Thermal and Photochemical Transformations of 1-(Arylazo)-*N*-arylidene-2-naphthylamines

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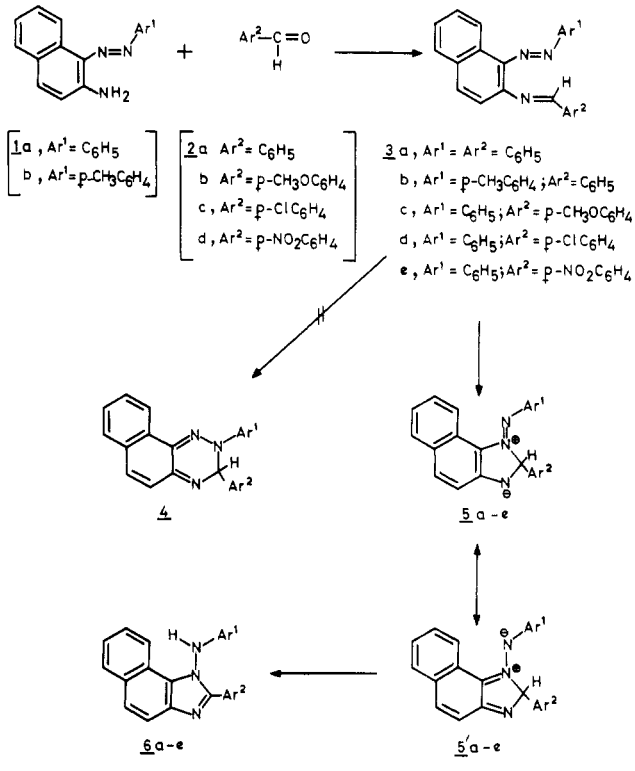
1-(Arylazo)-*N*-arylidene-2-naphthylamines **3a–e**, prepared by the reaction of 1-(arylazo)-2-naphthylamines **1a,b** with aromatic aldehydes **2a–d** on refluxing in toluene, gave the corresponding 1-(arylamino)-2-phenylnaphth[1,2-*d*]imidazoles **6a–e** in yields ranging between 50 and 60%. Refluxing of **3a** in *o*-dichlorobenzene, however, gave 1*H*-2-phenylnaphth[1,2-*d*]imidazole (**7**, 45%) and 2*H*-2-phenylnaphtho[1,2-*d*]triazole (**9**, 5%). Reaction of **3a** with dimethyl acetylenedicarboxylate gave dimethyl benzo[*f*]quinoxaline-2,3-dicarboxylate (**10**, 11%), dimethyl α-benzal-α′-[[1-(phenylazo)-2-naphthyl]imino]succinate (**11**, 7%), dimethyl [1-(phenylazo)-2-naphthyl]aminofumarate (**12**, 2%), and benzanilide (**13**, 6%). The reaction of 1-(phenylazo)-2-naphthylamine (**1a**) with DMAD, however, gave **10** (32%) and **12** (3%). Photolysis of **3a** in benzene gave 2*H*-2-phenylnaphtho[1,2-*d*]triazole (**9**, 5%) and *N*-benzoyl-1-(phenylazo)-2-naphthylamine (**19**, 41%), whereas the photolysis in methanol gave a mixture of **6a** (10%), **19** (25%), **1a** (1%), and the naphthotriazole **9** (4%). Reasonable mechanisms have been suggested for the formation of the various products in these reactions.

Heterohexa-1,3,5-trienes are reported to undergo pericyclic transformations, leading to five-membered heterocycles.[3] The object of the present investigation has been to examine the thermal and photochemical transformations of a few 1-(arylazo)-*N*-arylidene-2-naphthylamines (**3a–e**) and to see whether this class of compounds undergoes cyclization under these conditions to give five-membered heterocycles.

Results and Discussion

Synthesis of 1-(Arylazo)-*N*-arylidene-2-naphthylamines. One of the convenient methods for the synthesis of 1-(arylazo)-*N*-arylidene-2-naphthylamines (**3**) would be through the reaction of 1-(arylazo)-2-naphthylamines (**1**) with aldehydes (**2**). Several examples of the reaction of 1-(arylazo)-2-naphthylamines with aromatic aldehydes have been reported.[4-16] Goldschmidt and Rosell[4] and Meldola,[5] for example, have reported as early as 1890 that the reaction of 1-(arylazo)-2-naphthylamines (**1**) with aldehydes (**2**) leads to the formation of 2,3-dihydronaphtho[2,1-*e*][1,2,4]triazines **4** and not the expected 1-(arylazo)-*N*-benzylidene-2-naphthylamines (Scheme I). Although subsequent investigators[6] have continued to represent the products of the reaction of 1-(arylazo)-2-naphthylamines with aldehydes as 2,3-dihydronaphtho[2,1-*e*][1,2,4]triazines **4**, Fischer and co-workers[7,8] have

Scheme I



correctly identified these products as *N*-anilinonaphthimidazoles **6**. They had suggested that the initial products formed in these reactions are the Schiff bases **3**, which are subsequently transformed to the corresponding *N*-anilinonaphthimidazoles **6**.[8] However, their attempts to characterize Schiff bases **3** in these reactions have not been successful.

