Alkylaminonitrobenzenes by Vicarious Nucleophilic Animation with 4-(Alkylamino)-1,2,4-triazoles

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Alkylaminonitrobenzenes by Vicarious Nucleophilic Amination with 4-(Alkylamino)-1,2,4-triazoles

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A series of 4-(alkylamino)-1,2,4-triazoles transfer the alkylamino group to the 4-position of nitrobenzene and various 3-substituted nitrobenzenes, with no detectable ortho substitution. By contrast 2-nitrothiophene reacts in the 3-position and 2-nitronaphthalene in the 1-position; 1-nitronaphthalene gives a mixture of products derived from dominant 2- with some 4-substitution. The orientations are discussed and rationalized.

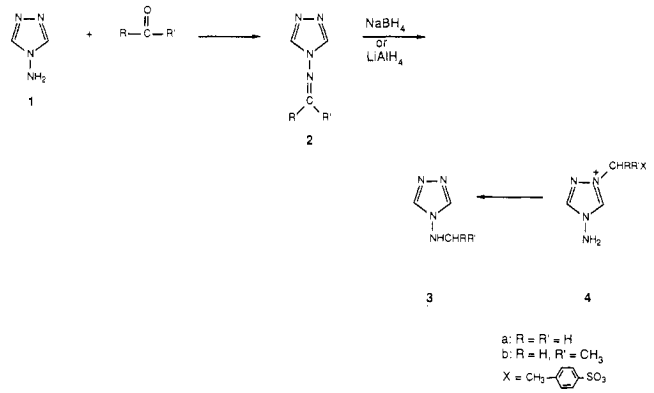
We recently reported[1] that nitrobenzene and a variety of 3-substituted nitrobenzenes could be efficiently aminated in the 4-position by 4-amino-1,2,4-triazole (**1**) in an extension of Makosza's vicarious substitution sequence. We now report extensions of this work in various directions.

Preparation of 4-(Alkylamino)-1,2,4-triazoles 3. We followed two literature methods: in the first,[2] the methyl *p*-toluenesulfonates of cation **4a** and of the ethyl analogue **4b** were prepared and rearranged into the corresponding 4-(methylamino)- (**3a**, 56%) and 4-(ethylamino)-1,2,4-triazoles (**3b**, 76%) (for the designation of various compounds of type **3** see Table I).

The second method for the preparation of compounds **3** is the reduction of imines **2**; the *N*-benzyl derivative **3d** was previously so obtained.[3] Reacting 4-amino-1,2,4-

(1) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1986**, *51*, 5039.

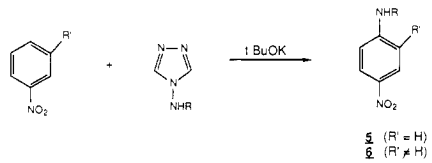
(2) Becker, H. G. O.; Timpe, H.-J. *J. Prakt. Chem.* **1969**, *311*, 9.



triazole with the appropriate aldehydes or ketones gave imines **2b–f**. Imine **2d** was reduced by $LiAlH_4$, the other imines by $NaBH_4$, giving the corresponding 4-(alkylamino)-1,2,4-triazoles **3a–f**. This second method was more convenient and gave higher purity products in better yields than by rearrangement (cf. Table I).

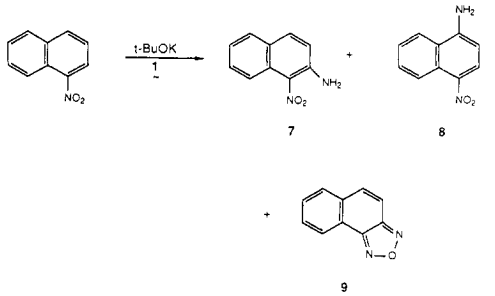
Properties of the 4-(alkylamino)-1,2,4-triazoles are recorded in Table I and significant spectral details in Table II.

Amination of Nitrobenzene with 4-(Alkylamino)-1,2,4-triazoles. Nitrobenzene reacted with the (alkylamino)triazoles in DMSO solution in the presence of potassium *tert*-butoxide at 20 °C, under conditions similar to those used previously for the conversion of nitrobenzenes into 4-nitroanilines.[1] The N-substituted 4-nitroanilines **5a–f** were obtained in good yields and had melting points in accord with literature data (Table III). The reaction was extended to several 3-substituted nitrobenzenes. The corresponding N,2-disubstituted 4-nitroanilines **6a–d** were also obtained in good yields (Table III).

