cals, Inc.) was dried overnight at 135 °C under vacuum before use. 4,7-Dihydroxy-1,10-phenanthroline was purchased from G. F. Smith. All other chemicals were used as received from commercial sources.

Elemental analyses were performed in the General Electric CR&D Microanalytical Laboratory. NMR spectra were recorded on a Varian FT80 spectrometer.

$[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$. The first phase of the reaction was carried out under nitrogen with dried solvents. A 1.58-g sample of sodium hydride (56.9% NaH, 39.3 mmol) was washed with petroleum ether to remove mineral oil and dried. After addition of 40 mL of Me_2SO, 3.29 g (49.9 mmol) of malononitrile was added in small portions with stirring. Finally, 1.58 g (6.36 mmol) of 4,7-dichloro-1,10-phenanthroline[17] was added and the solution volume increased to about 90 mL with Me_2SO. The mixture was heated at 90–95 °C for 16 h to give a deep-yellow solution. After the mixture was cooled to room temperature, the reaction was quenched with ~1 mL of H_2O and the Me_2SO removed under reduced pressure with a dry-ice condenser. This and subsequent operations were done in air. The solid residue was treated with 150 mL of H_2O, filtered, washed extensively with H_2O, and dried under vacuum at 80 °C: yield, 2.99 g; yellow-orange powder.

About 1.7 g of the crude product was dissolved in ~400 mL of 10% tetraethylammonium hydroxide solution. An insoluble residue was filtered off, and the filtrate was treated dropwise with 50% NaOH until precipitation ceased (~10 mL). The crude $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$ was collected and washed with a small portion of $(C_2H_5)_4NOH$ solution. Drying as above gave 1.56 g (1.52 mmol) of product or 85% based on the initial 4,7-dichloro-1,10-phenanthroline. This crude salt was taken into a minimum quantity of warm acetonitrile and any residue filtered off. The solution was warmed and the volume reduced to nearly cause precipitation followed by ether addition to the cloud point. Cooling to −20 °C gave clear yellow platelets, which were filtered and washed with cold 1:1 acetonitrile/ether. The cold crystals should be protected from moisture which turns them orange. The product was dried at 110 °C under vacuum. Several crops gave a total of 1.25 g (1.22 mmol, 68% overall yield). Anal. Calcd for $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$: C, 70.2; H, 7.1; N, 20.5; Na, 2.2. Found: C, 70.1; H, 7.2; N, 20.5; Na, 2.2. Absorption spectrum (CH_3CN) 213 nm (log ε 5.39), 250 (4.43), 273 (4.35), 391 (4.51), 411 (4.57).

$[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. The crude solid was obtained from tetraethylammonium hydroxide solution as above by addition of aqueous lithium chloride. Initially an oil formed which solidified on standing and was then filtered. A sample of 102 mg of initial reaction product gave 100 mg of crude $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. Recrystallization by slow addition of twice the volume of ether to a concentrated acetonitrile solution at 0 °C gave 60 mg of pure $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. Anal. Calcd: C, 70.4; H, 5.9; N, 22.1. Found: C, 70.0; H, 6.2; N, 22.1.

Metal-Free $C_{18}H_8N_6$. A 100-mg sample of the orange-yellow solid from the $HC(CN)_2^-$/4,7-dichloro-1,10-phenanthroline reaction was dissolved in 50 mL of 4:1 ethanol/water with warming followed after filtration by addition of 1.5 g of 18-crown-6 and 1.0 mL of 12 M HCl to the warm solution. The mass of fine yellow-orange crystals which formed on cooling to room temperature was collected by filtration, washed several times with ethanol containing 1 mL of 12 M HCl per 75 mL, and air-dried: yield, 91 mg. Anal. Calcd for $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)\cdot 3H_2O$: C, 61.7; H, 5.0; N, 18.0. Found: C, 61.7; H, 4.8; N, 18.4 A flame test for Na was negative.

