methoxyphenyl azide, 2101-87-3; 4-chlorophenyl azide, 3296-05-7; 3,4-dichlorophenyl azide, 66172-16-5; 2,4,6-trimethylphenyl azide, 14213-00-4; 5-methyl-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-2,1-benzisothiazole, 66172-17-6; *N*-ethyl-2-[3,3,3-trifluoro-2-(trifluoromethyl)propyl]aniline, 66172-00-7; methyl fluorosulfonate, 421-20-5; 2-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]benzothiazole, 66172-01-8; 2-aminobenzenethiol, 137-07-5; trimethyl phosphite, 121-45-9; triphenyl phosphite, 101-02-0; diphenyl 5,5-bis(trifluoromethyl)-2-(hexafluoroisopropylidene)-1,3-dithiolane-4-phosphonate, 66172-02-9; hexamethylbenzene, 87-85-4; durene, 95-93-2; 2-[1,1-bis(trifluoromethyl)-2-(2,4,5-trimethylphenyl)ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane, 66172-03-0; *p*-methylanisole, 104-93-8; 2-[1,1-bis(trifluoromethyl)-2-(*p*-methoxyphenyl)ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane, 66172-04-1; *p*-cresol, 106-44-5; *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)thiopropionate, 66172-05-2; butadiene, 106-99-0; 6-(hexafluoroisopropylidene)-5,6-dihydro-2*H*-thiopyran, 24515-61-5; 2,3-dichlorobutadiene, 1653-19-6; 3,4-dichloro-6-(hexafluoroisopropylidene)-5,6-dihydro-2*H*-thiopyran, 66172-06-3; pentamethyl-5-vinylcyclopentadiene, 20145-47-5; 3-(hexafluoroisopropylidene)-1,4,5,6,7-pentamethyl-7-vinyl-2-thiabicyclo[2.2.1]hept-5-ene, 35012-44-3; spiro[4.4]nona-1,3-diene, 766-29-0; 3-(hexafluoroisopropylidene)spiro[2-thiabicyclo[2.2.1]hept-5-ene-7,1′-cyclopentene, 35012-45-4; 6,6-diphenylfulvene, 2175-90-8; 7-(diphenylmethylene)-3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene, 24515-65-9; 1,3-cyclohexadiene, 592-57-4; anthracene, 120-12-7; 12-(hexafluoroisopropylidene)-11-thia-9,10-dihydro-9,10-ethanoanthracene, 24515-64-8; cyclooctatetraene, 629-20-9; 1,3-diphenylisobenzofuran, 5471-63-6; 1,2,4,7-tetrakis(methylene)cyclooctane, 35061-75-7; 3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]heptane, 35012-42-1; 4-(hexafluoroisopropylidene)-3-thiatricyclo-[4.2.2.0^{2,5}]deca-9-ene, 66172-07-4.

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Intramolecular Addition of Aryl Azides to the Azo Group. 2.[1] Synthesis and Properties of Benz[*cd*]indazole *N*-Arylimines

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Received November 14, 1977

Thermal and photochemical decomposition of 8-azido-1-arylazonaphthalenes results in intramolecular addition to the azo group to give previously unknown benz[*cd*]indazole *N*-arylimines in good yields by 1,5-cyclization. Only in one case 1,6-cyclization leading to a 2-arylnaphtho[1,8-*de*]triazine has also been observed. Chemical and spectroscopic properties of all *N*-imines are in accord with the proposed structures containing the stable 1,3-dipolar azimine system. Formation of products is discussed in terms of a possible concerted process not involving nitrene intermediates.

In a previous paper[1] we have reported what appears to be the first definite example of addition of aryl azides to the azo group leading to the formation of azimines, 1,3-dipolar valence tautomers of unknown triaziridines, presumably through the intermediacy of nitrenes. Photochemical decomposition of a number of 2-azido-2′-arylazobiphenyls (**1**, Ar = aryl) was in fact found to afford benzo[*c*]cinnoline *N*-arylimines (**2**) as major products as well as minor amounts of 4-arylazocarbazoles (**3**), 2-amino-2-arylazobiphenyls (**4**), and benzo[*c*]cinnoline (**5**).

These results prompted us to prepare a series of 1-azido-8-arylazonaphthalenes (**6**) and to investigate their thermal and photochemical decomposition in the hope that analogous intramolecular additions of the azido group (or nitrene) to the peri azo group would lead to the formation of 2-arylnaphtho[1,8-*de*]triazines (**7**) and/or benz[*cd*]indazole *N*-

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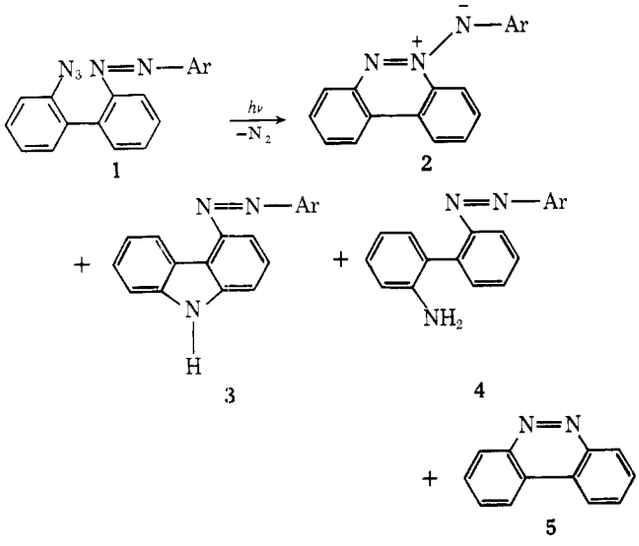
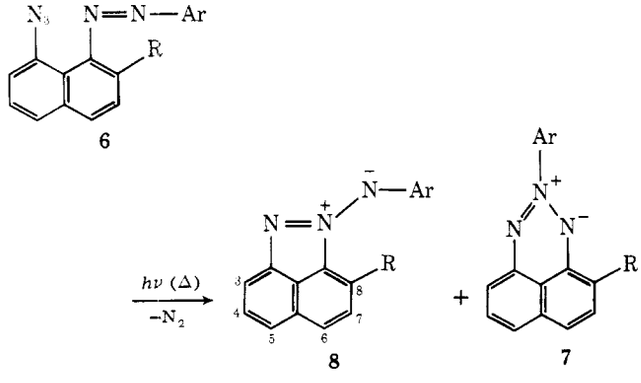


arylimines (8) by 1,6- or 1,5-cyclization, respectively. Reactions of peri-substituted 1-naphthyl azides are known[2,3b] and the stereochemistry appears to be favorable for intramolecular reaction in these cases.