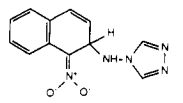


^{13}C and ^{1}H NMR data for compounds **5**, **6**, and **2** are recorded in Tables IV, V, and VI, respectively. The aryl ring carbons were assigned by comparing the observed chemical shifts to those calculated by means of substituent parameters.[4] In the 2-substituted 4-nitroaniline series, the observed shifts for C3 and C5 were often quite close. In these cases, ^{13}C–^{1}H heteronuclear correlation[5] allowed the unequivocal assignment of these carbons since the corresponding protons were easily assigned by means of the coupling patterns. Coupling between the amino and adjacent alkyl protons was observed for the N-substituted 4-nitroanilines (Table V) as well as for the 4-(alkylamino)-1,2,4-triazoles (Table II), due to the reduced basicity of the amino nitrogens, which causes slow proton exchange.[6]

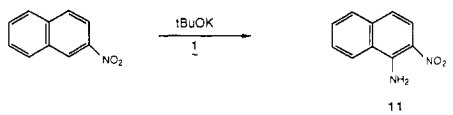
Reaction of Nitronaphthalenes with 4-Amino-1,2,4-triazole. 1-Nitronaphthalene was converted by 4-amino-1,2,4-triazole under the usual conditions into three products: 1-nitro-2-naphthalenamine (**7**) (36%), 4-nitro-1-naphthalenamine (**8**) (26%), and 1,2-naphthofurazan (**9**) (30%), all of which showed melting points and spectra in



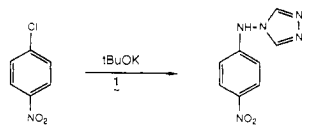
accord with literature data. Hence, the dominant substitution mode is at the position ortho to the nitro group (as **9** is presumably formed by a reductive cyclization either of **7** or of an intermediate of type **10**). Moreover, 2-



nitronaphthalene is converted readily into 2-nitro-1-naphthalenamine **11** (70%). On the other hand, 4-(isopropylamino)-1,2,4-triazole aminated 1-nitronaphthalene in the 4-position exclusively, giving *N*-isopropyl-4-nitro-1-naphthalenamine in 98% yield.



These results (except for the last) are in strong contrast to the nitrobenzene series where the reaction occurs only at the para position. If the para position is occupied, then the reaction either takes another course (e.g., *p*-chloronitrobenzene yields **12**) or more often no reaction occurs.



Makosza found that the ratio of ortho to para substitution in nitrobenzenes under VNS (vicarious nucleophilic substitution) conditions depends largely on the steric bulk of the incoming carbanion.[7] Para substitution was preferred for all but the smallest reagents; as the steric bulk increases, the o/p ratio decreased, thus with tertiary carbanions no ortho substitution was observed, and if the para position was blocked, no reaction occured. However, Makosza also found[8] that with 1-nitronaphthalene, substitution in the ortho position was generally preferred, although some para substitution was found for larger carbanions:[8] thus our results are in overall agreement with his.

Molecular orbital calculations at the INDO level[9] show that the π-electron density is significantly lower at the 2-position of 1-nitronaphthalene than at the 4-position, while in nitrobenzene, the π-electron densities at the ortho

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Table I. Preparation of 4-(Alkylamino)-1,2,4-triazoles 3

			imines 2		amines 3		
	R	R′	yield, %	mp, °C	yield,[a] %	mp,[b] °C	lit. mp, °C
a	H	H	[c]		56[d]	oil[e]	
b	H	Me	100	106–112[f]	71,[d] 94	74–77[g]	80[2]
c	Me	Me	89	oil[h]	98	99–101[i]	
d	H	Ph	87	170–171[j]	87	102–106	108[2]
e	H	*n*-Pr	87	oil	81	64–70	72[2]
f	$-(CH_2)_5-$[k]		84	96–101	68	169–171[l]	