Cyclic voltammetry was performed with a Pine Instruments Co. Model AFRDE3 potentiostat and a Hewlett-Packard 7034A X-Y recorder. The electrochemical cell consisted of three compartments separated by glass frits; the center compartment was used for the working electrode. The working and counter electrodes were platinum wires, and the reference electrode was a silver wire. The electrodes were inserted through rubber septa which were used to seal the top of each cell compartment. The cell, electrodes, and all other glassware were dried at 140 °C overnight and transferred to an argon-filled Vacuum Atmospheres glovebox for solution preparation while still hot. The cell was charged with freshly prepared 0.1 M $(n\text{-}C_4H_9)_4NBF_4$/acetonitrile solution. This electrolyte solution was also used to prepare a sample solution and a ferrocene solution in separate containers which were also sealed with rubber septa. Following preliminary scans of the electrolyte solution, the sample solution was added by using standard transfer techniques for oxygen and moisture-sensitive materials and mixed with the aid of a magnetic stir bar. When measurements on the sample were completed, the ferrocene standard was added, and further spectra were recorded for voltage calibration.[18]

Acknowledgment. M. N. Ackermann thanks Oberlin College for a sabbatical leave during which this work was completed and the National Science Foundation, through a Science Faculty Professional Development Award, and the General Electric Co. for financial support.

Registry No. $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$, 81315-62-0; $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$, 81315-63-1; $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)$, 81315-65-3; malononitrile, 109-77-3; 4,7-dichloro-1,10-phenanthroline, 5394-23-0.

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Intramolecular Cyclization of Peri-Substituted 1-Azidonaphthalenes. 3.[1] Structural and Chemical Investigation of 1-(Arylamino)benz[*cd*]indazol-8(and -6)(1*H*)-ones Produced by Decomposition of Hydroxy-Substituted 8-Azido-1-(arylazo)naphthalenes

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Thermal and photochemical decomposition of 8-azido-2-hydroxy-1-(arylazo)naphthalenes **3a–d** leads to 1-(arylamino)benz[*cd*]indazol-8(1*H*)-ones **4a–d** in good yields. Analogous results are obtained in the conversion of **5** into **6**. The reactions appear to proceed through 1,5-cyclization of the tautomeric hydrazone forms of the azides, and the absence of products that would be expected from nitrene intermediates suggests that the reactions proceed through a concerted mechanism. Evidence is presented to support the benzindazolone structures rather than the isomeric triazines. The ratios of *O*- and *N*-alkyl derivatives obtained on alkylation of **4a–d** depend on the type of substituent in the arylamino ring and on the bulk of the alkyl group.

The thermal and photochemical decomposition of 8-azido-1-(arylazo)naphthalenes (**1**, R = H or OCH_3) have been shown to lead to the corresponding benz[*cd*]indazole *N*-aryl imines **2**, apparently through a concerted cyclization

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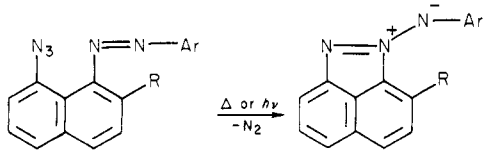


1 2

that does not involve nitrene intermediates.[1] The previously unknown compounds **2** are of interest as examples of heterocyclic *N*-imines containing the rare 1,3-dipolar azimine system. Analogous mono- and di-*N*-oxides are known.[2] We here report similar results in the thermal and photochemical decomposition of the 2- and 4-hydroxy-8-azido-1-(arylazo)naphthalenes **3a–d** and **5**.

The preparation of azides **3a** and **3b** has been described previously.[1] Azides **3c** and **3d** were prepared in similar fashion by coupling of the aryldiazonium chlorides with 8-azido-2-naphthol. Refluxing solutions of **3a–d** in toluene for 1 h led to the orange-yellow 1-(arylamino)benz[*cd*]-indazol-8(1*H*)-ones **4a–d** in yields of 80–85%, along with some polymeric material. There was no evidence for the formation of the isomeric aryl imines **8** (R = H), which might have been expected in light of the results of the thermal decomposition of **1** (R = H, OCH_3).[1] The formation of **4** is not unexpected in view of the known tautomerism of (arylazo)naphthols, which exist in both azo and hydrazone forms in solution and in the solid state.[3] The hydrazone forms **3B** evidently undergo 1,5-cyclization to **4** (Scheme I), in analogy to the thermal conversion of 2-azidobenzylidenamines to 2-substituted indazoles.[4]

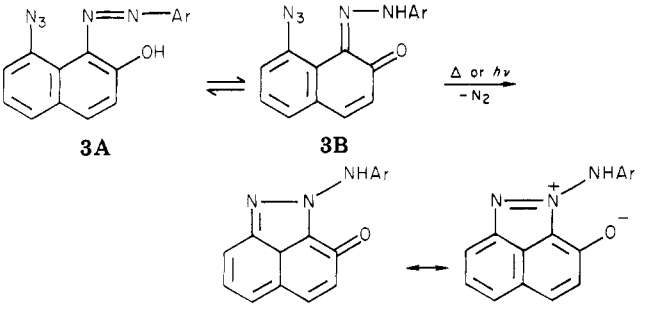
Likewise, azide **5**, prepared by coupling 4-tolyldiazonium chloride with 5-azido-1-naphthol, was converted to **6** in 80% yield on refluxing in toluene solution (Scheme II).

