Phthalazines. XV.[1] Ring Transformation of Phthalazines into Naphthalenes by Means of Inverse-Electron-Demand Diels–Alder Reaction

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The 1-substituted phthalazines 6 underwent inverse-electron-demand Diels–Alder reaction with the enamines 3 and ynamines 9, resulting in the formation of 1-substituted naphthalenes.

Thus, 1-phthalazinecarbonitrile (6b) reacted with 3a—i to give the corresponding 1-naphthonitriles 7a—e, g, h and 2,3-dihydro-1-naphthonitriles 8f, i, respectively. Similarly, reaction of 1-(methylsulfonyl)phthalazine (6c) with 3a, b, d, f gave the corresponding 1-(methylsulfonyl)naphthalenes 10a, b, d and 1-(methylsulfonyl)-2,3-dihydronaphthalene 11f. Furthermore, 1-methylthio- (6e), 1-phenyl- (6f), 1-methyl-(6b), 1-chlorophthalazines (6h) and phthalazine (6a) reacted with 3a to afford the corresponding 4-substituted 2,3-dihydro-1*H*-benz[*f*]indenes 12e—h, a, respectively.

A similar ring transformation was found to proceed between 1,4-phthalazinedicarbonitrile (14) and 1-methyl-1*H*-indole (13), giving the benzo[*b*]carbazoledicarbonitrile (15).

Compounds 6b and 6c also underwent inverse-electron-demand Diels–Alder reaction with the ynamines 9a, b to give the corresponding 1-cyano-16a,b and 1-(methylsulfonyl)naphthalenes 17a,b, respectively.

Keywords phthalazine; enamine; ynamine; inverse-electron-demand Diels–Alder reaction; ring transformation; naphthalene

Many reports on the inverse-electron-demand Diels–Alder reaction of monocyclic pyridazines have been published.[2,3] In the condensed pyridazine ring system, it has been reported by us that 7-(methylsulfonyl)-1-phenyl-1*H*-1,2,3-triazolo[4,5-*d*]pyridazine (**1**) and 7-(methylsulfonyl)-1-phenyl-1*H*-imidazo[4,5-*d*]pyridazine (**2**) react with electron-rich dienophiles, *i.e.*, the enamines **3**, giving the corresponding benzotriazoles **4** and indenoimidazoles **5** through the adducts A and B of the inverse-electron-demand Diels–Alder reaction.[4] In the phthalazine ring system, only one example has been reported of an inverse-electron-demand Diels–Alder reaction of a phthalazine (**6a**) with an electron-rich enamine (the 2-ethylideneimidazolidine **3j**), affording the naphthalene **7j**.[5] As an extension of the above work, we examined the inverse-electron-demand Diels–Alder reaction of the 1-substituted phthalazines **6** with enamines **3** or ynamines **9** and found that the expected inverse-electron-demand Diels–Alder reaction took place, resulting in the formation of the naphthalenes. In the present paper, we describe the above ring transformation in detail.