[a] By reduction of imine unless otherwise noted. [b] All microcrystals except **3c** and **3f**: needles from 1:1 hexane/dioxane. [c] Not prepared. [d] By rearrangement of the quaternary salts **4**; two-step yield. [e] M_r(calcd) = 98.0592, found 98.0598. [f] No lit. mp given.[11] [g] Product of reduction of imine. M_r(calcd) = 112.0748, found 112.0750. [h] No physical data given in the literature.[12] [i] Anal. Found: C, 47.54; H, 8.29; N, 45.53. Calcd for $C_5H_{10}N_4$: C, 47.60; H, 7.99; N, 44.41. [j] Lit. mp[13] 175 °C. [k] Compounds derived from cyclohexanone. [l] Anal. Found: C, 58.04; H, 8.55; N, 34.37. Calcd for $C_8H_{14}N_4$: C, 57.81; H, 8.43; N, 33.70.

Table II. ^{13}C and ^1H NMR Data for N-Substituted 4-Amino-1,2,4-triazoles 3[a]

	^1H NMR data			^{13}C NMR data	
	ring[b]	NH[c]	R	ring	R
a	8.6	6.2 (q)	3.05 (d, 3 H)	141.97	40.35
b	8.55	6.65 (br s)	3.2 (q, 2 H), 1.1 (t, 3 H)	143.05	48.17, 12.49
c	8.5	5.95 (d)	3.5 (m, 1 H), 1.1 (d, 6 H)	143.43	52.92, 20.18
d	8.6	7.1 (t)	4.45 (d, 2 H), 7.55 (s, 5 H)	136.81	51.03, 130.67, 122.77, 122.28, 121.60
e	8.4	5.85 (t)	3.15 (m, 2 H), 1.5 (m, 4 H), 0.9 (t, 3 H)	143.04	53.41, 29.38, 19.59, 13.55
f	8.4	5.8 (d)	3.0 (m, 1 H), 1.0–1.8 (m, 10 H)	143.53	60.38, 30.65, 25.48, 23.83

[a] In $CDCl_3$. [b] s, 2 H. [c] 1 H; the peaks are fairly broad; coupling with the adjacent alkyl protons is observed (multiplicity indicated in parentheses).

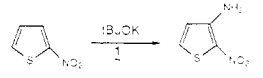
Table III. Amination with N-Substituted 4-Amino-1,2,4-triazoles

	R	R′	yield, %	mp, °C	lit. mp, °C
5a	CH_3	H	79	149–151	151–152[14]
5b	C_2H_5	H	81	94–96	96–94[14]
5c	$CH(CH_3)_2$	H	49	82–84	81–82[14]
5d	CH_2Ph	H	17 (52)[a]	145–146	147[15]
5e	$(CH_2)_3CH_3$	H	75	55–57	54–55[16]
5f	c-C_6	H	86	98–100	99–101[17]
6a	C_2H_5	Cl	82	62–64	59.5–60.5[18]
6b	CH_3	I	36	128–130[b]	
6c	C_2H_5	CH_3	86	95–97[c]	none given[19]
6d	CH_3	CO_2H	98	265–267 dec	258 dec[20] 263–264 dec[21]

[a] Based on nitrobenzene consumed. [b] Needles from 1:1 aqueous ethanol. Anal. Found: C, 29.92; H, 1.84; N, 9.69. Calcd for $C_7H_7IN_2O_2$: C, 30.24; H, 2.54; N, 10.07. [c] Needles from 1:1 aqueous ethanol. Anal. Found: C, 59.66; H, 7.06; N, 15.36. Calcd for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71; N, 15.55.

and para positions are comparable. Apparently, electronic factors favor nucleophilic substitution at the 2-position in 1-nitronaphthalene unless high steric demand overcomes the effect, while in nitrobenzene steric effects play the major role in determining regiochemistry. Thus, the anion of 4-amino-1,2,4-triazole is large enough to prevent ortho substitution in nitrobenzene, but not in 1-nitronaphthalene. In the 4-isopropylamino analogue, its larger size directs the substitution exclusively into the para position in both cases.