The low decomposition temperature of azides **3** and **5** (110 °C) and the absence of other products that would be expected from nitrene intermediates suggest that cyclization occurs by a concerted mechanism that does not involve nitrenes (see Table I). Such a mechanism is consistent with the results of thermal decomposition of phenyl azides that have α,β-unsaturated ortho substituents, which undergo intramolecular cyclization by a concerted process in which the ortho substituent provides anchimeric assistance for the elimination of nitrogen.[5]

Photolysis of **3** and **5** with a 100-W high-pressure mercury lamp in benzene solution for 24–48 h (until disappearance of starting material was indicated by TLC) gave indazoles **4** and **6** in 70–80% yields.

Evidence that **4a–c** are benzindazolones rather than the isomeric triazines was obtained by methylation of **4a–c** with methyl iodide and K_2CO_3 (Scheme III). Although the principal products were the *N*-methyl derivatives **7a–c**, small amounts of **8a–c** were formed and shown to be identical with the indazole *N*-imines prepared by thermolysis or photolysis of 8-azido-2-methoxy-1-(arylazo)-naphthalenes.[1] Likewise, methylation of **6** gave 78% **9** and 18% **10** (Scheme IV), the latter being identical with the

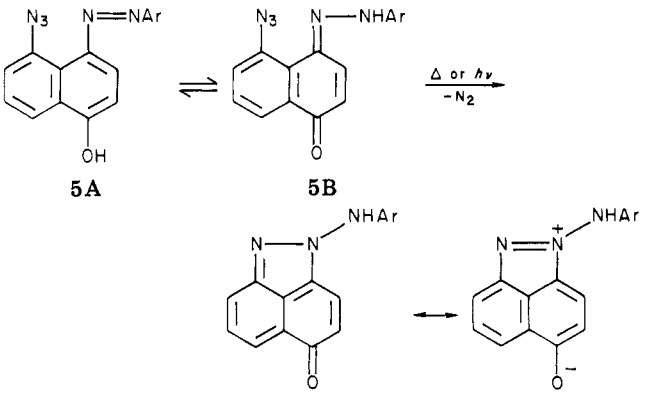
Scheme I[a]



3A 3B 4

[a] a, Ar = C_6H_5; b, Ar = 4-$CH_3C_6H_4$; c, Ar = 4-$CH_3OC_6H_4$; d, Ar = 4-$O_2NC_6H_4$.

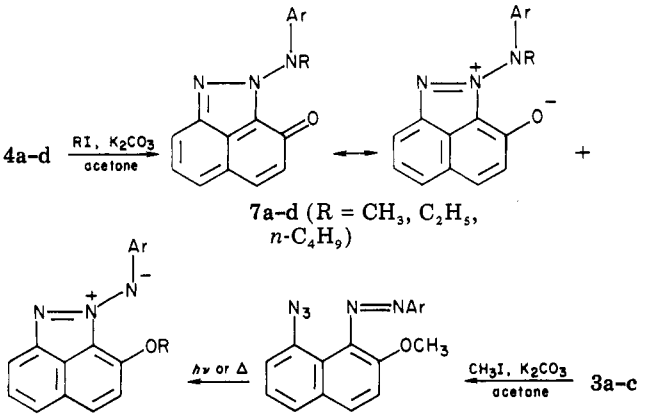
Scheme II[a]



5A 5B 6

[a] Ar = 4-$CH_3C_6H_4$.

Scheme III



7a–d (R = CH_3, C_2H_5, n-C_4H_9)

8a–c (R = CH_3)

compound prepared by methylation of the hydroxy group of **5** followed by photolysis in benzene. Methylation of **4d** gave only **7d**.

The benzindazolone structures for **4a–d** and **6** and their *N*-methyl derivatives **7a–d** and **9** are also consistent with spectroscopic data. The mass spectra of **4** and **6** showed fragment ions $ArNH_2^+$, $ArNH^+$, and ArN^+ and the benzindazole fragments at m/e 171 ($C_{10}H_7N_2O^+$) and 170 ($C_{10}H_6N_2O^+$). Similarly, the mass spectra of **7** and **9** (R = CH_3) showed the fragment ions $ArNHCH_3^+$, $ArNH{=}CH_2^+$, and $ArN{=}CH_2^+$ and the peaks at m/e 171 and 170. In addition, **7** gave relatively prominent peaks at m/e 172, which did not appear in the spectra of **4**, **6**, and **9**.