Whereas several 2-substituted naphtho[1,8-*de*]triazines [7, Ar = alkyl or aryl; R = H] have been reported[4] and have been shown to be formed by alkylation and arylation of the 1*H*-naphtho[1,8-*de*]triazine,[4] benz[*cd*]indazoles *N*-arylimines (8) (if formed at all) would provide the first examples of the as yet unknown benz[*cd*]indazoles *N*-imines [8, Ar = H, alkyl, or aryl; R = H], which appear to be particularly interesting as members of heterocyclic *N*-imines[5,6] containing the rare 1,3-dipolar azimine function.[7,8] Moreover, benz[*cd*]indazole *N*-arylimines (8) would be representatives of the benz[*cd*]-indazole system whose synthesis has not as yet succeeded in spite of several attempts performed.[2,3] Although several of its dihydro derivatives are known,[3] so far the only authenticated examples of the benz[*cd*]indazole system are offered by the mono-[2] and di-*N*-oxide.[2]

Azides **6a–c** were obtained by diazotization of the readily available 1-amino-8-azidonaphthalene,[9] coupling of the diazonium salt with phenol or 1- and 2-naphthol, and methylation. Azides **6d–f** were prepared by coupling of the appropriate aryldiazonium chloride with 8-azido-2-naphthol and subsequent methylation of the coupling products with methyl iodide–silver oxide. Attempted preparation of 8-azido-1-arylazonaphthalenes (6) by condensation of 1-amino-8-azidonaphthalene with aryl nitroso compounds was unsuccessful.

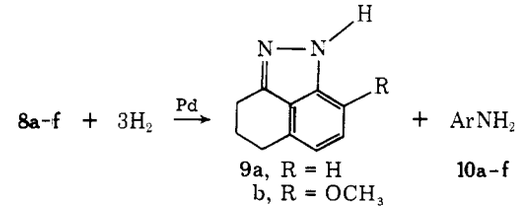


a, R = H; Ar = 4-$OCH_3C_6H_4$
b, R = H; Ar = 2-OCH_3-1-naphthyl
c, R = H; Ar = 4-OCH_3-1-naphthyl
d, R = OCH_3; Ar = Ph
e, R = OCH_3; Ar = 4-$CH_3C_6H_4$
f, R = OCH_3; Ar = 2PhC_6H_4

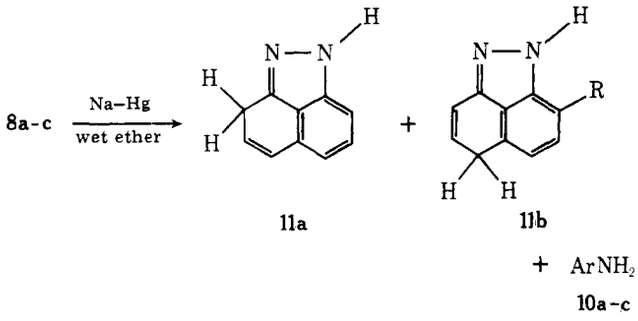
Photolysis of azides **6a–f** with a 100-W high-pressure mercury lamp in benzene solution for 24–36 h (until TLC showed complete decomposition of starting material) led to the isolation of the stable, red-violet benz[*cd*]indazole *N*-arylimines (**8a–f**) in 70–85% yields together with minor unidentified colored products and some polymeric material. No evidence of formation of 2-arylnaphtho[1,8-*de*]triazines (7) was found in any cases examined except for photolysis of azide **6b** which afforded the blue 2-(2-methoxy-1-naphthyl)naphtho[1,8-*de*]triazine (**7b**) albeit in very low yield (5%).

Thermolysis of azides **6a–f** took place readily in refluxing toluene (2–3 h) and was found to lead substantially to the same results as obtained from photolysis, *N*-imines 8 being isolated in comparable yields and no evidence of triazines 7 being obtained in any cases. The only exception was furnished by thermolysis of azide **6b** which gave only tars. Since control experiments (see later) showed azimine **8b** to be not capable of surviving the reaction conditions needed to bring about thermal decomposition of azide **6b**, whereas triazine **7b** was found to be quite stable, formation of **7b** in photolysis of **6b** and its absence in the corresponding thermolysis appeared to be possibly indicative of a photochemical rearrangement of *N*-imine **8b** to the valence tautomeric triazine **7b**. In order to check this point we effected irradiation of *N*-imine **8b** for the same time as employed in photochemical decomposition of azide **6b**, but TLC showed *N*-imine **8b** to be quite unaffected. However, when triazine **7b** was irradiated under the same conditions slow rearrangement to **8b** was observed, ca. 20% conversion taking place after the same irradiation time as employed to effect decomposition of azide **6b**. It thus appears that *N*-imine **8b** is a photoisomer of triazine **7b**. Since triazines **7a,c–f** could not be isolated from photolysis of the corresponding azides 6 their photochemical formation (and their possible conversion to *N*-imines **8a,c–f**) remains an open question, but it appears that photochemical rearrangement of 2-substituted naphthotriazines is not a general process since 2-methylnaphthotriazine (7, Ar = CH_3; R = H)[10] and 2-(2-nitropheny)naphthotriazine (7, Ar = $2NO_2C_6H_4$; R = H)[11] were found to be quite stable on irradiation for several days. On the other hand our observation that 2-methylnaphthotriazine (7, Ar = CH_3; R = H), 2-(2-nitrophenyl)naphthotriazine (7, Ar = 2-$NO_2C_6H_4$; R = H), and triazine **7b** are all thermally stable at least up to 180 °C (together with previous relevant findings[4,8c]) and the results obtained from thermolysis of all azides **6a–f** would lead to the conclusion that triazines 7 are not formed from thermolysis of 6, since they would be expected to be quite stable and isolable in such conditions.