In the present studies we have investigated the reactions of **1a** and **1b** with aromatic aldehydes under controlled conditions with a view to isolating the corresponding 1-(arylazo)-*N*-arylidene-2-naphthylamines. Treatment of **1a** with excess benzaldehyde (**2a**) at room temperature (30 °C) for 12 h, for example, gave a 75% yield[17] of a product

(1) (a) Indian Institute of Technology. (b) University of Notre Dame.
(2) This is Document No. NDRL 2004 from the Notre Dame Radiation Laboratory.
(3) For some pertinent references on the thermal and photochemical transformations of heterohexa-1,3,5-trienes, see: (a) Sukumaran, K. B.; Angadiyavar, C. S.; George, M. V. *Tetrahedron* **1972**, *28*, 3987; (b) Mitra, A. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1980; (c) George, M. V.; Mitra, A.; Sukumaran, K. B. *Angew. Chem., Int. Ed. Engl.*, in press.
(4) Goldschmidt, H.; Rosell, Y. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 487.
(5) Meldola, R. *J. Chem. Soc.* **1890**, *57*, 328.
(6) (a) Neri, A. *Gazz. Chim. Ital.* **1937**, *67*, 282, 284, 448, 473, 513; *Chem. Abstr.* **1937**, *32*, 174, 1265. (b) Neri, A.; Grimaldi, G. *Gazz. Chim. Ital.* **1937**, *67*, 273, 453, 468; *Chem. Abstr.* **1937**, *32*, 173, 1266. (c) Neri, A. *Chim. Ind. (Milan)* **1941**, *23*, 11; *Chem. Abstr.* **1941**, *35*, 3261.
(7) Fischer, O.; Meier, W.; Schwappacher, H.; Kracker, H. *J. Prakt. Chem.* **1922**, [2] *104*, 102; *Chem. Abstr.* **1924**, *18*, 1902.
(8) Fischer, O.; Theil, E.; Stanbar, F.; Hild, W.; Senfert, G.; Hojer, H.; Mantiechler, F.; Elflein, F.; Müller, K. *J. Prakt. Chem.* **1924**, [2] *107*, 16; *Chem. Abstr.* **1924**, *18*, 1652.
(9) Wright, J. B. *Chem. Rev.* **1951**, *48*, 397.
(10) Messmer, A.; Sziman, O. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 250.
(11) Goldschmidt, H.; Poltzer, A. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 1000.
(12) Sachs, F.; Goldmann, M. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 3319.
(13) Meldola, R.; Forester, M. O. *J. Chem. Soc.* **1891**, *59*, 678.
(14) Witt, F. H. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2557.
(15) Busch, M.; Bergmann, E. *Chem. Zentralbl.* **1905**, *76*, 1, 1103.
(16) Noelting, E.; Wegelin, F. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2595.

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melting at 141–142 °C which was identified as 1-(phenylazo)-N-benzylidene-2-naphthylamine (**3a**, Scheme I). It has been observed that even traces of acids, including benzoic acid, accelerate the transformation of **3** to other products. Also, care had to be taken to ensure that the reaction mixture was not heated above room temperature, even while the solvents were removed under vacuum.

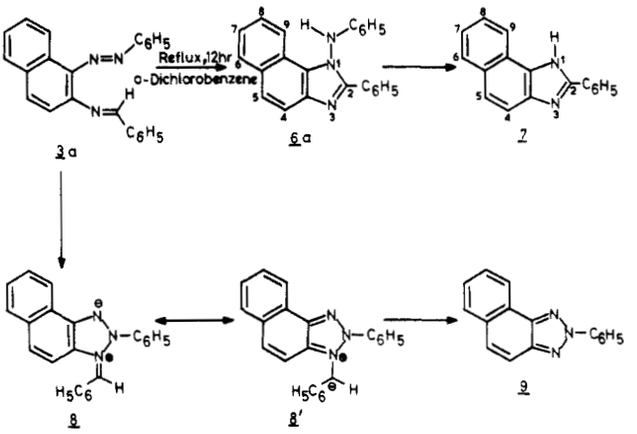
Similarly, the reaction of **1b** with benzaldehyde gave a 89% yield of **3b**. Likewise, the reaction of **1a** with anisaldehyde (**2b**), *p*-chlorobenzaldehyde (**2c**), and *p*-nitrobenzaldehyde (**2d**) gave the corresponding Schiff bases **3c** (86%), **3d** (78%), and **3e** (84%), respectively.

The structures of Schiff bases **3a–e** have been confirmed on the basis of analytical data and spectral evidence. The UV spectra of these compounds, for example, showed several absorption maxima, characteristic of highly conjugated chromophores. The NMR spectrum of **3a**, for example, showed two doublets around δ 6.75 (1 H) and 7.12 (1 H) and two complex multiplets centered around δ 7.32 (14 H) and 8.10 (1 H), respectively. Of these, the complex multiplet around δ 8.10 has been assigned to the H_9 proton of the naphthalene ring in **3a**, as this proton will be considerably deshielded due to the magnetic anisotropy of the phenylazo group at the C_1 position. Such a deshielding effect has been observed in the cases of different benzoquinolines[18] and naphthazolotriazines.[19,20] The doublets around δ 7.12 and 6.75 ($J_{3,4}$ = 9.0 Hz) are assigned to the H_3 and H_4 protons, respectively, and the downfield shift of H_3 in this case is attributed again to the deshielding effect of the aldimino functional group at the C_2 position of the naphthalene ring. The complex multiplet around δ 7.32, accounting for 14 protons, is attributed to the ten phenyl protons, the aldiminic proton (N=CH) of the C_2 functional group and the H_5, H_6, and H_7 protons of the naphthalene ring in **3a**. It might be mentioned in this connection that the aldiminic proton in benzylideneaniline ($C_6H_5CH{=}NC_6H_5$), for example, is reported to appear at δ 8.35.[21]

The mass spectrum of **3a** showed the molecular ion peak at *m/e* 335, and the fragmentation patterns are in agreement with the assigned structure.