The IR spectra of **4** and **6** in reasonably concentrated solution in $CHCl_3$ or CH_2Cl_2 showed fairly sharp bands in

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(4) Kzbechek, L.; Takimoto, H. *J. Org. Chem.* **1964**, *29*, 1150. Sakai, K.; Anselme, J. P. *Ibid.* **1972**, *37*, 2351.

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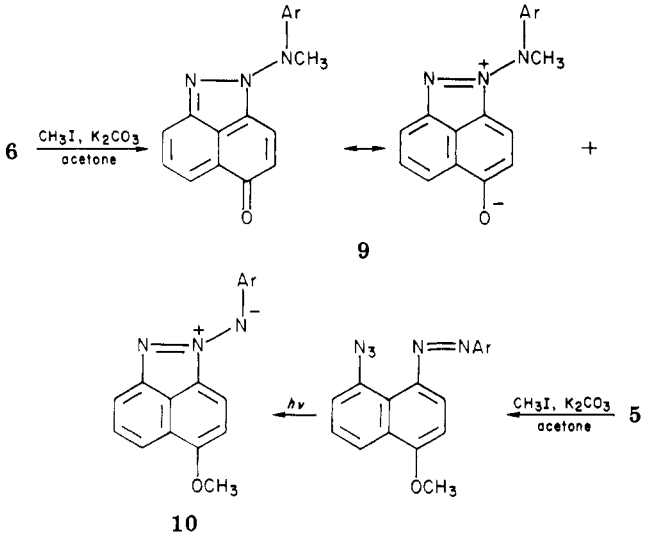
Table I. Decomposition of Azides 3a-d and 5

azide	product[c]	yield, % thermolysis	yield, % photolysis	mp, °C	IR, cm^{-1}
3a	4a	80	77	166-168	3320, 3250, 1620[a]
3b	4b	79	75	150-152	3320, 3240, 1630[a]
3c	4c	85	80	133-134	3320, 3240, 1625[b]
3d	4d	81	78	220-221	3340, 3220, 1630, 1530, 1345[b]
5	6	80	70	148-150	3325, 3200, 1620[a]

[a] $CHCl_3$. [b] CH_2Cl_2. [c] Analytical, UV, and mass spectral data are presented as supplementary material.

Scheme IV[a]



10

[a] Ar = 4-$CH_3C_6H_4$.

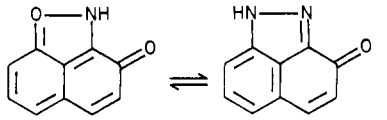
the region 3340–3320 cm^{-1} as well as broad bands at 3240–3200 cm^{-1}. These are attributed to free and intermolecular hydrogen-bonded NH, respectively, since only the former bands appeared in spectra taken in dilute solution. The carbonyl stretching absorptions for **4a–d** and **6** occurred in the range 1630–1620 cm^{-1}; virtually identical values were observed for **7** (R = CH_3) and **9**. Apparently there is no intramolecular hydrogen bonding between the NH and CO groups of **4** because such bonding should shift the carbonyl bands to lower frequencies than those of **7** (R = CH_3). The relatively low carbonyl stretching frequencies in all these compounds suggest that they have some betaine character, probably arising from resonance stabilization of the 12-π-electron benz[*cd*]indazolium system, which is isoelectronic with the stable phenalenium ion.[6] In fact, benz[*cd*]indazole derivatives,[1,2] which are closely related to the benz[*cd*]indazolium system, are much more stable than the parent benz[*cd*]indazole, which has not yet been isolated.[2,7]

The UV spectra of **4** and their *N*-methyl derivatives **7** were virtually identical, showing intense absorption in the region 300–420 nm. The most intense band was usually the longest wavelength band, which had a maximum near 385 nm (350 nm for **4d** and **7d**) and extended up to about 540 nm. The spectra of **6** and **9** were similar except that the long-wavelength absorption was shifted to a longer wavelength. The strong resemblance of the UV spectra of **4** and **7** and the fact that the spectra of **4** did not show any bands characteristic of **8** (R = CH_3) suggest that if there is any tautomeric equilibrium between **4** and **8** (R = H), it lies strongly toward **4**, at least in ethanol solution. The UV and IR spectra of **6** lead to a similar conclusion.