Catalytic hydrogenation of *N*-imines (**8a–f**) led to 1,3,4,5-tetrahydrobenz[*cd*]indazoles[2] **9a** and **9b**, respectively, and the corresponding arylamines **10a–f**. Attempts to stop the reactions at an uptake of 1 or 2 molar equiv of hydrogen gave complex mixtures consisting of starting material, dihydrobenzindazoles (11), tetrahydrobenzindazole (**9a** or **9b**), and arylamine (10). These findings are in agreement with previous reports[2] of the catalytic reduction of benzindazole *N*-oxide and its 3-methoxy derivative, which afforded tetrahydrobenzindazoles **9a** and **9b**, respectively, in fairly good yields, and with similar N–N reductive cleavage reported for other azimines.[7b,12]

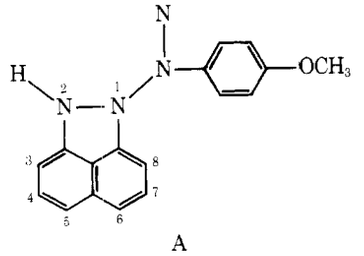


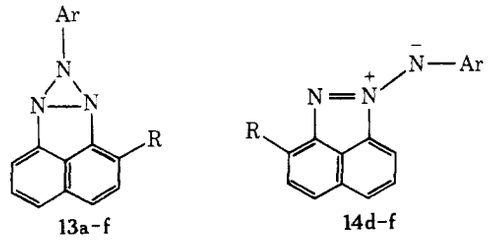
Treatment of *N*-imines **8a–c** with sodium amalgam in wet ether also led to reductive cleavage of the exocyclic N–N bonds with formation of a mixture of 1,3- and 1,5-dihydrobenzindazole, **11a** and **11b**, and arylamines, **10a–c**. Similar behavior was shown by benzindazole *N*-oxide which was found to furnish dihydrobenzindazole **11a** and **11b** under the same reductive conditions.[2]



N-Imines **8a–f** were insoluble in concentrated hydrochloric acid and were unchanged by it; however, when hydrogen chloride was passed into a methylene chloride solution of benz[*cd*]indazole *N*-(4-methoxyphenyl)imine (**8a**) and the precipitate formed was filtered off and treated with an aqueous solution of sodium carbonate, TLC showed that starting azimine **8a** had been largely converted in a reddish product. Chromatography led to the isolation of this compound, **12**, whose elemental analysis and parent ion in the mass spectrum were consistent with the molecular formula $C_{17}H_{14}ClN_3O$, thus pointing to a product deriving from hydrogen chloride addition to azimine **8a**. The mass spectrum of product **12** showed, in addition to the parent ion at *m/e* 311, predominant fragment ions at *m/e* 189 ($C_{10}H_6ClN_2^+$) and 123 ($C_7H_9NO^+$), clearly indicating that the chloride ion had entered the benzindazole ring of **8a**. The NMR spectrum consisted, in the aromatic region, of a two-proton AB quartet, with J_{AB} values of 8.2 Hz unmistakably ortho, superimposed on an AA′ BB′ and an ABX pattern. Finally the IR spectrum showed two sharp NH stretching absorptions at 3460 and 3320 cm^{-1}. All these data suggest a 1,2-dihydrobenzindazole structure such as A, with the halogen atom to be placed at positions 3, 5, 6, or 8.

Unfortunately a definite choice cannot be made between positions 3, 8 or 5, 6 for the chlorosubstituent on the basis of the observed J_{AB} values of 8.2 Hz since the available data for coupling constants for 1,8-disubstituted naphthalenes[2,13] (including some with a 1,8 bridge) would lead to expect $J_{3,4}$ and $J_{7,8}$ values of ca. 6.7–8.2 Hz and comparable values of ca. 7.8–8.6 Hz for $J_{4,5}$ and $J_{6,7}$.





However, a structure of type A, in which the halogen atom is placed either at the 3 or 5 position, seems to be possibly preferable for compound **12** to account for its preference to exist in a 1,2-dihydrobenzindazole form, whereas all known dihydrobenzindazoles[3] appear to exist in the 1,3- and 1,5-tautomeric forms. A slight stabilization of the ring nearer to the 2-nitrogen by the substituent in positions 3 or 5 might offer a possible explanation. Formation of product **12** can be most reasonably accounted for by a nucleophilic attack by chloride ion on azimine **8a** protonated at the imino nitrogen and subsequent prototropy induced by base. Qualitative experiments performed with the other *N*-imines **8b–f** showed hydrogen chloride addition to be a general process.

The UV spectra of *N*-imines **8a–f** showed intense absorption in the visible region between 500 and 600 nm as expected for dipolar compounds having easily polarizable valence electrons,[4,5] thus providing strong evidence (apart from lack of precedent) contrary to alternative unlikely triaziridine structures **13a–f**. Moreover their UV spectra showed similarity with that of benz[*cd*]indazole *N*-oxide[2] with its long wavelength absorptions shifted to notably longer wavelength.

NMR data are also in accord with the proposed structures **8**. In fact the NMR spectrum of **8a** showed a complex pattern of six protons in the aromatic region consisting of two overlapping ABC systems (the interpretation of which was not performed) which are in agreement with an unsymmetrical benzindazole ring. On the other hand the aromatic region of NMR spectra of compounds **8d–f** showed the low field half of the AB quartet, expected from the protons ortho and meta to the methoxy group, always to fall at lower field than any other benzindazole hydrogens. This pattern is consistent with structures **8d–f** if it is granted the reasonable assumption that protons 6–8 in the ring nearer to the arylimino group should be deshielded more than protons 3–5. Such assumption, which is consistent with previous reports[2] of NMR investigation of benzindazole *N*-oxide, would lead to exclude alternative tautomeric azimine structures **14d–f**.

Mass spectra of *N*-imines **8a–c** showed, in addition to the parent ion, characteristic ($M^+ - 1$) ions which were also observed in benzo[*c*]cinnoline *N*-arylimines[1] (**2**), together with predominant peaks due to loss of the methoxy fragment from the molecular ion and to N–N bond cleavage of the parent ion affording $ArNH_2^+$, $ArNH^+$, and ArN^+ fragments and fragments corresponding to loss of nitrogen from benzindazole ions. *N*-Imines **8d–f** showed an analogous fragmentation pattern, the only noticeable difference being that peaks at *m/e* 185 and 184, apparently deriving by loss of the arylimino fragment from the parent ion, were clearly more abundant in these cases. The corresponding ions at *m/e* 155 and 154 were almost absent in the mass spectra of *N*-imines **8a–c**.

As for the blue triazine **7b**, its structure was promptly assigned on the basis of spectroscopic and chemical evidence. Its mass spectrum showed the molecular ion as the base peak, its UV spectrum was as expected for a 2-substituted naphthotriazine,[10,11] and its NMR spectrum showed the two high-field aromatic protons (δ 5.8–6.0) characteristic of the 4-hydrogen atoms of the 2-substituted naphthotriazine system.[10,8c] Finally chemical proof came from its ready hydrogenolysis which resulted, as expected,[10] in the formation of 1,8-diaminonaphthalene and 2-methoxy-1-naphthylamine.