Thermal Transformations of 1-(Arylazo)-N-arylidene-2-naphthylamines. Thermolysis of 1-(phenylazo)-N-benzylidene-2-naphthylamine (**3a**), by refluxing in toluene for 12 h, in the absence of any catalyst gave a 60% yield of 1-anilino-2-phenylnaphth[1,2-*d*]imidazole (**6a**).[12] Similarly, the thermolysis of **3b–e** under identical conditions gave the corresponding N-(arylamino)naphthimidazoles **6b** (65%), **6c** (55%), **6d** (55%), and **6e** (50%), respectively. The structures of all these products have been confirmed by analytical results and spectral data. The UV spectra of these compounds, for example, showed several absorption maxima, characteristic of the naphthimidazole chromophore and quite distinctly different from those of the starting materials (**3a–e**). The NMR spectrum of **6a**, for example, showed a broad singlet at δ 3.15 (1 H) corresponding to the NH proton (D_2O exchangeable). Other signals were observed at δ 6.55 (2 H, m, H_4 and H_5), 6.75 (1 H, m, aromatic), 7.06 (2 H, m, aromatic), 7.24 (5 H, m, aromatic), 7.95 (5 H, m, aromatic), and 8.50 (1 H, m, H_9). The mass spectrum of **6a** showed a molecular ion peak at *m/e* 335, and the fragmentation patterns are in agreement with the assigned structure.

Scheme II



The formation of the 1-(arylamino)-2-arylnaphth[1,2-*d*]imidazoles **6a–e** in the thermolysis of 1-(arylazo)-N-arylidene-2-naphthylamines **3a–e** can be rationalized in terms of a pentadienyl anion type of ring-closure reaction[22] leading to the zwitterionic intermediate **5** which can be represented by an alternative resonance form, **5'**. Further transformations of **5** will lead to the N-(arylamino)-naphthimidazole **6**, as shown in Scheme I.

The thermolysis of **3a** in refluxing *o*-dichlorobenzene (180 °C) for 12 h, however, gave a mixture of products consisting of a 45% yield of 1*H*-2-phenylnaphth[1,2-*d*]-imidazole (**7**) and a 5% yield of 2*H*-2-phenylnaphtho-[1,2-*d*]triazole (**9**) (Scheme II).

The formation of **7** in the thermolysis of **3a** at elevated temperatures, however, may be understood in terms of the loss of a phenylnitrene moiety, whereas the triazole **9** may arise through the loss of a phenylcarbene moiety, as shown in Scheme II. In support of the suggestion that **7** is formed through the thermal fragmentation of **6a**, we have shown in a separate experiment that a 57% yield of **7** is obtained when **6a** is refluxed in *o*-dichlorobenzene for 12 h.

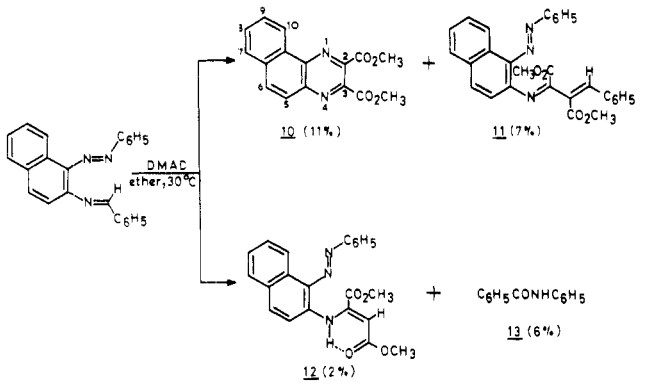
Reaction of 1-(Phenylazo)-N-benzylidene-2-naphthylamine (3a) with Dimethyl Acetylenedicarboxylate (DMAD). The thermal transformations of 1-(arylazo)-N-arylidene-2-naphthylamines **3a–e** have been assumed to involve dipolar intermediates such as **5a–e** (Scheme I). If such dipolar intermediates are actually involved, then it may be possible to trap them in presence of very reactive dipolarophiles such as DMAD. With this view, we have examined the reaction of **3a** with DMAD.

The reaction of Schiff bases with DMAD has been reported to give different products, depending on the nature of the substituents present in the starting material.[23–26] Snyder and co-workers[24] have shown that the reaction of benzylideneaniline with DMAD, for example, gives α-benzyl-α'-(phenylimino)succinate, whereas benzylidenemethylamine gives dihydropyridine derivatives.[24,25]

