromatography 10 mg of recovered VIIIc, 12 mg of 2-aminobiphenyl, and 17 mg of benzocinnoline.

When *N*-imides VIIIa–d were refluxed in *o*-dichlorobenzene in the presence of an excess of the coresponding 2-azido-2′-arylazobiphenyls VIa–d (1:2–5 molar ratio) rapid decomposition of the *N*-imides occurred, TLC showing that no trace was left after 1 h refluxing.

Refluxing in *o*-dichlorobenzene of *N*-imides VIIIa–d in the presence of a threefold molar excess of *p*-chlorophenyl azide also led to rapid decomposition of VIIIa–d, benzocinnoline being the only recognizable product. (2-Aminobiphenyl was also formed in the case of the *N*-imide VIIIc.)

Thermolysis of 2-Azido-2′-arylazobiphenyls VIa–d in Bromobenzene. Thermal decomposition of azides VIa–d in refluxing bromobenzene was much slower than in *o*-dichlorobenzene. Qualitative experiments showed that the *N*-imides VIIIa–d were formed at the beginning of the reactions and survived for ca. 2 h after which time the starting azides were considerably unchanged whereas only trace amounts of the *N*-imides were left.

From two experiments carried out on a preparative scale (1 g of starting azide) benzo[*c*]cinnoline *N*-(2-biphenylyl)imide (VIIIc) (15% yield, 30% decomposition of azide VIc) and benzo[*c*]cinnoline *N*-(4-chlorophenyl)imide (VIIId) (13% yield, 25% decomposition of azide VId) were isolated by chromatography.

***N*-Methyl-*N*-(2′-azido-2-biphenylylazo)aniline (XIII).** 2-Amino-2′-azidobiphenyl[12] (1.9 g) was dissolved in 30 ml of water containing 3 ml of concentrated hydrochloric acid. The solution was cooled to 0 °C and diazotized with 0.7 g of sodium nitrite in 10 ml of water. The diazonium salt solution was filtered into an ice-cold solution of *N*-methylaniline (11 g) in 50 ml of water containing 3 ml of concentrated hydrochloric acid. Sodium acetate (5 g) was added to the solution. After 1 h stirring, the reaction mixture was extracted with ether and the extracts were washed with water, then dried (Na_2SO_4) and evaporated. The residue was chromatographed on alumina (pentane as eluent) to afford 2.25 g of XIII as sulfur-colored plates: mp 48–50 °C; IR ν_{max} 2075 cm^{-1} (N_3); mass spectrum *m/e* 328 (M^+), 300, 222, 195, 181, 180, 166, 152, 139, 106, 77.

Anal. Calcd for $C_{19}H_{16}N_6$: C, 69.50; H, 4.91; N, 25.59. Found: C, 69.72; H, 4.85; N, 25.12.

Photolysis of *N*-Methyl-*N*-(2′-azido-2-biphenylylazo)aniline (XIII). A solution of 1 g of azide XIII in 350 ml of N_2-saturated cyclohexane was irradiated for 5 h, after which time TLC showed the starting material to be absent. Solvent was evaporated and the residue chromatographed on silica gel to give carbazole (35%) together with trace amounts of benzocinnoline and other unidentified products accompanied by much polymeric material.

Thermolysis of *N*-Methyl-*N*-(2′-azido-2-biphenylylazo)aniline (XIII). A solution of 0.5 g of XIII in chlorobenzene was heated under reflux for 6 h. Chlorobenzene was distilled off under vacuum and the residue chromatographed to give carbazole (30%) together with traces of benzocinnoline and much polymeric material.

Registry No.—VIa, 60595-17-7; VIb, 60595-18-8; VIc, 60595-19-9; VId, 60595-20-2; VIIa, 60595-21-3; VIIb, 60595-22-4; VIIc, 60595-23-5; VIId, 60595-24-6; VIIIa, 54507-87-8; VIIIb, 60595-25-7; VIIIc, 60595-26-8; VIIId, 60595-27-9; IXa, 60595-28-0; IXb, 60595-29-1; IXc, 60595-30-4; IXd, 60595-31-5; XIII, 60595-32-6; XIV, 54147-64-7; 2,2′-diaminobiphenyl, 1454-80-4; nitrosobenzene, 586-96-9; 4-

methylnitrosobenzene, 623-11-0; 2-nitrosobiphenyl, 21711-71-7; 4-chloronitrosobenzene, 932-98-9; sodium nitrite, 7632-00-0; 4-aminocarbazole, 18992-64-8.