In principle benz[*cd*]indazole *N*-arylimines (**8a–f**) could undergo thermal or photochemical fragmentation to benzindazole (or 3-methoxybenzindazole, respectively) and a formal aryl nitrene fragment.[5,6]

On heating in refluxing toluene all *N*-imines **8** were found to be stable for several hours, with the exception of *N*-imine **8b** which was shown to be completely destroyed after 1 h in refluxing toluene and after several hours in boiling benzene. In refluxing *o*-dichlorobenzene (in the absence and in the

presence of suitable compounds expected to be able to trap either benzindazole or 1,8-dehydronaphthalene which might be formed by spontaneous decomposition of benzindazole), azimines **8** exhibited rapid decomposition with formation of tarry products and traces of arylamines **10**. These findings did not provide much diagnostic evidence for fragmentation of *N*-imines **8**. However, formation of arylamines **10** only in trace amounts and in particular the absence of carbazole in the pyrolysis of **8f** would at least indicate that nitrene fragments are practically not formed in these cases in analogy with what is observed with benzocinnoline *N*-arylimines.[1,7b]

On UV irradiation all *N*-imines **8** were found to be largely unchanged for a few days, slow decomposition (to tars) being noticed with further increasing irradiation time. In the presence of acetophenone their decomposition took place readily (24 h) affording traces of arylamines **10** (no trace of carbazole from **8f**) and intractable material. As from pyrolysis we did not manage to detect or intercept either benzindazole or 1,8-dehydronaphthalene from suitable trapping experiments.

The results obtained from photochemical and thermal decomposition of 8-azido-1-arylazonaphthalenes (**6**) provide a new definite example of formation of azimines by intramolecular addition of aryl azides to the azo group in addition to that previously offered by 2-azido-2-arylazobiphenyls[1] (**1**). However, in contrast with results obtained from decomposition of these latter azides which appeared to provide evidence in favor of a nitrene mechanism in the formation of benzo[*c*]cinnoline *N*-arylimines (**2**), decomposition of azides **6** is more likely to lead to products **8** without the actual intermediacy of nitrenes. A concerted cyclization mechanism, in which the peri-azo group provides anchimeric assistance for the elimination of nitrogen, is much more plausible, at least in thermolysis, to account for the absence of other products expected from nitrene intermediates and, more significantly, for the low reaction temperatures. In fact azides **6a–f** were found to decompose smoothly at 110 ° whereas 1-azidonaphthalenes have been reported to decompose above 150 °C.[3b,14] Steric destabilization of the azido group by the peri-arylazo substituent might be an explanation alternative to that involving concerted cyclization for the decomposition temperatures of 8-azido-1-arylazonaphthalenes (**6**), but this possibility appears to be ruled out by previous findings[3b] that decomposition temperatures of 1-azidonaphthalenes are not affected by peri substituents, even if bulky, unless intramolecular catalysis is involved. As for photochemical decomposition of azides **6**, the only evidence against a nitrene mechanism is based on the following findings: (a) yields of *N*-imines **8** are comparable to those obtained from thermolysis, (b) absence of other products diagnostic for the intermediacy of nitrenes, (c) irradiation at 254, 300, and 350 nm (in the last case in the presence and in the absence of acetophenone) does not produce any detectable change.

Finally we wish to point out that thermal and photochemical decomposition of 8-azido-1-arylazonaphthalenes (**6**) represents a general synthetic route to benz[*cd*]indazole *N*-arylimines (**8**), which do not appear to be otherwise accessible at the moment; studies are in progress to further explore the chemical reactivity of these interesting compounds.

Experimental Section

All melting points are uncorrected. UV spectra are for solutions in ethanol and IR and NMR spectra for solutions in carbon disulfide unless otherwise stated. 1-Amino-7-naphthol was a commercial product; 1-amino-8-azidonaphthalene was prepared as described in the literature.[9] Reaction products such as aniline, *p*-anisidine, *p*-toluidine, and 2-aminobiphenyl were characterized by spectral comparison with authentic commercial samples.

8-Azido-2-naphthol. A suspension of 1-amino-7-naphthol (2 g) in 8 mL of concentrated hydrochloric acid and 70 mL of water was cooled to 0–5 °C and diazotized with a solution of 0.9 g of sodium nitrite in 10 mL of water. After standing for 15 min, the resulting solution was treated with 0.9 g of sodium azide in water (10 mL), stirred for 1 h at 0–5 °C, and then extracted with ether. The dried extracts were evaporated and the residue was chromatographed on silica gel. Elution with 5% ether–pentane afforded 1.3 g (57%) of 8-azido-2-naphthol: mp 127–129 °C; IR ν_{max} 3580 (OH) and 2100 cm^{-1} (N_3); mass spectrum *m/e* 185 (M^+) and 157 ($M^+ - N_2$). Anal. Calcd for $C_{10}H_7N_3O$: C, 64.86; H, 3.81; N, 22.69. Found: C, 64.81; H, 3.86; N, 22.74.

Preparation of 8-Azido-2-hydroxy-1-arylazonaphthalenes (6: R = OH; Ar = Ph, 4-$CH_3C_6H_4$, 2-PhC_6H_4). The preparation of these compounds was accomplished by coupling of the appropriate aryldiazonium chloride with 8-azido-2-naphthol by means of the following general procedure.

8-Azido-2-hydroxy-1-phenylazonaphthalene (6: R = OH; Ar = Ph). Aniline (3.6 g) was dissolved in 120 mL of water containing 12 mL of concentrated hydrochloric acid and diazotized with 3 g of sodium nitrite at 0 °C. The diazonium salt solution was filtered into a stirred solution of 8-azido-2-naphthol (7.4 g) in 400 mL of water containing 4.8 g of sodium hydroxide. After stirring 1 h, the reaction mixture was acidified and the bright red solid was filtered and washed with water. The crude material was purified through a silica gel column to give 8-azido-2-hydroxy-1-phenylazonaphthalene (6, R = OH; Ar = Ph) (10.4 g, 93%): mp 115–116 °C dec; IR ν_{max} 2080 cm^{-1} (N_3); mass spectrum *m/e* 289 (M^+). Anal. Calcd for $C_{16}H_{11}N_5O$: C, 66.43; H, 3.81; N, 24.22. Found: C, 66.34; H, 3.85; N, 24.35.

8-Azido-2-hydroxy-1-(4-tolylazo)naphthalene (6, R = OH; Ar = 4-$CH_3C_6H_4$) was obtained in 91% yield as bright red plates: mp 118–120 °C dec; IR ($CHCl_3$) ν_{max} 2110 and 2090 (N_3) cm^{-1}; mass spectrum *m/e* 303 (M^+). Anal. Calcd for $C_{17}H_{13}N_5O$: C, 67.32; H, 4.32; N, 23.09. Found: C, 67.42; H, 4.28; N, 22.98.