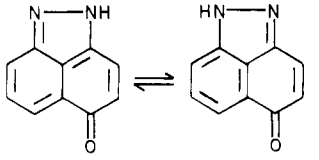
Table II. Alkylation of Benzindazolones with RI and K_2CO_3 in Dry Acetone at Room Temperature

benzindazolone	R	yield, % total	yield, % *O*-alkyl	yield, % *N*-alkyl
4a	CH_3	95	3	92
	C_2H_5	96	19	77
	n-C_4H_9	92	23	69
4b	CH_3	98	5	93
	C_2H_5	90	18	72
	n-C_4H_9	92	29	63
4c	CH_3	98	9	89
	C_2H_5	90	27	63
	n-C_4H_9	90	39	51
	sec-C_4H_9	93	76	17
4d	CH_3	96	0	96
	C_2H_5	95	0	95
	n-C_4H_9	93	0	93
6	CH_3	96	18	78

Catalytic hydrogenation of **7a–d** (R = CH_3) over Pd/C was carried out until 2 equiv of hydrogen had been absorbed, and TLC indicated disappearance of starting material. Chromatographic separation of the products gave *N*-methylarylamines in yields of 60–80% and about 35% of a light yellow solid. The principal peak in the mass spectrum of this solid was at *m/e* 170, and the elemental analysis was consistent with the composition $C_{10}H_6N_2O$. The IR spectrum showed a broad band in the range 3200–3000 cm^{-1}, consistent with hydrogen-bonded NH, and a carbonyl band at 1630 cm^{-1}. Its low solubility precluded obtaining an NMR spectrum. It is tentatively assigned structure **11**. Similar results were obtained on hydrogenation of **9**, giving 66% *N*-methyl-4-toluidine and 33% of a yellow product that appeared isomeric with **11** and is believed to be **12**.



11



12

The alkylation of **4a–d** with ethyl and butyl iodides was investigated to explore the effects of different alkyl groups and of the aryl substituent on the relative proportions of O- and N-alkyl products formed (Table II). The proportion of O-alkylation is increased by electron-donating groups on the arylamino ring, whereas the strongly electron-withdrawing nitro group in **4d** leads exclusively to the *N*-alkyl derivative. We believe that the mesomeric anion

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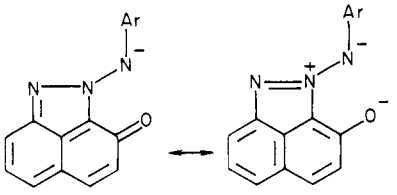
Table III. Alkylation of Benz[*cd*]indazolones with Alkyl Iodides (RI)

compd	R	chromatography[a]	products[b]	mp, °C	MS, *m/e* (M^+)	IR, cm^{-1}
4a	CH_3	SiO_2 (5)	8a	*f*	*f*	*f*
		(10)	7a	174-176	275	1625[c]
4b	CH_3	SiO_2 (3)	8b	*f*	*f*	*f*
		(5)	7b	91-92	289	1625[c]
4c	CH_3	SiO_2, CH_2Cl_2	8c	*g*	*g*	*g*
			7c	84-86	305	1630[d]
4d	CH_3	Al_2O_3, Et_2O	7d	205-207	320	1635[d]
4a	C_2H_5	Al_2O_3 (5)	8a	63-65		1275, 1050[e]
		(10)	7a	150-152		1625[c]
4b	C_2H_5	Al_2O_3 (10)	8b	133-135		1585, 1510, 1060[d]
			7b	93-95		1630[d]
4c	C_2H_5	SiO_2 (10)	8c	135-137		2830, 1250, 1055, 1035[e]
			7c	91-92		1630[d]
4d	C_2H_5	Al_2O_3 (20)	7d	137-139		1640[d]
4a	*n*-C_4H_9	Al_2O_3 (5)	8a	82		1275, 1060[e]
		(10)	7a	89-90		1625[c]
4b	*n*-C_4H_9	Al_2O_3 (10)	8b	100-102		1580, 1505, 1060[d]
			7b	55-57		1630[d]
4c	*n*-C_4H_9	SiO_2 (5)	8c	69-71		2830, 1250, 1055, 1035[e]
		(10)	7c	100-101		1630[d]
4c	*sec*-C_4H_9	SiO_2 (5)	8c	80-82		2825, 1250, 1060, 1030[e]
		(10)	7c	oil		1630[d]
4d	*n*-C_4H_9	Al_2O_3 (20)	7d	115-117		1635[d]
6	CH_3	Al_2O_3 (5)	10	*h*	*h*	*h*
			9	146-148	289	1620[c]