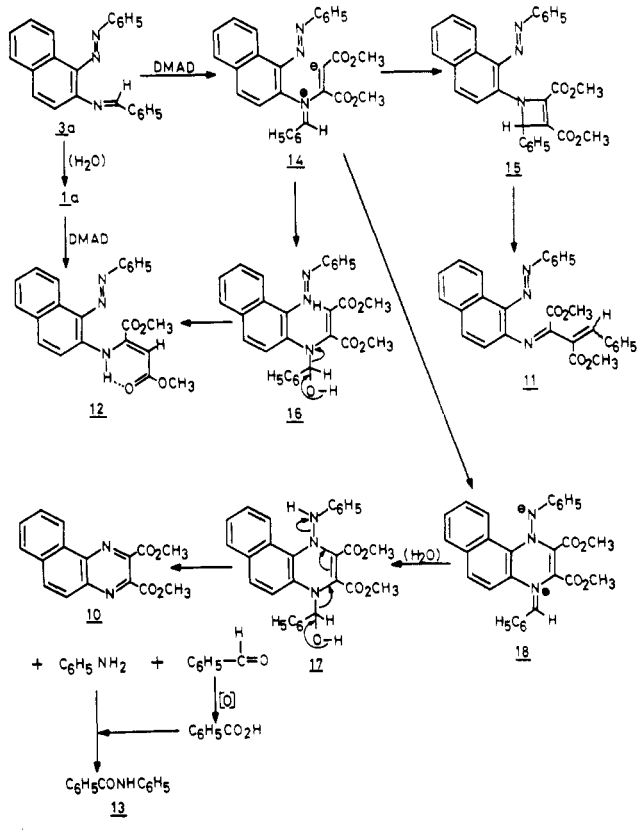
Treatment of an equimolar mixture of **3a** with DMAD in ether at room temperature gave a mixture of dimethyl

(17) The yields of these products have been calculated on the basis of the reacted starting materials.
(18) Donckt, E. V.; Martin, R. H.; Geerts-Evrard, F. *Tetrahedron* **1964**, *20*, 1495.
(19) Klemm, L. H.; Klopfenstein, C. E.; Zell, R. *J. Heterocycl. Chem.* **1970**, *7*, 751.
(20) Vilarrasa, J.; Granados, R. *J. Heterocycl. Chem.* **1974**, *11*, 867.
(21) King, J. F.; Durst, T. *Can. J. Chem.* **1962**, *40*, 882.
(22) For examples of pentadienyl anion type of cyclization, see: (a) Taylor, E. C.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181; (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.*, in press.
(23) For recent reviews on the reactions of nucleophiles with dimethyl acetylenedicarboxylate, see: (a) George, M. V.; Khetan, S. K.; Gupta, R. K. *Adv. Heterocycl. Chem.* **1976**, *19*, 279; (b) Acheson, R. M.; Elmore, N. F. *Ibid.* **1978**, *23*, 263.
(24) Snyder, H. R.; Cohen, H.; Tapp, W. J. *J. Am. Chem. Soc.* **1939**, *61*, 3560.
(25) Gagan, J. M. F. *J. Chem. Soc. C* **1966**, 1121.
(26) Huisgen, R.; Herbig, K. *Justus Liebigs Ann. Chem.* **1965**, *688*, 98.

Scheme III



Scheme IV



benzo[*f*]quinoxaline-2,3-dicarboxylate (**10**), dimethyl α-benzal-α′-[[1-(phenylazo)-2-naphthyl]imino]succinate (**11**), dimethyl [[1-(phenylazo)-2-naphthyl]amino]fumarate (**12**), and benzanilide (**13**) (Scheme III). The structures of all these products have been established on the basis of analytical data, spectral information, and chemical evidence. The IR spectrum of **10**, for example, showed two absorption bands at 1735 and 1725 cm^{-1} due to ester carbonyl groups, whereas its NMR spectrum showed a sharp singlet at δ 4.10 (6 H) due to the ester methoxyl protons. In addition, the spectrum showed three complex multiplets centered around δ 7.78 (3 H, H_7, H_8, and H_9), 8.0 (2 H, H_5 and H_6), and 9.15 (1 H, H_{10}). The mass spectrum of **10** showed a molecular ion peak at *m/e* 296 (relative intensity 71), and the fragmentation patterns are in support of the assigned structure. Further confirmation was derived by refluxing **10** in ethanolic potassium hydroxide to give a 75% yield of benzo[*f*]quinoxaline-2,3-dicarboxylic acid [mp 195 °C dec (lit.[27] mp 195 °C dec)], which in turn was converted to benzo[*f*]quinoxaline-2,3-dicarboxylic anhydride [mp 234 °C (lit.[27] mp 235 °C)] in an 86% yield on being heated to around 200 °C for 15 min.

The IR spectrum of **11** likewise showed the presence of two ester carbonyl groups at 1765 and 1735 cm^{-1}, respectively, whereas its NMR spectrum showed the presence of two singlets at δ 3.75 (3 H) and 3.87 (3 H), assigned to two sets of ester methoxy protons. The vinylic proton in **11** appeared as a singlet at δ 6.00 (1 H), whereas the aromatic protons appeared as several multiplets centered around δ 6.24 (1 H), 6.81 (1 H), 7.30 (3 H), 7.51 (8 H), and 8.20 (3 H). The mass spectrum of **11** showed a molecular ion peak at *m/e* 477, in agreement with the assigned structure.

The structure of **12** likewise has been deduced as dimethyl [[1-(phenylazo)-2-naphthyl]amino]fumarate on the basis of spectral information. The IR spectrum of **12** showed an NH absorption band at 3400 cm^{-1} and two carbonyl absorption bands at 1748 (C=O, free) and 1705 cm^{-1} (C=O, hydrogen bonded), respectively, in agreement with the fumarate geometry for this product.[28,29] The NMR spectrum of **12** showed a sharp singlet at δ 4.05 (6 H), assigned to the ester methoxy protons, and a broad peak centered around δ 6.90 (2 H), assigned to the NH and vinylic protons.