2-Nitrothiophene was converted in poor yield to 3-amino-2-nitrothiophene (**13**) (15%) as the only isolated



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product. Makosza also found that 2-nitrothiophene and chloromethyl phenyl sulfone gave only the 2,3-disubstituted product.[10]

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Experimental Section

Melting points were determined on a Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were obtained at 60 MHz on a Varian EM 360L NMR spectrometer, with TMS as internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-100 NMR spectrometer at 25 MHz, referenced to solvent (δ ($CDCl_3$) = 77.0, δ (DMSO-d_6) = 39.5). Two-dimensional NMR spectra were obtained on a Varian XL-200 NMR spectrometer at 200 MHz for proton and 50 MHz for carbon. High resolution mass spectra were obtained on an AEI MS30 mass spectrometer. Combustion analyses were performed on a Carlo Erba 1106 elemental analyzer.

Reagents were obtained from Aldrich with the exception of 4-amino-1,2,4-triazole which was the generous gift of Reilly Tar and Chemical Co. Nitrobenzene was distilled from P_2O_5 and stored over molecular sieves. 4-Amino-1,2,4-triazole and substituted nitrobenzenes were dried in vacuo over P_2O_5 immediately before use, with the exception of 4-(methylamino)-1,2,4-triazole and 3-nitrotoluene which were dried over molecular sieves. Potassium *tert*-butoxide was stored and weighed in a drybox. DMSO was obtained in an Aldrich Sure-Seal bottle and was transferred via syringe under inert atmosphere (N_2 or Ar). All amination reactions were carried out under dry N_2 or argon.

(4-Amino-1,2,4-triazol-1-yl)alkyl *p*-Toluenesulfonates 4. 4-Amino-1,2,4-triazole (0.84 g, 10 mmol) and methyl *p*-toluene-

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Table IV. ^{13}C NMR Chemical Shifts and Assignments for N-Substituted 4-Nitroanilines 5 and 6[a]

	C1	C2	C3	C4	C5	C6	R
5a	155.15	110.27	126.01	135.66	*b*	*c*	29.07
5b	154.37	110.51	126.16	135.46	*b*	*c*	37.01, 13.86
5c	152.74	111.07	126.37	137.04	*b*	*c*	44.10, 22.32
5d	152.99	111.32	126.38	137.34	*b*	*c*	47.67, 138.41, 128.95, 127.88, 127.34
5e	153.66	111.78	126.32	137.4	*b*	*c*	42.98, 30.99, 20.03, 13.64
5f	152.64	110.97	126.32	136.85	*b*	*c*	51.36, 32.55, 24.56, 25.34
6a	148.84	117.50	125.25	137.04	124.71	108.58	38.06, 14.18
6b	153.64	81.37	134.59	136.54	125.76	107.73	30.44
6c[d]	151.57	120.72	125.88	137.09	124.62	107.51	38.06, 14.38
6d[e]	155.30	109.19	128.45	134.54	129.27	111.14	29.56

[a] **5a**, **5b**, **6b**, and **6d** in DMSO, others in $CDCl_3$. [b] Equivalent to C3. [c] Equivalent to C2. [d] R′ = CH_3: δ 11.65. [e] R′ = CO_2H: δ 168.46.

Table V. ^1H NMR Chemical Shifts and Assignments for N-Substituted 4-Nitroanilines 5 and 6[a]

	H2	H3	H5	H6	R	NH[b]
5a	8.15 (d, 2 H)	6.65 (d, 2 H)	H3	H2	2.85 (d, 3 H)	7.3 (q)
5b	8.15 (d, 2 H)	6.75 (d, 2 H)	H3	H2	3.2 (m, 2 H), 1.2 (t, 3 H)	7.35 (t)
5c	8.25 (d, 2 H)	6.65 (d, 2 H)	H3	H2	3.8 (m, 1 H), 1.25 (d, 3 H)	4.6 (d)
5d	8.1 (d, 2 H)	6.8 (d, 2 H)	H3	H2	4.6 (d, 2 H), 7.45 (s, 5 H)	*c*
5e	8.0 (d, 2 H)	6.7 (d, 2 H)	H3	H2	3.15 (m, 2 H), 1.5 (m, 4 H), 0.9 (t, 3 H)	6.5 (t)
5f	8.05 (d, 2 H)	6.5 (d, 2 H)	H3	H2	3.35 (m, 1 H), 1.1–2.1 (m, 10 H)	4.75 (d)
6a		8.2 (d, 1 H)	8.08 (dd, 1 H)	6.62 (d, 1 H)	3.32 (m, 2 H), 1.35 (t, 3 H)	5.02 (s)
6b		8.55 (d, 1 H)	8.2 (dd, 1 H)	6.6 (d, 1 H)	2.9 (d, 3 H)	6.4 (q)
6c		7.9 (d, 1 H)	8.02 (dd, 1 H)	6.5 (d, 1 H)	3.3 (m, 2 H), 1.35 (t, 3 H)	4.4 (s)
6d		8.55 (d, 1 H)	8.05 (dd, 1 H)	6.7 (d, 1 H)	2.9 (s, 3 H)[d]	8.6 (s, 2 H)[e]