8-Azido-2-hydroxy-1-(2-biphenylylazo)naphthalene (6, R = OH; Ar = 2-PhC_6H_4) was obtained in 89% yield as dark red plates: mp 101–103 °C dec; IR ν_{max} 2080 cm^{-1} (N_3); mass spectrum *m/e* 365 (M^+). Anal. Calcd for $C_{22}H_{15}N_5O$: C, 72.31; H, 4.14; N, 19.17. Found: C, 73.02; H, 4.21; N, 19.33.

Synthesis of 8-Azido-2-methoxy-1-arylazonaphthalenes (6d–f). Azides **6d–f** were prepared from the corresponding hydroxy derivatives by methylation with methyl iodide–silver oxide in dimethylformamide at room temperature. The following procedure is representative.

8-Azido-2-methoxy-1-phenylazonaphthalene (6d). To a stirred mixture of 8-azido-2-hydroxy-1-phenylazonaphthalene (**6**, R = OH; Ar = Ph) (5.5 g) in dry dimethylformamide (DMF) (400 mL) was added silver oxide (5.5 g) and after 15 min methyl iodide (10 mL). Stirring was continued at room temperature until TLC showed complete absence of the starting material (24–30 h), then the reaction mixture was poured into water and extracted with methylene chloride. The extracts were washed with water and evaporated to give an oily residue which was chromatographed on silica gel. Elution with 10% ether–pentane afforded 8-azido-2-methoxy-1-phenylazonaphthalene (**8d**) (3.5 g, 61%) as dark red needles: mp 96–98 °C dec; IR ν_{max} 2835 (OCH_3) and 2090 cm^{-1} (N_3); mass spectrum *m/e* 303 (M^+) and 275 ($M^+ - N_2$). Anal. Calcd for $C_{17}H_{13}N_5O$: C, 67.32; H, 4.32; N, 23.09. Found: C, 67.45; H, 4.37; N, 23.35.

8-Azido-2-methoxy-1-(4-tolylazo)naphthalene (6e) was obtained in 55% yield as dark red needles: mp 101–103 °C dec; IR ν_{max} 2830 (OCH_3) and 2095 cm^{-1} (N_3); mass spectrum *m/e* 317 (M^+) and 289 ($M^+ - N_2$). Anal. Calcd for $C_{18}H_{15}N_5O$: C, 68.12; H, 4.76; N, 22.07. Found: C, 68.14; H, 4.73; N, 21.45.

8-Azido-2-methoxy-1-(2-biphenylylazo)naphthalene (6f) was obtained in 30% yield as a dark red, thick oil which did not solidify: IR ν_{max} 2835 (OCH_3) and 2095 cm^{-1} (N_3); mass spectrum *m/e* 379 (M^+) and 351 ($M^+ - N_2$). Anal. Calcd for $C_{23}H_{17}N_5O$: C, 72.8; H, 4.51; N, 18.46. Found: C, 73.15; H, 4.53; N, 18.38.

Synthesis of 8-Azido-1-arylazonaphthalenes (6a–c). These compounds were prepared by coupling of the diazonium chloride of 1-amino-8-azidonaphthalene with phenol, 1- and 2-naphthol, and subsequent methylation of the crude coupling product either with methyl iodide–silver oxide in DMF or with methyl iodide–potassium carbonate in dry acetone.

8-Azido-1-(4-methoxyphenylazo)naphthalene (6a). 1-Amino-8-azidonaphthalene (1.85 g) was suspended in a solution of concentrated hydrochloric acid (3 mL) and water (30 mL) and diazotized at 0 °C by dropwise addition of sodium nitrite (0.75 g) in water (10 mL). After the addition was complete, the diazonium salt solution was filtered dropwise into an ice-cold solution of 0.95 g of phenol in 100 mL of water containing 1.2 g of sodium hydroxide. After standing 1 h the mixture was acidified and the red precipitate was filtered off

and washed several times with water. The crude product (1.5 g) was directly methylated without further purification.

Methylation was accomplished by stirring it in a solution of dry acetone (50 mL) and methyl iodide (3 mL), containing 2 g of potassium carbonate. Stirring was effected at room temperature for 24 h, after which time the mixture was filtered and the filtrate was evaporated. The dark oily residue was chromatographed on alumina (20% benzene–pentane as eluant) to give 8-azido-1-(4-methoxyphenylazo)naphthalene (6a) (0.6 g) as dark red needles: mp 78–80 °C dec; IR ν_{max} 2840 (OCH_3) and 2100 cm^{-1} (N_3); mass spectrum *m/e* 303 (M^+) and 275 ($M^+ - N_2$). Anal. Calcd for $C_{17}H_{13}N_5O$: C, 67.32; H, 4.32; N, 23.09. Found: C, 67.55; H, 4.31; N, 22.89.

8-Azido-4′-methoxy-1,1′-azonaphthalene (6c). The above procedure, starting from 1.85 g of 1-amino-8-azidonaphthalene and 1.45 g of 1-naphthol, gave 1.8 g of azide **6c** as dark red needles; mp 130–132 °C dec; IR ν_{max} 2840 (OCH_3) and 2095 cm^{-1} (N_3); mass spectrum *m/e* 353 (M^+) and 325 ($M^+ - N_2$). Anal. Calcd for $C_{21}H_{15}N_5O$: C, 71.40; H, 4.25; N, 19.82. Found: C, 70.98; H, 4.53; N, 19.35.

8-Azido-2′-methoxy-1,1′-azonaphthalene (6b). Coupling of 2-naphthol (2.8 g) with the diazonium chloride of 1-amino-8-azidonaphthalene (from 3.6 g of amine) led to 6.5 g of crude azo compound which was methylated with methyl iodide–silver oxide in DMF to afford 5.5 g of azide 6b as dark red needles: mp 106–108 °C dec; IR ν_{max} 2840 (OCH_3) and 2090 cm^{-1} (N_3); mass spectrum *m/e* 353 (M^+) and 325 ($M^+ - N_2$). Anal. Found: C, 70.90; H, 4.18; N, 19.27.

Photolysis of 8-Azido-1-arylazonaphthalenes (6a–f). General Procedure. Stirred solutions of azides **6a–f** (1 g) in 400 mL of benzene were purged with nitrogen for 1 h and then irradiated at room temperature with a 100-W high-pressure mercury lamp. The progress of the reactions was monitored by TLC and irradiation was stopped after TLC showed absence of starting material (24–36 h). The excess solvent was distilled off and the residue was chromatographed on silica gel.