[a] Two products were separated by sequential elution with solvents in the order listed or by two elutions with the same solvent. The solvent composition (% Et_2O-C_5H_{12}) is given in parentheses. [b] Yields are given in Table II. Analytical, UV, and mass spectral data are given as supplementary material. [c] $CHCl_3$. [d] CH_2Cl_2. [e] CS_2. [f] See ref 1. [g] See **8c** of this work. [h] See **10** of this work.

13 is the nucleophilic species attacking the alkyl iodide because of the intense dark red color that develops immediately on addition of K_2CO_3 to the orange-yellow solutions of **4a–d** and because there is no reaction in the absence of K_2CO_3. The observed substituent effect could result from varying contributions of **13b** to the resonance



13A 13B

hybrid of ion **13**, depending on the substituent on the arylamino ring. The contribution of **13B** should diminish as the electron-withdrawing character of that substituent increases.

The results of the alkylation of **4a–c** (Table II) imply that the O/N ratio increases with the bulk of the alkyl group. However, we believe that the data are insufficient to support this conclusion, and further studies on this effect are in progress.

Experimental Section

All melting points are uncorrected. UV spectra are for solutions in 95% ethanol. Reaction products such as *N*-methylaniline, *N*-methyl-4-toluidine, *N*-methyl-4-methoxyaniline and *N*-methyl-4-nitroaniline were characterized by spectral comparison with authentic samples which were commercially available or prepared according to the literature. 8-Azido-2-hydroxy-1-(phenylazo)naphthalene (**3a**) and 8-azido-2-hydroxy-1-(4-tolylazo)naphthalene (**3b**) were prepared as described.[1]

Preparation of 8-Azido-2-hydroxy-1-[(4-methoxyphenyl)azo]naphthalene (3c) and 8-Azido-2-hydroxy-1-[(4-nitrophenyl)azo]naphthalene (3d). These compounds were prepared by coupling of the appropriate aryldiazonium chloride with 8-azido-2-naphthol by means of the procedure reported in part 2.[1] Azide **3c** was obtained in 88% yield as bright red plates: mp 122–126 °C dec; IR (CH_2Cl_2) ν_{max} 2100 cm^{-1} (N_3); mass spectrum, *m/e* 319 (M^+). Anal. Calcd for $C_{17}H_{13}N_5O_2$: C, 63.94; H, 4.10; N, 21.93. Found: C, 64.15; H, 4.13; N, 21.66.

Azide **3d** was obtained in 83% yield as bright red plates: mp 215–217 °C dec; IR (KBr) ν_{max} 2110 and 2090 cm^{-1} (N_3); mass spectrum, *m/e* 334 (M^+). Anal. Calcd for $C_{16}H_{10}N_6O_3$: C, 57.48; H, 3.01; N, 24.14. Found: C, 57.61; H, 3.02; N, 25.34.

5-Azido-1-naphthol. A suspension of 1-amino-5-naphthol[8] (3 g) in 10 mL of concentrated hydrochloric acid and 90 mL of water was cooled at 0–5 °C and diazotized with a solution of 1.4 g of sodium nitrite in 10 mL of water. After being allowed to stand for 15 min, the resulting solution was treated with 1.5 g of sodium azide in water (15 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 2 g (59%) of 5-azido-1-naphthol:[9] mp 158–160 °C dec; IR (CS_2) ν_{max} 3570 (OH) and 2090 cm^{-1} (N_3); mass spectrum, *m/e* 185 (M^+), 157, 156. Anal. Calcd for $C_{10}H_7N_3O$: C, 64.86; H, 3.81; N, 22.69. Found: C, 64.78; H, 3.86; N, 22.45.

5-Azido-1-hydroxy-4-(*p*-tolylazo)naphthalene (5). *p*-Toluidine (2.1 g) was dissolved in 60 mL of water containing 6 mL of concentrated hydrochloric acid and diazotized with 1.5 g of sodium nitrite at 0–5 °C. The diazonium salt solution was filtered into a stirred solution of 5-azido-1-naphthol (3.7 g) in 250 mL of water containing 4 g of sodium hydroxide. After being stirred 1 h, the reaction mixture was filtered and then acidified with 10% hydrochloric acid to give a bright red solid which was filtered off and washed with water. The crude material was purified through a silica gel column with 20% ether–pentane as the eluant to afford **5**: 4.8 g (80%); mp 135–137 °C dec; IR (KBr) ν_{max} 3420, 3220, 3160, 2085 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, 67.12; H, 4.36; N, 22.77.