[a] **5c** in acetone-d_6; **5a**, **5b**, **6b**, and **6d** in DMSO; all others in $CDCl_3$. [b] 1 H; coupling with the adjacent alkyl protons is observed (multiplicity indicated in parentheses). [c] Resonance not observed (possibly very broad). [d] R′ = CH_3: δ 2.1 (s, 3 H). [e] NH and CO_2H are superimposed.

Table VI. ^{13}C and ^1H NMR Data for 4-(Alkylideneamino)-1,2,4-triazoles 2[a]

compd			^1H NMR data				^{13}C NMR data			
	R	R′	ring[b]	R = H[c]	R ≠ H	R′	ring	C=N	R	R′
2b	H	Me	8.9	8.6 (q)		2.2 (d, 3 H)	138.76	161.37	18.62	16.03
2c	Me	Me	8.4		2.1 (s, 3 H)	2.3 (s, 3 H)	139.04	177.98	25.29	19.49
2d	H	Ph	9.1	9.05 (s)		7.85 (m, 2 H)	138.92	157.93	132.15	132.05
						7.4 (m, 3 H)			129.83	128.30
2e	H	*n*-Pr	9.1	8.5 (t)		2.4 (q, 2 H)	138.72	174.42	34.05	18.53
						1.5 (m, 1 H)			13.51	
						0.95 (t, 3 H)				
2f	$-(CH_2)_5-$[d]		8.85		2.2–2.8 (m, 4 H)		139.74	183.29	34.90	28.96
					1.7–2.0 (br s, 6 H)				26.65	26.02
									24.52	22.09

[a] In $CDCl_3$. [b] s, 2 H. [c] 1 H, multiplicity in parentheses. [d] Compound derived from cyclohexanone.

sulfonate (1.86 g, 10 mmol) were dissolved in absolute ethanol (3 mL) and heated to reflux for 4 h. The ethanol was evaporated to give a quantitative yield of **4a** as a white solid, mp 144–147 °C. The crude product was recrystallized from 1:1 ethanol/dioxane to give 2.28 g (85%) of white plates, mp 151–153 °C (lit.[3] 88%, mp 157 °C): ^1H NMR (DMSO) δ 10.1 (s, 1 H, triazole H2), 9.15 (s, 1 H, triazole H4), 7.5 (d, 2 H, aryl H2,6), 7.15 (d, 2 H, aryl H3,5), 6.6 (br s, 2 H, NH_2), 4.0 (s, 3 H, NCH_3), 2.9 (s, 3 H, $ArCH_3$); ^{13}C NMR (DMSO) δ 144.97 (triazole ring), 142.97 (C1), 138.10 (C4), 128.20 (C3,5), 125.38 (C2,6), 38.82 (NCH_3), 20.74 ($ArCH_3$).

Similarly, using ethyl *p*-toluenesulfonate, **4b** was obtained in quantitative yield as a light yellow oil which slowly crystallized on standing to an off-white hygroscopic solid, mp 64–70 °C. No yield or physical properties of this compound were reported in the literature;[2,3] it was used without further purification: ^1H NMR ($CDCl_3$) δ 10.15 (s, 1 H, triazole H2), 8.65 (s, 1 H, triazole H4), 7.55 (d, 2 H, aryl H2,6), 7.0 (d, 2 H, aryl H3,5), 6.9 (br s, 2 H, NH_2), 4.15 (q, 2 H, NCH_2), 2.3 (s, 3 H, $ArCH_3$), 1.3 (t, 3 H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 145.11 (triazole ring), 142.34 (C1), 138.10 (C4), 128.25 (C3,5), 125.42 (C2,6), 47.30 (NCH_2), δ20.79 ($ArCH_3$), 13.67 (CH_2CH_3).