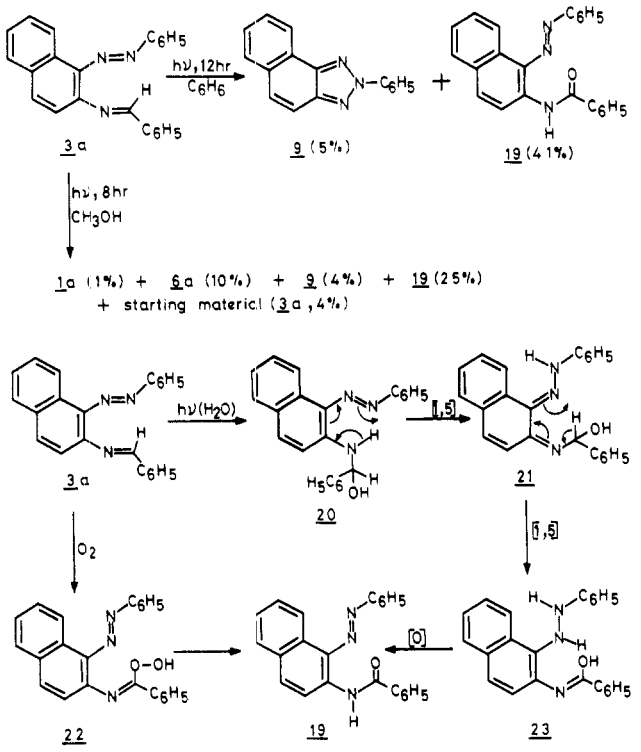
The formation of products such as **10**–**13** in the reaction of **3a** with DMAD can be understood in terms of the pathways shown in Scheme IV. It is assumed that the initial reaction of **3a** with DMAD results in the formation of the zwitterionic intermediate **14**, which undergoes cyclization to give **15**, and a subsequent ring opening of **15** will ultimately give rise to **11**. An alternative pathway for the reaction of **14** is to give the cyclized intermediate **18**, which can combine with moisture under the reaction conditions to give the intermediate **17**, and subsequent fragmentation of **17** will give the benzo[*f*]quinoxaline derivative **10** and products such as benzaldehyde and aniline. Air oxidation of benzaldehyde would give rise to benzoic acid, which in turn can combine with aniline under the reaction conditions to give benzanilide (**13**). The formation of **12**, on the other hand, can be explained in terms of the reaction of the initially formed zwitterion **14** with moisture to give the adduct **16**, which can subsequently fragment to give **12** and benzaldehyde. An alternative mode of formation of **12** is through the reaction of **1a**, formed through the hydrolysis of **3a** under the reaction conditions, with DMAD. In a separate experiment, we have shown that the reaction of **1a** with DMAD in ether at room temperature gives a mixture of the benzo[*f*]quinoxaline derivative **10** (32%) and the fumarate **12** (3%).

Photochemical Transformations of 1-(Phenylazo)-*N*-benzylidene-2-naphthylamine (3a). Heterohexa-1,3,5-trienes such as **3a-e** should, in principle, undergo the photochemically allowed $[_\pi4_s + _\pi2_a]$- or $[_\pi4_a + _\pi2_s]$-type of additions, leading ultimately to products which may resemble the thermal transformation products.

Photolysis of a benzene solution of **3a** for 12 h gave a mixture of the triazole **9** (5%) and *N*-benzoyl-1-(phenylazo)-2-naphthylamine (**19**, 41%). When the photolysis of **3a**, however, was carried out in methanol, a mixture of products consisting of **9** (4%), **19** (25%), **1a** (1%), and **6a** (10%) was formed (Scheme V). The formation of products such as the naphthoimidazole **6a** and the triazole **9** from **3a** may involve pathways similar to those of the thermal transformations of **3a** shown in Schemes I and II. Small amounts of **1a** in these reactions may arise through

(27) Crippa, G. B.; Perroncito, G. *Ann. Chim. Appl.* **1935**, *25*, 618; *Chem. Abstr.* **1936**, *30*, 5532.
(28) Huisgen, R.; Herbig, K.; Siegl, A.; Huber, H. *Ber. Dtsch. Chem. Ges.* **1966**, *99*, 2526.
(29) Hendrickson, J. B.; Rees, R.; Templeton, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 107.

Scheme V



the hydrolysis of **3a**, whereas the formation of **19** may be explained in terms of the pathway shown in Scheme V. It has been assumed that **3a** reacts with the moisture present in the mixture to give **20**, which subsequently is converted to **23** through [1,5] sigmatropic shifts. Subsequent air oxidation of **23** will lead to **19**. An alternative pathway, involves the initial conversion of **3a** to the hydroperoxy derivative **22**, which can subsequently give **19**. However, it might be pointed out here that when the photolysis of **3a** was carried out in moist benzene, no appreciable increase in the yield of **19** was observed, thereby casting doubts on the involvement of **20** in these transformations.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 137 and Model 521 infrared spectrometers. The electronic spectra were taken on a Beckman DB spectrophotometer. NMR traces were recorded on a Varian A-60 NMR spectrometer using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 mass spectrometer at 70 eV. All irradiation experiments were carried out either in a 150-W Srinivasan-Griffin-Rayonet photochemical reactor (λ 3500 Å) or by using a Hanovia 450-W, medium-pressure, mercury lamp in a quartz-jacketed immersion well.