Photolysis of 8-Azido-1-(4-methoxyphenyl)naphthalene (6a). Chromatography with 5% ether–pentane afforded trace amounts of unreacted azide. Further elution with 10% ether–pentane gave benz[*cd*]indazole *N*-(4-methoxyphenyl)imine (**8a,** 82%) as dark red-violet needles: mp 139–140 °C (from pentane–benzene); IR ν_{max} 2840 (OCH_3), 1260, 1240, 1150, 1060 cm^{-1}; NMR δ 3.60 (OCH_3), 6.3 (2 H, d, J = 8.8 Hz), 6.43–7.3 (6 H, m), and 7.7 (2 H, d, J = 8.8 Hz); mass spectrum *m/e* 275 (M^+), 274, 260, 244, 232, 204, 140, 126, 123, 121, 106, 78; UV λ_{max} 293, 302, 352, 531, 554 nm (log ϵ 4.32, 4.25, 3.98, 4.39, 4.35). Anal. Calcd for $C_{17}H_{13}N_3O$: C, 74.17; H, 4.76; N, 15.26. Found: C, 73.98; H, 4.81; N, 14.98. Elution with ether afforded a violet product which was not identified.

Photolysis of 8-Azido-2′-methoxy-1,1′-azonaphthalene (6b). Chromatography (benzene–petroleum 2:3 as eluant) gave (1) trace amounts of unreacted azide, (2) 2-(2-methoxy-1-naphthyl)naphtho[1,8-*de*]triazine (**7b**), (3) benz[*cd*]indazole *N*-(2-methoxy-1-naphthyl)imine, and (4) a mixture of unidentified colored products. **7b** (5%) appeared as dark blue needles: mp 238–240 °C; NMR ($CDCl_3$) δ 3.78 (OCH_3), 5.8–6.0 (2 H, dd), and 6.32–7.7 (10 H, m); mass spectrum *m/e* 325 (M^+), 310, 294, 266, 254, 241, 168, 155; UV λ_{max} 341, 356, 584, 633, 693 nm (log ϵ 4.10, 4.15, 2.93, 2.90, 2.71). Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.64; N, 12.91. Found: C, 77.65; H, 4.61; N, 12.97.

Hydrogenation of **7b** in methylene chloride with palladium–charcoal (10%) at room temperature and atmospheric pressure led to 1,8-diaminonaphthalene and 1-amino-2-methoxynaphthalene,[15] whose R_f's (SiO_2 and Al_2O_3) were identical to those of authentic compounds.

Benz[*cd*]indazole N-(2-methoxy-1-naphthyl)imine (**8b,** 85%) appeared as dark violet needles, which softened without melting at ca. 170 °C and then were converted to unmelting tarry material: IR ν_{max} 2840 (OCH_3), 1370, 1275, 1255, 1168, 1100, 1070 cm^{-1}; NMR δ 3.75 (OCH_3) and 6.9–7.9 (12 H, m); mass spectrum *m/e* 325 (M^+), 324, 294, 173, 158, 130, 126; UV λ_{max} 265, 326, 521 nm (log ϵ 4.27, 3.91, 3.99). Anal. Found: C, 77.54; H, 4.66; N, 12.78.

Photolysis of 8-Azido-4′-methoxy-1,1′-azonaphthalene (6c). Chromatography (25% benzene–pentane) afforded (1) traces of unreacted azide, (2) violet oily product not identified, and (3) benz[*cd*]indazole *N*-(4-methoxy-1-naphthyl)imine (**8c,** 75%) as dark violet needles, which were converted to tar on heating without melting: IR ν_{max} 2835, 1360, 1325, 1092, 1070 cm^{-1}; mass spectrum *m/e* 325 (M^+), 324, 310, 294, 173, 171, 158, 130, 126; UV λ_{max} 279, 299, 364, 556, 597 nm (log ϵ 4.19, 4.23, 3.92, 4.47, 4.52). Anal. Found: C, 77.34; H, 4.68; N, 12.84.

Photolysis of 8-Azido-2-methoxy-1-phenylazonaphthalene (6d). Chromatography (5% ether–pentane) gave (1) traces of unreacted azide, (2) violet oily product not identified, and (3) 8-methoxybenz[*cd*]indazole *N*-phenylimine (**8d,** 70%) as red-violet needles: mp 111–112 °C (from benzene–pentane); IR ν_{max} 2840 (OCH_3), 1280, 1060 cm^{-1}; NMR δ 4.08 (OCH_3), 6.98–7.45 (7 H, m), 7.7 (1 H, d, J = 8.6 Hz), and 8.1–8.35 (2 H, m); mass spectrum *m/e* 275, 274, 260, 185, 184, 126, 77; UV λ_{max} 295, 305, 348, 498, 526, 560 nm (log ϵ 4.27, 4.20, 3.83, 4.18, 4.20, 4.02). Anal. Calcd for $C_{17}H_{13}N_3O$: C, 74.16; H, 4.76; N, 15.26. Found: C, 74.10; 4.78; N, 14.96.

Photolysis of 8-Azido-2-methoxy-1-(4-tolylazo)naphthalene (6e). Chromatography (5% ether–pentane) gave (1) traces of unreacted azide, (2) a mixture of colored products, and (3) 8-methoxybenz[*cd*]indazole *N*-(4-tolyl)imine (**8e,** 70%) as bright red-violet needles: mp 150–152 °C (from benzene–pentane); IR ν_{max} 2840 (OCH_3), 1280, 1060 cm^{-1}; NMR δ 2.37 (CH_3), 4.1 (OCH_3), 6.95–7.4 (6 H, m), 7.73 (1 H, d, J = 8.6 Hz), and 8.16 (2 H, d, $J \approx$ 8.7 Hz); mass spectrum *m/e* 289 (M^+), 288, 274, 260, 259, 185, 184, 126, 107, 106, 91; UV λ_{max} 295, 308, 349, 500, 527, 562 nm (log ϵ 4.33, 4.26, 3.91, 4.22, 4.31, 4.15). Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.73; H, 5.22; N, 14.52. Found: C, 74.04; H, 5.20; N, 14.34.