Rearrangement of 4 into 4-(Alkylamino)-1,2,4-triazoles 3. For the rearrangement reaction, **4a** was prepared on a larger scale (0.5 mol) and used without further purification. The tosylate was dissolved in a minimum amount of H_2O and NaOH (4.0 g, 0.1 mol) dissolved in a minimum amount of H_2O was added. The solution was heated to 75 °C for 3 h and then evaporated to dryness in vacuo at 75 °C. The solid residue was extracted with $CHCl_3$ (3 × 50 mL) and the solvent was removed in vacuo to give 2.59 g (53%) of **3a** as a light brown oil which was not purified further. The product reportedly decomposes on distillation.[2]

Similarly, tosylate **4b** (6.2 g, 21.8 mmol) was dissolved in H_2O (6.5 mL) and NaOH (1.74 g, 43.6 mmol) dissolved in a minimum amount of water was added. The solution was heated to 75 °C for 3 h, then the pH was adjusted to 12 with NaOH, and the aqueous phase was continuously extracted, first with ether and then with chloroform until no more product could be recovered. Total yield was 1.7 g (71%) of a light yellow waxy solid.

Preparation of Imines 2: General Synthetic Procedure. 4-Amino-1,2,4-triazole (4.2 g, 0.05 mol) and the aldehyde or ketone (0.05 mol) were dissolved in absolute ethanol (40 mL) and heated to reflux in the presence of one drop of concentrated H_2SO_4 [a two- to threefold excess of the carbonyl component was used when it was volatile (acetaldehyde, acetone)]. Five hours at reflux was sufficient to complete the reaction with aldehydes, while the ketones needed to reflux for 24 h in the presence of some 3A molecular sieves. The crude imines were isolated by evaporation of the solvent and used without further purification.

Reduction of Imines. (a) 4-(Benzylamino)-1,2,4-triazole (3d). Imine **2d** (0.52 g, 3.0 mmol) was dissolved in THF (20 mL, distilled from CaH_2 under Ar) in the drybox. $LiAlH_4$ (0.17 g, 4.5 mmol) was added in portions. After 30 min at room temperature, the reaction was quenched by adding a bit of ethyl acetate followed by water. The whole was then added to NaOH solution (final pH was 12) and the aqueous phase was continuously extracted with ether for 24 h. The ether phase was dried (Na_2SO_4) and

evaporated to give 0.45 g (89%) of light yellow oil which slowly crystallized: mp 102–106 °C (lit.[2] 68%, mp 108 °C).

(b) Reduction with $NaBH_4$. The preparation of 4-(ethylamino)-1,2,4-triazole (**3b**) will serve as an example of the general synthetic procedure. Imine **2b** (4.4 g, 0.04 mol) was dissolved in methanol (distilled from CaH_2, 40 mL). Sodium borohydride powder (1.51 g, 0.04 mol) was added portionwise. After the initial vigorous gas evolution had subsided, the mixture was heated to reflux for 15 min. The solvent was then evaporated and the residue was dissolved in a minimum amount of 1 N NaOH (final pH was 12). The solution was evaporated to dryness and the residual solids were extracted with $CHCl_3$ (3 × 50 mL). Evaporation of the solvent gave 4.4 g (98%) of white solid, mp 74–77 °C (lit.[2] 73%, mp 80 °C).

Amination of Nitrobenzenes with 4-(Alkylamino)-1,2,4-triazoles: General Synthetic Procedure. A solution of potassium *tert*-butoxide (0.56 g, 5.0 mmol) in DMSO (5 mL) was added dropwise to a solution of the 4-(alkylamino)-1,2,4-triazole (3.0 mmol) and the nitrobenzene (2.5 mmol) in DMSO (10 mL) over 10–15 min at 20–25 °C. The highly colored solution was stirred at room temperature for 15 min and then quenched in saturated NH_4Cl (50 mL). The aqueous phase was extracted with ether (3 × 50 mL). The combined ether phases were washed once with water (50 mL) and then dried ($MgSO_4$) and the solvent was removed in vacuo. The crude products were purified by flash chromatography using 230–400-mesh silica gel and petroleum ether/diethyl ether mixtures of varying proportions (1:1 to 4:1), with the exception of **6d** which was purified by recrystallization from 1:1 aqueous ethanol. If necessary, the other products were also further purified by recrystallization. The products were light to deep yellow needles with the exception of *N*-benzyl-4-nitroaniline (**5d**), which gave deep yellow plates.