Starting Materials. 1-(Phenylazo)-2-naphthylamine (**1a**, mp 100–101 °C) and 1-(*p*-tolylazo)-2-naphthylamine (**1b**, mp 114 °C) were prepared by a reported procedure.[30] Benzaldehyde (**2a**, bp 178 °C), *p*-anisaldehyde (**2b**, bp 249 °C), and *p*-chlorobenzaldehyde (**2c**, mp 47 °C, bp 214 °C) were freshly distilled before use. A commercially available sample of *p*-nitrobenzaldehyde (**2d**) was recrystallized from aqueous alcohol before use (mp 106 °C). Dimethyl acetylenedicarboxylate [bp 100 °C (5 mm)] was prepared by a reported procedure.[31] The petroleum ether used was the fraction with a boiling point of 60–80 °C.

Preparation of 1-(Arylazo)-*N*-arylidene-2-naphthylamines (3a–e). In a typical experiment, 0.01 mol of the 1-(arylazo)-2-naphthylamine (**1**) was mixed with a tenfold excess of the aldehyde (**2**), and the mixture was stirred at room temperature under a nitrogen atmosphere for 12 h. The unchanged aldehyde was removed under vacuum, and the residue was chromatographed over neutral alumina. Elution with petroleum ether gave the unchanged aldehyde as the initial fraction, whereas continued elution with the same solvent gave the corresponding 1-(arylazo)-*N*-arylidene-2-naphthylamines (**3a–e**). The product, in each case, was recrystallized from a suitable solvent such as ethanol. Details of the yields and melting points of **3a–e** are listed in Table I, whereas the UV absorption data are given in Table II.

(30) Hodgson, H. H.; Foster, C. K. *J. Chem. Soc.* **1942**, 30.
(31) Huntress, E. H.; Lesslie, T. E.; Bornstein, J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. 4, p 329.

Table I. Physical Data of 1-(Arylazo)-*N*-arylidene-2-naphthylamines[a]

compd	mp, °C	yield, %	mol formula
3a	141–142	75	$C_{23}H_{17}N_3$
3b	131	89	$C_{24}H_{19}N_3$
3c	125–126	86	$C_{24}H_{19}N_3O$
3d	124–125	78	$C_{23}H_{16}N_3Cl$
3e	139–140	84	$C_{23}H_{16}N_4O_2$

[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all compounds.

Table II. UV Absorption Characteristics of Some 1-(Arylazo)-*N*-arylydene-2-naphthylamines

compd	absorption maxima (CH_3OH), λ_{max}, nm (ε)
3a	232 (23 340), 242 (32 250), 308 (13 200), 388 (3 300), 396 (sh, 3250), 492 (10 100)
3b	230 (sh, 25 100), 242 (37 300), 252 (sh, 23 900), 306 (13 450), 382 (3600), 394 (3550), 402 (sh, 3200), 492 (10 850)
3c	240 (39 950), 256 (sh, 21 650), 305 (15 000), 360 (3500), 382 (3950), 392 (3900), 492 (10 500)
3d	232 (sh, 26 750), 244 (35 800), 252 (sh, 24 850), 306 (13 950), 365 (sh, 2630), 388 (3450), 396 (3450), 492 (10 700)
3e	232 (sh, 24 800), 242 (31 900), 258 (sh, 22 600), 298 (13 650), 377 (sh, 3400), 385 (3500), 394 (sh, 3500), 492 (8350)

Thermal Transformation of 1-(Arylazo)-*N*-arylidene-2-naphthylamines. In a typical run, 1 mmol of the 1-(arylazo)-*N*-arylidene-2-naphthylamine (**3**) was refluxed in 10 mL of toluene for 12 h under a nitrogen atmosphere. After removal of the solvent under reduced pressure, the residual product was triturated with petroleum ether and later recrystallized from benzene.

1-Anilino-2-phenylnaphth[1,2-*d*]imidazole (**6a**): mp 201 °C (lit.[12] mp 198 °C); 60% yield; IR (KBr) ν_{max} 3224, 3074 cm^{-1} (ν_{NH}, hydrogen bonded); UV (CH_3OH) λ_{max} 234 nm (ε 36 480), 269 (31 480), 287 (sh, 16 000), 332 (sh, 8700), 339 (9370).

2-Phenyl-1-(*p*-toluidino)naphth[1,2-*d*]imidazole (**6b**): mp 192 °C dec; 65% yield; IR (KBr) ν_{max} 3165, 3084 cm^{-1} (ν_{NH}, hydrogen bonded); UV (CH_3OH) λ_{max} 232 nm (ε 50 500), 265 (36 700), 282 (sh, 19 950), 330 (sh, 10 800), 335 (11 550).

Anal. Calcd for $C_{24}H_{19}N_3$: C, 82.52; H, 5.44; N, 12.03. Found: C, 82.15; H, 5.21; N, 12.01.

1-Anilino-2-(*p*-anisyl)naphth[1,2-*d*]imidazole (**6c**): mp 204–205 °C; 55% yield; IR (KBr) ν_{max} 3208, 3175, 3110 cm^{-1} (ν_{NH}, hydrogen bonded); UV (CH_3OH) λ_{max} 228 nm (ε 75 500), 274 (37 850), 292 (sh, 18 300), 332 (sh, 11 950), 338 (12 400).

Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.90; H, 5.20; N, 11.50. Found: C, 79.38; H, 5.53; N, 11.26.