Thermolysis of 8-Azido-2-hydroxy-1-(arylazo)naphthalenes (3a–d) and 5-Azido-1-hydroxy-4-(*p*-tolyl-

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azo)naphthalene (5). General Procedure. Solutions of azides **3a–d** and **5** (1 g) were refluxed in toluene (50 mL) until TLC showed absence of starting material (ca. 1 h). On cooling the reaction mixture the yellow precipitate was filtered off and recrystallized from toluene. Results are summarized in Table I.

Photolysis of 8-Azido-2-hydroxy-1-(arylazo)naphthalenes (3a–d) and 5-Azido-1-hydroxy-4-(*p*-tolylazo)naphthalene (5). General Procedure. Stirred solutions of azides **3a–d** and **5** (1 g) in 300 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 virtually complete absence of starting material (24–48 h). The excess solvent was distilled off, and the residue was chromatographed on silica gel with using 20% ether–pentane as the eluant. Yields are collected in Table I.

Synthesis of 1-(4-Methoxyphenyl)-8-methoxybenz[*cd*]indazol-1-imine (8c, R = CH_3). 8-Azido-2-methoxy-1-[(4-methoxyphenyl)azo]naphthalene was obtained in 60% yield[1] as dark red needles: mp 137–139 °C dec; IR (CH_2Cl_2) ν_{max} 2100 cm^{-1} (N_3); mass spectrum, *m/e* 333 (M^+), 305 ($M^+ - N_2$). Anal. Calcd for $C_{18}H_{15}N_5O_2$: C, 64.85; H, 4.53; N, 21.01. Found: C, 64.31; H, 4.48; N, 20.85.

Thermolysis in toluene solution gave **8c** (R = CH_3) in 70% yield as bright red-violet needles: mp 135–137 °C; IR (CS_2) ν_{max} 2830, 1275, 1250, 1055 cm^{-1}; mass spectrum, *m/e* 305 (M^+), 304. Anal. Calcd for $C_{18}H_{15}N_3O_2$: C, 70.80; H, 4.95; N, 13.76. Found: C, 70.71; H, 5.01; N, 13.65.

Synthesis of 1-*p*-Tolyl-6-methoxybenz[*cd*]indazol-1-imine (10). Methyl iodide (1 mL) was added to a stirred solution of **5** (150 mg) in dry acetone (20 mL) containing anhydrous potassium carbonate (300 mg). The resulting mixture was stirred at room temperature for 4 h, after which time TLC showed virtually complete absence of starting material, and then was filtered, and the solvent was distilled off. The crude methylation product was dissolved in benzene (100 mL) and photolyzed at room temperature for 24 h. The excess benzene was removed, and the residue was chromatographed on basic alumina with 5% ether–pentane as the eluant to give 120 mg (84%) of **10** as bright red-violet needles: mp 195–197 °C; IR (CS_2) ν_{max} 2830, 1268, 1072, 1055, 820, 750 cm^{-1}; mass spectrum *m/e* 289 (M^+), 288, 274, 259, 185, 184, 107, 106, 105, 104, 91. Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.73; H, 5.22; N, 14.52. Found: C, 74.37; H, 5.30; N, 14.66.

Alkylation of 1-(Arylamino)benz[*cd*]indazolones 4a–d and 6. General Procedure. To stirred solutions of the benzindazolone (2×10^{-3} M) in dry acetone (60 mL) containing anhydrous potassium carbonate (1 g) was added a 20-fold molar excess of the appropriate alkyl iodide, and the resulting mixture was stirred at room temperature for 10–48 h, until TLC showed disappearance of starting material. The reaction mixture was filtered and concentrated under reduced pressure, and the resulting residue was chromatographed on silica gel or basic alumina. Yields of O- and N-alkylation products are reported in Table II and details in Table III.

Hydrogenation of 1-(Methylarylamino)benz[*cd*]indazolones 7a–d (R = CH_3) and 9. The following procedure is typical of that used in the hydrogenation of compounds **7a–d** (R = CH_3) and **9**.