Photolysis of 8-Azido-2-methoxy-1-(2-biphenylylazo)naphthalene (6f). Chromatography (10% ether–pentane) afforded (1) traces of unreacted azide, (2) a mixture of colored products, and (3) 8-methoxybenz[*cd*]indazole *N*-(2-biphenylyl)imine (**8f**) (72%) as bright red-violet plates: mp 141–143 °C; IR ν_{max} 2830 (OCH_3), 1280, 1055 cm^{-1}; NMR δ 3.95 (OCH_3), 7.06 (1 H, d, J = 8 Hz), 7.15–7.60 (11 H, m), 7.71 (1 H, d, J = 8 Hz), and 8.75–8.9 (1 H, m); mass spectrum *m/e* 351 (M^+), 350, 336, 184, 169, 168, 167, 166, 126; UV λ_{max} 298, 308, 505, 534, 574 nm (log ϵ 4.34, 4.23, 4.13, 4.15, 3.93). Anal. Calcd for $C_{23}H_{17}N_3O$: C, 78.61; H, 4.88; N, 11.96. Found: C, 78.27; H, 4.90; N, 11.77.

Thermolysis of 8-Azido-1-arylazonaphthalenes (6a–f). General Procedure. Solutions of azides **6a–f** (1 g) were refluxed in toluene (40 mL) until TLC showed that no starting material was left (1–2 h). Solvent was distilled off under reduced pressure and the residue was chromatographed as described above for the corresponding photolyses.

Azide **6a** gave benz[*cd*]indazole *N*-(4-methoxyphenyl)imine (**8a**) in 80% yield; azide **6c** afforded benz[*cd*]indazole *N*-(4-methoxy-1-naphthyl)imine (**8c**) in 77% yield; azide **6d** furnished 8-methoxybenz[*cd*]indazole *N*-phenylimine (**8d**) in 55% yield (this reaction was accompanied by much tarring); azide **6e** gave 8-methoxybenz[*cd*]-indazole *N*-(4-tolyl)imine (**8e**) in 70% yield. Decomposition of azide **6f** was not carried out on a preparative scale; however, the reaction performed on a qualitative scale was shown by TLC to follow the general trend, i.e., considerable formation of the corresponding *N*-imine (**8f**) and some tarring.

Thermolysis of azide **6b** did not furnish any isolable material but led to formation of a great amount of tars. Qualitative experiments showed initial formation of benz[*cd*]indazole *N*-(2-methoxy-1-naphthyl)imine (**8b**) (but not of triazine **7b**) and subsequent decomposition to tars. When decomposition of azide **6b** was carried out in boiling benzene formation of *N*-imine **8b** became more evident, but yield of isolable product appeared to be still too poor for the reaction to have a synthetic utility.

Hydrogenation of Benz[*cd*]indazole *N*-Arylimines (8a–f). The following procedure is typical of that used in the hydrogenation of *N*-imines **8a–f.**

Hydrogenation of Benz[*cd*]indazole *N*-(4-Methoxyphenyl)-imine (8a). The *N*-imine **8a** (500 mg) was dissolved in 50 mL of methylene chloride and hydrogenated at room temperature and atmospheric pressure using palladium–charcoal (10%, 100 mg) as catalyst. Hydrogenation led to the uptake of ca. 3 molar equiv of hydrogen in 0.5 h. After removal of the catalyst and the excess solvent the residue was chromatographed on silica gel.

Elution with 5% ether–pentane furnished *p*-anisidine (**10a,** 56%).

Elution with ether gave 1,3,4,5-tetrahydrobenz[*cd*]indazole (**9a,** 46%), mp 120–121 °C (lit.[2] mp 120–121 °C), identical in all respects with a sample prepared by hydrogenation of benzindazole *N*-oxide:[2] IR (CCl_4) 3490 cm^{-1} (NH); mass spectrum *m/e* 158 (M^+) and 157.

Hydrogenation of *N*-(2-Methoxy-1-naphthyl)imine (8b) gave 1-amino-2-methoxynaphthalene (**10b,** 77%), mp and mmp 53–54 °C (lit.[15] 54 °C) and IR spectrum identical with that of an authentic specimen, and 1,3,4,5-tetrahydrobenzindazole (**9a,** 60%).

Hydrogenation of *N*-(4-Methoxy-1-naphthyl)imine (8c) gave 1-amino-4-methoxynaphthalene (**10c,** 66%), mp and mmp 38–40 °C (lit.[16] 39–40 °C) and IR spectrum identical with that of an authentic specimen, and 1,3,4,5-tetrahydrobenzindazole (**9a,** 59%).

Hydrogenation of 8-Methoxybenz[*cd*]indazole *N*-Phenylimine (8d) furnished aniline (**10d,** 40%) and 8-methoxy-1,3,4,5-tetrahydrobenzindazole (**9b,** 38%), mp and mmp 121–122 °C (lit.[2]

164–166 °C), identical in all respects with a specimen prepared by hydrogenation of 3-methoxybenzindazole *N*-oxide as described by Alder and co-workers,[2] who reported for the compound **9b** a melting point 164–166 °C; in our hands the same compound (**9b**) had mp 121–122 °C: IR (CCl_4) 3495 (NH) and 2840 cm^{-1} (OCH_3); NMR ($CDCl_3$) δ 2.12 (2 H), 2.87 (2 H), 2.99 (2 H), 3.9 (OCH_3), 6.63 (1 H, d, J = 7.5 Hz), and 6.7 (1 H, d, J = 7.5 Hz); mass spectrum m/e 188 (M^+), 187, 173; UV δ_{max} 258, 266, 297 (log ϵ 3.67, 3.65, 3.73).

Hydrogenation of 8-Methoxybenz[*cd*]indazole *N*-(4-Tolyl)-imine (8e) afforded *p*-toluidine (**10e,** 45%) and 8-methoxy-1,3,4,5-tetrahydrobenzindazole (**9b,** 36%).

Hydrogenation of 8-Methoxybenz[*cd*]indazole *N*-(2-Biphenylyl)imine (8f) gave 8-aminobiphenyl (**10f,** 75%) and 8-methoxy-1,3,4,5-tetrahydrobenzindazole (**9b,** 40%).

Reduction of Benz[*cd*]indazole *N*-Arylimines (8a–c) with Sodium Amalgam in Wet Ether. The following procedure is typical of that employed in reduction of *N*-imines **8a–c.**

Reduction of Benz[*cd*]indazole *N*-(4-Methoxyphenyl)imine (8a). Compound **8a** (500 mg) was dissolved in diethyl ether saturated with water (100 mL) and treated with 1.2% sodium amalgam (12 g). After stirring 3 h and further addition of sodium amalgam (6 g), the reaction mixture was allowed to stand for 10 h. The solution was decanted, dried, and evaporated to give a dark oily residue which was chromatographed on silica gel. Elution with 10% ether–pentane afforded *p*-anisidine (**10a,** 68%); elution with 50% ether–pentane gave a mixture of 1,3- and 1,5-dihydrobenzindazole, **11a** and **11b** (54%), mp 152–156 °C after sublimation. The IR, NMR, and UV spectra of this mixture were practically identical with those of a mixture of **11a** and **11b** obtained by reduction of benz[*cd*]indazole *N*-oxide as described by Alder and co-workers:[2] IR ($CHCl_3$) 3475 cm^{-1} (NH); mass spectrum m/e 156 (M^+), 155.