1-Anilino-2-(*p*-chlorophenyl)naphth[1,2-*d*]imidazole (**6d**): mp 321–322 °C (lit.[8] mp 321 °C); 55% yield; IR (KBr) ν_{max} 3230, 3200, 3115, 3060 cm^{-1} (ν_{NH}, hydrogen bonded); UV (CH_3OH) λ_{max} 236 nm (ε 41 100), 270 (sh, 33 350), 276 (33 950), 289 (sh, 18 400), 335 (sh, 12 100), 337 (12 800).

1-Anilino-2-(*p*-nitrophenyl)naphth[1,2-*d*]imidazole (**6e**): mp 229–230 °C (lit.[13] mp 228–229 °C); 50% yield; IR (KBr) ν_{max} 3364 (ν_{NH}, free), 3224, 3076 cm^{-1} (ν_{NH}, hydrogen bonded); UV (CH_3OH) λ_{max} 234 nm (ε 49 000), 244 (sh, 42 000), 272 (sh, 16 700), 328 (sh, 10 550), 364 (16 850).

Thermal Transformation of 1-(Phenylazo)-*N*-benzylidene-2-naphthylamine (3a) in Refluxing *o*-Dichlorobenzene. A solution of 300 mg (0.9 mmol) of **3a** in 15 mL

of o-dichlorobenzene was refluxed for 12 h, and the solvent was removed under reduced pressure. The residue was chromatographed over silica gel. Elution with petroleum ether gave 10 mg (5%) of 2*H*-2-phenylnaphtho[1,2-*d*]triazole (**9**, mp 106–107 °C) after recrystallization from ethanol. There was no depression in the melting point of **9** when it was mixed with an authentic sample prepared by a reported procedure.[32]

Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 100 mg (45%) of **7**, mp 218 °C. The melting point of **7** was not depressed when some of the product was mixed with an authentic sample.[33]

Thermal Transformation of 1-Anilino-2-phenylnaphth[1,2-*d*]imidazole (6a) in Refluxing *o*-Dichlorobenzene. A solution of **6a** (1.01 g, 3 mmol) in o-dichlorobenzene (25 mL) was refluxed for 12 h, and the solvent was removed under vacuum. The reaction mixture was chromatographed over alumina, and elution with a mixture (1:1) of benzene and petroleum ether gave 420 mg (57%) of 1*H*-2-phenylnaphth[1,2-*d*]imidazole (**7**, mp and mmp 218 °C) after recrystallization from a mixture (1:1) of benzene and methylene chloride.

Reaction of 1-(Phenylazo)-*N*-benzylidene-2-naphthylamine (3a) with Dimethyl Acetylenedicarboxylate. A solution of DMAD (1.42 g, 10 mmol) in diethyl ether (10 mL) was added to an ether solution of **3a** (3.35 g, 10 mmol in 20 mL) over a period of 15 min. Afterward, the reaction mixture was stirred at room temperature for 20 h, and, subsequently, the solvent was removed under vacuum. The dark red, viscous mass that was obtained was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 120 mg (6%) of benzanilide (**13**, mp and mmp 162 °C) after recrystallization from petroleum ether.

Further elution of the column with a mixture (1:1) of petroleum ether and benzene gave a crude product (400 mg), melting over the range 95–98 °C. Recrystallization from methanol gave 340 mg (11%) of dimethyl benzo[*f*]quinoxaline-2,3-dicarboxylate (**10**): mp 155–156 °C; IR (KBr) ν_{max} 2970 (ν_{CH}, aliphatic), 1735, 1725 cm^{-1} ($\nu_{C=O}$); UV (CH_3OH) λ_{max} 236 nm (ϵ 36 000), 286 (32 000).

Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 64.86; H, 4.05; N, 9.46; mol wt 296. Found: C, 64.98; H, 3.83; N, 9.70; mol wt 296 (mass spectrometry).

Subsequent elution of the column with benzene gave a product which on recrystallization from methanol yielded 80 mg (2%) of dimethyl [[1-(phenylazo)-2-naphthyl]amino]fumarate (**12**): mp 255–256 °C; IR (KBr) ν_{max} 3400 (ν_{NH}, free), 3060 (ν_{NH}, hydrogen bonded), 2960 (ν_{CH}, aliphatic), 1748 ($\nu_{C=O}$, free), 1705 ($\nu_{C=O}$, hydrogen bonded), 1620, 1605 cm^{-1} ($\nu_{C=C}$ and ν_{NH}); UV (CH_3OH) λ_{max} 232 nm (ϵ 25 000), 252 (34 000), 298 (19 000), 362 (15 600), 430 (11 350); NMR ($CDCl_3$) δ 4.05 (s, 6 H, methoxy), 6.90 (m, 2 H, NH and vinylic), 7.35 (m, 6 H, aromatic), 7.78 (m, 4 H, aromatic), 9.15 (m, 1 H, aromatic).

Anal. Calcd for $C_{22}H_{19}N_3O_4$: C, 67.87; H, 4.88; N, 10.80. Found: C, 67.82; H, 4.82; N, 10.50.