Amination of 1-Nitronaphthalene. (A) 1-Nitronaphthalene (0.43 g, 2.5 mmol) was added to a solution of potassium *tert*-butoxide (0.56 g, 5.0 mmol) and 4-amino-1,2,4-triazole (0.84 g, 10 mmol) in DMSO (10 mL). After 15 min at room temperature, the reaction was worked up as described above. Three products were isolated from the crude product mixture by flash chromatography using 1:1 petroleum ether/diethyl ether. 1-Nitro-2-naphthalenamine (**7**) was the major product: 0.17 g (36%), R_f 0.23, mp 124.5–125 °C (lit.[22] mp 126–27 °C). After recrystallization from 50% aqueous ethanol the melting point was 125–126 °C. Anal. Found: C, 64.12; H, 4.24; N, 14.82. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.26; N, 14.89. ^1H NMR (acetone-d_6): δ 8.55 (dd, 1 H), 7.86 (d, 1 H), 7.78 (dd, 1 H), 7.59 (m, 1 H), 7.36 (m, 1 H, plus NH_2, broad), 7.22 (d, 1 H). ^{13}C NMR (DMSO): δ 146.87, 135.61, 129.03, 128.15, 127.76, 126.45, 124.35, 123.18, 122.16, 119.28.

Also obtained was 4-nitro-1-naphthalenamine (**8**), 0.12 g (26%), mp 184.5–87 °C (lit.[23] mp 190.5–91.5 °C). After two recrystallizations from 50% aqueous ethanol the melting point was 190–191 °C. Anal. Found: C, 63.76; H, 4.25; N, 15.02. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.26; N, 14.89. ^1H NMR (acetone-d_6): δ 8.94 (dd, 1 H), 8.38 (d, 1 H), 8.28 (dd, 1 H), 7.75 (m, 1 H), 7.56 (m, 1 H), 6.82 (d, 1 H, plus NH_2, broad). ^{13}C NMR (DMSO): δ 153.69, 131.76, 130.40, 127.96, 124.99, 123.57, 123.38, 120.65, 105.34.

The third product was 1,2-naphthofurazane (**9**), 0.13 g (30%), R_f 0.58, mp 77–77.5 °C (lit.[24] mp 78–79 °C). After recrystallization from 50% aqueous ethanol, white needles were obtained, mp 78–79 °C. Anal. Found: C, 70.35; H, 3.53; N, 16.24. Calcd for $C_{10}H_6N_2O$: C, 70.59; H, 3.52; N, 16.47. ^1H NMR ($CDCl_3$): δ 8.2 (m, 1 H, H3), 7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$): δ 148.35, 148.21, 132.90, 130.66, 129.15, 125.54, 121.25, 113.11.

(B) A solution of potassium *tert*-butoxide (0.56 g, 5.0 mmol) in DMSO (10 mL) was added dropwise to a solution of 1-nitronaphthalene (0.43 g, 2.5 mmol) and 4-(isopropylamino)-1,2,4-triazole (0.38 g, 3 mmol) in DMSO (10 mL) over 10–15 min at 25–30 °C. After 15 min at room temperature, the reaction mixture was poured into 50 mL of saturated NH_4Cl and extracted with ether (3 × 50 mL). The organic phase was washed with H_2O (50 mL), dried ($MgSO_4$), and evaporated. The crude product was purified by flash chromatography using 1:1 petroleum ether/ether) to give 0.54 g (93%) of *N*-isopropyl-4-nitronaphthalenamine, mp 134–136 °C. Anal. Found: C, 67.42; H, 6.38; N, 11.92. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. ^1H NMR ($CDCl_3$): δ 9.15 (dd, 1 H, H8), 8.6 (d, 1 H, H2), 7.6–8.1 (m, 3 H, H5,6,7), 6.55 (d, 1 H, H3), 5.3 (br s, 1 H, NH), 4.0 (m, 1 H, CH), 1.5 [s, 6 H, $(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 148.89, 134.27, 129.64, 127.88, 125.54, 124.86, 121.59, 119.99, 101.42, 44.54, 22.46.