Reduction of Benz[*cd*]indazole *N*-(2-Methoxy-1-naphthyl)-imine (8b) afforded 1-amino-2-methoxynaphthalene (**10b,** 88%) and a mixture of **11a** and **11b** (55%).

Reduction of Benz[*cd*]indazole *N*-(4-Methoxy-1-naphthyl)-imine (8c) led to 1-amino-4-methoxynaphthalene (**10c,** 70%) and to a mixture of **11a** and **11b** (50%).

Treatment of Benz[*cd*]indazole *N*-(4-Methoxyphenyl)imine (8a) with Acid. Hydrogen chloride was passed into a solution of *N*-imine **8a** (500 mg) in methylene chloride (15 mL) to give an orange-red precipitate which was filtered off, washed several times with methylene chloride, and then treated with 10% aqueous sodium carbonate. Extraction with methylene chloride and chromatography on silica gel using 5% ether–pentane as eluant gave trace amounts of starting imine **8a** and then 450 mg (80%) of compound **12** as reddish-brown needles: mp 144–146 °C; IR ν_{max} 3460 (NH), 3320 (NH), and 2825 cm^{-1} (OCH_3); NMR δ 3.87 (OCH_3), 6.67 (1 H, d, J = 8.2 Hz), 7.01 (2 H, d, J = 8.9 Hz), 7.24–7.36 (5 H, m), and 8.36 (1 H, dd); mass spectrum m/e 311 (M^+), 189, 123, 108; UV λ_{max} 295, 354, 476 nm (log ϵ 4.07, 4.41, 3.73). Anal. Calcd for $C_{17}H_{14}ClN_3O$: C, 65.49; H, 4.53; Cl, 11.37; N, 13.48. Found: C, 65.65; H, 4.48; Cl, 11.43; N, 13.24.

Experiments to Determine Photosensitivity of Benz[*cd*]indazole *N*-Arylimines (8a–f). Solutions of *N*-imines **8a–f** in benzene (or cylcohexane) were irradiated for 3–6 days, after which time TLC showed **8a–f** to be largely unchanged, decomposition to tars having occurred to a very small extent. When irradiations were conducted at 350 nm in the presence of acetophenone as sensitizer (threefold molar excess) complete decomposition of *N*-imines **8a–f** took place in ca. 24 h, traces of arylamines **10a–f** and much tarry material being observed. Finally sensitized irradiations of *N*-imines **8a–f** in the presence of excess diethyl acetylendicarboxylate, methyl propiolate, or dimethyl azodicarboxylate did not lead to formation of identifiable products.

Pyrolyses of Benz[*cd*]indazole *N*-Arylimines (8a–f). All *N*-imines **8a–f** were found to be largely unchanged in refluxing toluene for several hours with the exception of *N*-imine **8b** which smoothly decomposed to tars and traces of 1-amino-2-methoxynaphthalene. The *N*-imine **8b** could be completely decomposed also in boiling benzene in ca. 24 h. Pyrolyses of *N*-imines **8** in refluxing *o*-dichlorobenzene (or decalin) brought about their rapid decomposition which was complete in 20–30 min to afford arylamines **10** in trace amounts (TLC) and much tarry material. No evidence of carbazole nor of azo-2-biphenyl could be obtained from pyrolysis of *N*-imine **8f.** Finally pyrolyses of *N*-imines **8** in DMF (at 150 °C, sealed tube) in the presence of a tenfold excess of diethyl acetylenedicarboxylate, vinyl acetate, or tetraphenylcyclopentadienone did not furnish any isolable product.

Control Experiments to Determine Thermal and Photochemical Sensitivity of 2-(2-Methoxy-1-naphthyl)-naphtho[1,8-*de*]triazine (7b). Triazine **7b** was found to be quite stable in refluxing toluene for 1 week and largely unchanged after refluxing in *o*-dichlorobenzene for 1 day. Irradiation of **7b** in benzene solution for 36 h led to its partial conversion to *N*-imine **8b.**

Chromatography on silica gel indicated that ca. 20% conversion had occurred. Rearrangement of **7b** to **8b** appeared to increase slowly with increasing irradiation time and after 1 week's irradiation triazine **7b** was still noticeably present.

No evidence of any rearrangement could be obtained from 1 week's irradiation of 2-methylnaphthotriazine[10] (**7,** R = H; Ar = CH_3) and 2-(2-nitrophenyl)naphthotriazine[11] (**7,** R = H; Ar = 2-$NO_2C_6H_4$). These two latter compounds were also recovered largely unchanged after refluxing in *o*-dichlorobenzene for 1 day.

Acknowledgment. The authors thank CNR for a research grant.

Registry No.—**6** (R = OH; Ar = Ph), 65832-01-1; **6** (R = OH; Ar = 4-$CH_3C_6H_4$), 65832-02-2; **6** (R = OH; Ar = 2-PhC_6H_4), 65832-03-3; **6a,** 65832-04-4; **6b,** 65832-05-5; **6c,** 65832-06-6; **6d,** 65832-07-7; **6e,** 65832-08-8; **6f,** 65898-26-2; **7b,** 65832-09-9; **8a,** 65898-25-1; **8b,** 65832-10-2; **8c,** 65832-11-3; **8d,** 65832-12-4; **8e,** 65832-13-5; **8f,** 65832-14-6; **9a,** 65832-15-7; **9b,** 26574-20-9; **10a,** 104-94-9; **10b,** 2246-42-6; **10c,** 16430-99-2; **10d,** 62-53-3; **10e,** 106-49-0; **10f,** 90-41-5; **11a,** 25262-27-5; **11b,** 25262-26-4; **12,** 65832-27-1; 8-azido-2-naphthol, 36519-80-9; 1-amino-7-naphthol, 118-46-7; phenyldiazonium chloride, 100-34-5; *p*-tolyldiazonium chloride, 2028-84-4; 2-biphenylyldiazonium chloride, 52500-12-6; 1-amino-8-azidonaphthanene, 2112-98-3; 8-azido-1-naphthyldiazonium chloride, 65832-16-8; phenol, 108-95-2; 1-naphthol, 90-15-3; 2-naphthol, 135-19-3.

References and Notes

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