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Synthesis of 1-α-Cumyl-1,2,3,6-tetrahydropyridazine-3,6-dione

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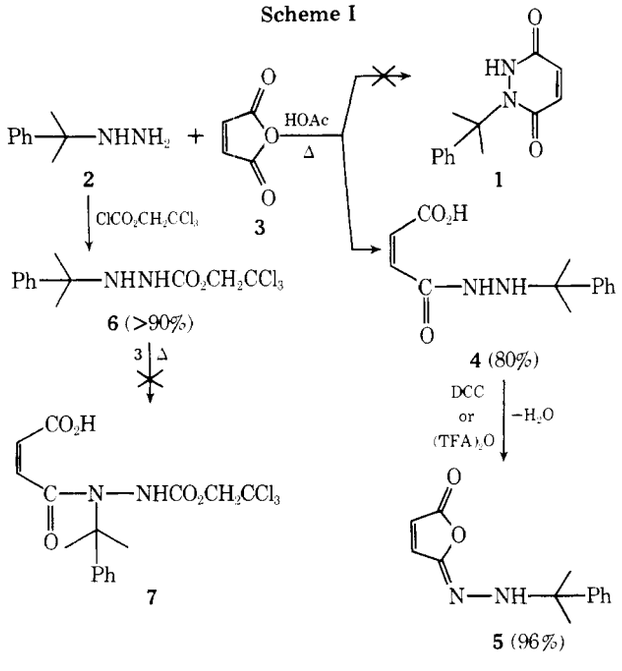
The title compound **1** cannot be prepared from reaction of α-cumylhydrazine (**2**) and maleic anhydride (**3**) in a manner analogous to the preparation of the 1-phenyl analogue. Instead, this reaction affords maleamic acid **4** and, after dehydration, isomaleimide **5**. When the unsubstituted nitrogen of **2** is protected by conversion to the trichloroethyl carbazate **6**, the substituted nitrogen is inert toward maleic anhydride, but not toward the more reactive maleoyl chloride **10**. The latter can be prepared by the reaction of lithium trichloroethoxide with excess maleic anhydride, followed by treatment with phosphorus trichloride. Maleic anhydride, which is unreactive toward 2,2,2-trichloroethanol, affords the isomeric fumarate **9** when treated with excess alkoxide ion. Treatment of carbazate **6** with maleoyl chloride **10** affords maleamate **11**. The latter diectly affords the desired tetrahydropyridazinedione **1** upon treatment with zinc in acetic acid.

1-α-Cumyl-1,2,3,6-tetrahydropyridazine-3,6-dione[1-4] (**1**), a precursor of a cyclic diacylhydrazyl radical which we desired, could not be prepared from α-cumylhydrazine[5] (**2**) and maleic anhydride (**3**). This unsuccessful approach is similar to that used to prepare the analogous 1-phenyltetrahydropyridazinedione[6] from phenylhydrazine. However, in the present case, α-cumylaminomaleamic acid (**4**) is obtained as the only product (Scheme I). Dehydration of **4** with either dicyclohexylcarbodiimide or trifluoroacetic anhydride affords the yellow isomaleimide **5** rather than the desired tetrahydropyridazinedione **1**. NMR chemical shifts (δ 6.13 and 7.20 ppm), vinyl coupling constant (J = 5.5 Hz), and ir carbonyl (1784 and 1757 cm^{-1}) and imine (1618 cm^{-1}) absorption peaks are in agreement with those observed for other isomaleimides.[7]

Scheme I



At this point, we felt that if the unsubstituted nitrogen of the hydrazine were protected, the maleic anhydride would be forced to react at the less reactive substituted nitrogen. Trichloroethoxycarbonyl[8] was chosen for this role since it could be removed under mild conditions that would not affect any of the other functionality present. To this end, α-cumylhydrazine was treated with 2,2,2-trichloroethyl chloroformate affording trichloroethyl carbazate **6** as a light, brown oil that could not be crystallized or distilled. The NMR spectrum of the oil is consistent with the assigned structure and showed it to be relatively pure. Reaction of carbazate **6** with maleic anhydride in refluxing toluene for 3 days failed to produce any detectable (NMR) quantity of the desired product **7**; extensive decomposition of the carbazate, however, was indicated.

We thought that a more reactive form of maleic acid could be obtained by protecting one carboxyl group and converting the other to the acid chloride. The trichloroethyl ester was chosen as the protecting group since this would allow removal of both protecting groups in one step. Heating maleic anhydride with trichloroethanol at 100 °C for 1 h (Scheme II) failed to produce any reaction (as judged by NMR), although methanol or ethanol react under these conditions.[9] Continued heating at 150 °C for 5 h afforded a colorless solid having an NMR spectrum inconsistent with that expected of the desired maleate **8**. Treatment of the anhydride with excess sodium trichloroethoxide affords the isomeric trichloroethyl hydrogen fumarate **9** [NMR, J_{vinyl} = 16.1 Hz (trans **HC**=**CH**);[10] ir 982 cm^{-1} (trans C=C)[11]]. Presumably, excess alkoxide ion allows the maleate isomerize to the sterically less congested fumarate