Amination of 2-Nitronaphthalene. A solution of potassium *tert*-butoxide (0.56 g, 5.0 mmol) in DMSO (10 mL) was added dropwise to a solution of 2-nitronaphthalene (0.43 g, 2.5 mmol) and 4-amino-1,2,4-triazole (0.84 g, 10 mmol) in DMSO (10 mL) over 10–15 min at 25–30 °C. After 15 min at room temperature, the reaction mixture was poured into 75 mL of saturated NH_4Cl. An orange solid precipitated which was filtered and dried; yield 0.51 g (109%). A portion of the crude product (0.37 g) was recrystallized from aqueous ethanol to give 0.24 g (66% recovery, overall 70% yield) of 2-nitro-1-naphthalenamine (**11**) as orange-brown needles, mp 139.5–140.5 °C (lit.[25] mp 144 °C). A second recrystallization including treatment with decolorizing charcoal gave orange needles, mp 140–141 °C. Anal. Found: C, 63.70; H, 4.30; N, 15.70. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.26; N, 14.89. ^1H NMR (acetone-d_6): δ 8.48 (d, 1 H), 8.28 (br s, 2 H), 8.02 (d, 1 H), 7.86 (dd, 1 H), 7.75–7.58 (m, 2 H), 7.12 (d, 1 H). ^{13}C NMR (acetone-d_6): δ 146.04, 137.36, 131.03, 129.32, 127.13, 124.64, 124.45, 122.16, 117.09.

Amination of 2-Nitrothiophene. A solution of potassium *tert*-butoxide (0.56 g, 5.0 mmol) in DMSO (10 mL) was added dropwise to a solution of 2-nitrothiophene (0.32 g, 2.5 mmol) and 4-amino-1,2,4-triazole (0.84 g, 10 mmol) in DMSO (10 mL) over 10–15 min at 25–30 °C. The reaction was more exothermic than usual; the temperature was controlled by means of a cool water bath. After 15 min at room temperature, the dark brown reaction mixture was poured into 75 mL of saturated NH_4Cl. A brown-black solid precipitated which was filtered out to facilitate the separation of layers; then the aqueous phase was extracted as usual. After purification by flash chromatography, 54 mg (15%) of 2-nitro-3-thiophenamine (**13**) was obtained, mp 158–159 °C (lit.[26] mp 158 °C). Anal. Found: C, 33.55; H, 2.72; N, 19.04. Calcd for $C_4H_4N_2O_2S$: C, 33.33; H, 2.78; N, 19.44. ^1H NMR ($CDCl_3$): δ 7.5 (d, 1 H, H-5), 6.6 (d, 1 H, H-4).

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Registry No. **1**, 584-13-4; **2b**, 33761-49-8; **2c**, 114274-06-5; **2d**, 18998-48-6; **2e**, 35554-57-5; **2f**, 114274-07-6; **3a**, 21614-53-9; **3b**, 21614-54-0; **3c**, 114274-08-7; **3d**, 6111-75-7; **3e**, 21724-51-6; **3f**, 114274-09-8; **4a**, 6086-02-8; **4b**, 114274-11-2; **5a**, 100-15-2; **5b**, 3665-80-3; **5c**, 25186-43-0; **5d**, 14309-92-3; **5e**, 58259-34-0; **5f**, 13663-59-7; **6a**, 6085-93-4; **6b**, 114274-12-3; **6c**, 88374-25-8; **6d**, 3484-33-1; **7**, 606-57-5; **8**, 776-34-1; **9**, 233-64-7; **11**, 607-23-8; **13**, 52003-20-0; *m*-$D_2NC_6H_4Cl$, 121-73-3; *m*-$O_2NC_6H_4I$, 645-00-1; *m*-$O_2NC_6H_4Me$, 99-08-1; *m*-$O_2NC_6H_4CO_2H$, 121-92-6; methyl *p*-toluenesulfonate, 80-48-8; ethyl *p*-toluenesulfonate, 80-40-0; 1-nitronaphthalene, 86-57-7; *N*-isopropyl-4-nitronaphthalenamine, 114274-13-4; 2-nitronaphthalene, 581-89-5; 2-nitrothiophene, 609-40-5; acetaldehyde, 75-07-0; acetone, 67-64-1; benzaldehyde, 100-52-7; butanal, 123-72-8; nitrobenzene, 98-95-3.

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