Further elution with a mixture (10:1) of benzene and ethyl acetate gave 340 mg (7%) of a product identified as α-benzal-α'-[[1-(phenylazo)-2-naphthyl]imino]succinate (**11**): mp 226–227 °C (after recrystallization from methanol); IR (KBr) ν_{max} 1765, 1735 cm^{-1} ($\nu_{C=O}$); UV (CH_3OH) λ_{max} 245 nm (ϵ 20 100), 275 (sh, 19 100), 282 (19 900), 315 (sh, 5700), 358 (sh, 3900), 402 (sh, 7650), 466 (28 250); NMR ($CDCl_3$) δ 3.75 (s, 3 H, OCH_3), 3.87 (s, 3 H, methoxy), 6.00 (s, 1 H, vinylic), 6.24 (m, 1 H, aromatic), 6.81 (m, 1 H, aromatic), 7.30 (m, 3 H, aromatic), 7.51 (m, 8 H, aromatic), 8.20 (m, 3 H, aromatic).

Anal. Calcd for $C_{29}H_{23}N_3O_4$: C, 72.95; H, 4.82; N, 8.81. Found: C, 72.69; H, 4.34; N, 8.51.

Reaction of 1-(Phenylazo)-2-naphthylamine (1a) with DMAD in Ether. To a solution of **1a** (2.47 g, 10 mmol) in ether (50 mL) was added 1.42 g (10 mmol) of DMAD dropwise with stirring, and the reaction mixture was kept at room temperature for 24 h. After removal of the solvent under vacuum, the product mixture was chromatographed over a silica gel column. Elution of the column with petroleum ether gave 400 mg (16%) of the starting amine, **1a**, mp and mmp 100–101 °C.

Further elution of the column with benzene gave 800 mg (32%) of **10**, mp and mmp 155–156 °C.

Subsequent elution of the column with a mixture (20:1) of benzene and ethyl acetate gave 90 mg (3%) of dimethyl [[1-(phenylazo)-2-naphthyl]amino]fumarate (**12**), mp and mmp 255–256 °C.

Hydrolysis of Dimethyl Benzo[*f*]quinoxaline-2,3-dicarboxylate (10). A solution of **10** (296 mg, 1 mmol) in ethanol (5 mL) was mixed with 5 mL of 20% potassium hydroxide solution, and the mixture was refluxed for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in water. The aqueous solution was carefully acidified with dilute hydrochloric acid to give 200 mg (75%) of benzo[*f*]quinoxaline-2,3-dicarboxylic acid (mp 195 °C dec) after recrystallization from ethanol. There was no depression in the melting point of this acid when it was mixed with an authentic sample.[27]

Preparation of Benzo[*f*]quinoxaline-2,3-dicarboxylic Anhydride. A sample of benzo[*f*]quinoxaline-2,3-dicarboxylic acid (100 mg, 0.37 mmol) was heated in an oil bath at around 200 °C for 15 min. The reaction mixture was recrystallized from ethanol to give 80 mg (86%) of the anhydride, mp 234 °C (lit.[27] mp 235 °C).

Photolysis of 1-(Phenylazo)-*N*-benzylidene-2-naphthylamine (3a) in Benzene. A solution of 700 mg (2.1 mmol) of **3a** in 350 mL of dry benzene was irradiated for 12 h in a Srinivasan-Griffin-Rayonet photochemical reactor. Removal of the solvent under vacuum gave a product which was chromatographed over silica gel. Elution with petroleum ether gave 25 mg (5%) of 2*H*-2-phenylnaphtho[1,2-*d*]triazole (**9**, mp and mmp 106–107 °C) after recrystallization from ethanol. Further elution of the column with a mixture (1:1) of petroleum ether and benzene gave 300 mg (41%) of an orange-red crystalline solid (mp 163–164 °C) which was identified as *N*-benzoyl-1-(phenylazo)-2-naphthylamine (**19**). There was no depression in the melting point of **19** when it was mixed with an authentic sample:[34] IR (KBr) ν_{max} 3100, 3065 (ν_{NH}, hydrogen bonded), 3035 (ν_{CH}, aromatic), 1684 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 7.50 (m, 8 H, aromatic), 7.83 (m, 6 H, aromatic), 8.92 (m, 2 H, aromatic), 13.87 (br s, 1 H, NH proton).

In a repeat run, a solution of **3a** (300 mg, 0.9 mmol) was photolyzed in moist benzene (150 mL) for 12 h. Workup of the mixture as in the earlier case gave 10 mg (5%) of **9** (mp and mmp 106–107 °C) and 150 mg (47%) of **19** (mp and mmp 162–163 °C).

Photolysis of 1-(Phenylazo)-*N*-benzylidene-2-naphthylamine (3a) in Methanol. A solution of 500 mg (1.5 mmol) of **3a**, in 170 mL of dry methanol, was photolyzed for 8 h under a nitrogen atmosphere by using a Hanovia medium-pressure mercury lamp. Removal of the solvent under vacuum gave a pasty residue which was chromatographed over neutral alumina.

Elution of the column with petroleum ether gave 15 mg (4%) of **9** (mp and mmp 106–107 °C), 5 mg (1%) of 1-(phenylazo)-2-naphthylamine (**1a**, mp and mmp 100–101 °C), 20 mg (4%) of the unchanged starting material (**3a**, mp and mmp 141–142 °C), and 125 mg (25%) of **19** (mp and mmp 163–164 °C) in this sequence.

Subsequent elution of the column with a mixture (1:4) of benzene and petroleum ether gave 50 mg (10%) **6a**, mp and mmp 200–201 °C.

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(32) Ferrania, Italian Patent 781 504; *Chem. Abstr.* **1969**, *76*, 57906.
(33) Fischer, O.; Reindl, L.; Fezer, O. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 930.
(34) Lawesson, T. A. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 796.