Hydrogenation of 7b (R = CH_3). Benzindazolone **7b** (R = CH_3) (500 mg) was dissolved in 50 mL of methylene chloride and hydrogenated at room temperature and atmospheric pressure by using palladium/charcoal (10%, 50 mg) as the catalyst for 0.5 h with an uptake of ca. 2 equiv of hydrogen. TLC showed absence of starting material. After removal of the catalyst and the excess solvent, the residue was chromatographed on silica gel.

Elution with 5% ether–pentane gave *N*-methyl-*p*-toluidine (70%). Further elution gave a mixture of unidentified colored products (60 mg). Elution with ether afforded **11**: 100 mg (34%); mp 261–265 °C; IR (KBr) ν_{max} 3200–3000 (br), 2900, 1650, 1630, 1610 cm^{-1}; UV λ_{max} 308 nm (log ϵ 3.62), 360 (3.85), 373 (3.84); mass spectrum, *m/e* (relative intensity) 174 (4), 172 (12), 170 (100), 142 (35). Anal. Calcd for $C_{10}H_6N_2O$: C, 70.58; H, 3.55; N, 16.46. Found: C, 69.97; H, 3.71; N, 16.26.

Hydrogenation of 7a (R = CH_3) gave *N*-methylaniline (60%) and **11** (35%).

Hydrogenation of 7c (R = CH_3) gave *N*-methyl-4-methoxyaniline (69%) and **11** (34%).

Hydrogenation of 7d (R = CH_3) furnished *N*-methyl-4-nitroaniline (80%) and **11** (38%).

Hydrogenation of 9 gave *N*-methyl-*p*-toluidine (66%) and **12**: 33%; mp 258–262 °C; IR (KBr) ν_{max} 3200–3000 (br), 1640, 1630, 1590 cm^{-1}; UV λ_{max} 256 nm (log ϵ 3.57), 297 (3.72), 344 (3.85), 398 (3.94); mass spectrum, *m/e* (relative intensity) 172 (5), 170 (100), 142 (20). Anal. Calcd for $C_{10}H_6N_2O$: C, 70.58; N, 3.55; N, 16.46. Found: C, 69.48; H, 3.57; N, 16.25.

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Registry No. 3a, 65832-01-1; **3b**, 65832-02-2; **3c**, 81044-44-2; **3d**, 81044-45-3; **4a**, 81044-46-4; **4b**, 81044-47-5; **4c**, 81044-48-6; **4d**, 81044-49-7; **5**, 81064-07-5; **6**, 81044-50-0; **7a** (R = Me), 81044-51-1; **7a** (R = Et), 81044-52-2; **7a** (R = Bu), 81044-53-3; **7b** (R = Me), 81044-54-4; **7b** (R = Et), 81044-55-5; **7b** (R = Bu), 81044-56-6; **7c** (R = Me), 81044-57-7; **7c** (R = Et), 81044-58-8; **7c** (R = Bu), 81044-59-9; **7c** (R = *sec*-Bu), 81044-60-2; **7d** (R = Me), 81044-61-3; **7d** (R = Et), 81044-62-4; **7d** (R = Bu), 81044-63-5; **8a** (R = Me), 65832-12-4; **8a** (R = Et), 81044-64-6; **8a** (R = Bu), 81044-65-7; **8b** (R = Me, 65832-13-5; **8b** (R = Et), 81044-66-8; **8b** (R = Bu), 81044-67-9; **8c** (R = Me), 81044-68-0; **8c** (R = Et), 81044-69-1; **8c** (R = Bu), 81044-70-4; **8c** (R = *sec*-Bu), 81044-71-5; **9**, 81044-72-6; **10**, 81044-73-7; **11** (isomer I), 81044-74-8; **11** (isomer II), 81044-75-9; **12** (isomer I), 81044-76-0; **12** (isomer II), 81044-77-1; *N*-methyl-*p*-toluidine, 623-08-5; *N*-methylaniline, 100-61-8; *N*-methy-4-methyxyaniline, 5961-59-1; *N*-methyl-4-nitroaniline, 100-15-2; 5-azido-1-naphthol, 51642-27-4; 1-amino-5-naphthol, 83-55-6.

Supplementary Material Available: Mass spectral data of benzindazolones **4a–d** and **6** and the *N*-methyl derivatives **7a–d** (R = CH_3) and **9** (Table IV), UV and combustion analytical data of **4a–d** and **6** and their alkylation products **7a–d**, **8a–c**, **9**, and **10** (Tables V and VI) (5 pages). Ordering information is given on any current masthead page.