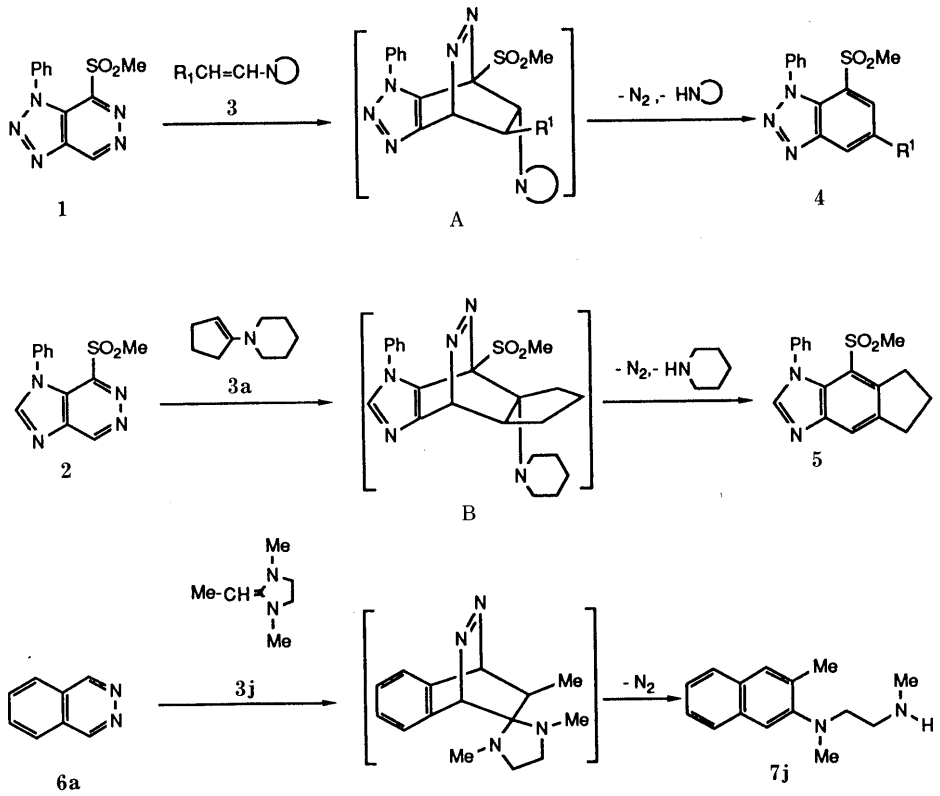


Chart 1

6	R	3	R^1	R^2	R^3	NR^4_2	7 or 10	yield (%)	8 or 11	yield (%)
6b[6]	CN	3a	H	$-(CH_2)_3-$		piperidino	7a[6a]	86		
6b	CN	3b	H	$-(CH_2)_4-$		piperidino	7b[9]	82		
6b	CN	3c	H	H	Ph	piperidino	7c[10]	76		
6b	CN	3d	H	Ph	H	piperidino	7d	77		
6b	CN	3e	H	H	iso-Bu	morpholino	7e	69		
6b	CN	3f	Me	Me	H	morpholino			8f	74
6b	CN	3g	H	H	iso-Pr	morpholino	7g[11]	75		
6b	CN	3h	H	Me	Ph	morpholino	7h	78		
6b	CN	3i	Me	H	Et	morpholino			8i	70
6c[7]	SO_2Me	3a	H	$-(CH_2)_3-$		piperidino	10a	79		
6c	SO_2Me	3b	H	$-(CH_2)_4-$		piperidino	10b	71		
6c	SO_2Me	3d	H	Ph	H	piperidino	10d	59		
6c	SO_2Me	3f	Me	Me	H	morpholino			11f	63

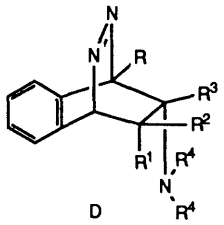


Chart 2

The enamines **3a**—**i** used in this study are listed in Chart 2. 1-Phthalazinecarbonitrile (**6b**)[6] underwent an inverse-electron-demand Diels–Alder reaction with **3a**—**i** for 10 min at 120 °C without any solvent. Compounds **3a**—**e**, **g** and **3h** gave the corresponding fully aromatized 1-naphthonitriles **7a**—**e**, **g**, and **7h** in good yields. On the other hand, **3f** and **3i** afforded the corresponding 2,3-dihydro-1-naphthonitriles **8f**, and **8i**.

As with the reported inverse-electron-demand Diels–Alder reaction of **1** and **2**,[4] the successive elimination of a nitrogen molecule and an amine from the primary regioselective cycloadduct (D) led to the naphthonitriles **7**, and the elimination of nitrogen alone resulted in the formation of the 2,3-dihydro-1-naphthonitriles **8**. In order to recycle the eliminated amine, the following reaction was examined. When **6b** was refluxed for 24 h with an equimolar amount of cyclopentanone and a quarter equimolar amount of piperidine in the presence of potassium carbonate in xylene, 2,3-dihydro-1*H*-benz[*f*]indene-4-carbonitrile (**7a**)[6a] was obtained in 40% yield. This finding shows that the enamine **3a**, which is first generated by the reaction between cyclopentanone and piperidine, cycloadds to **6b**, giving eventually **7a**. The recycling process for the formation of **7a** is shown in Chart 3.

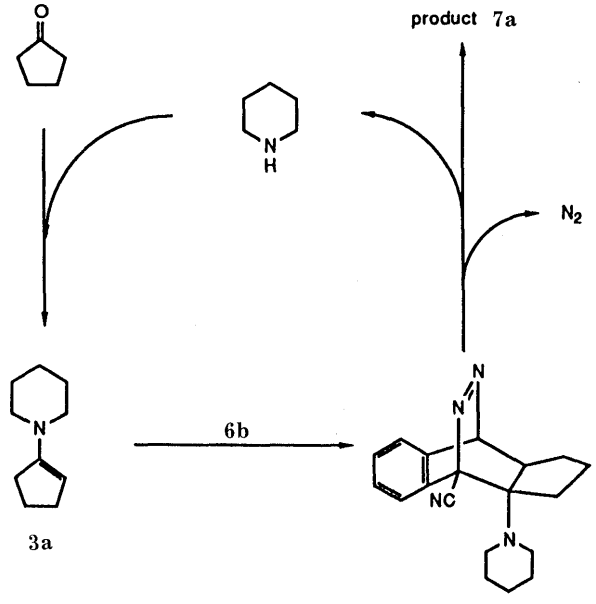
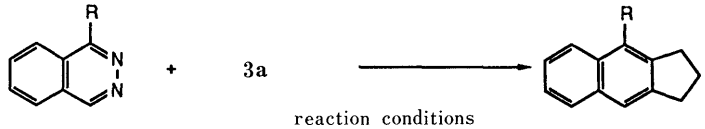


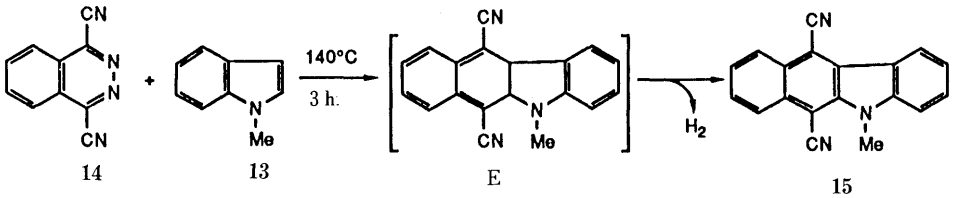
Chart 3

In view of the above results, we expected that 1-(methylsulfonyl)phthalazine (**6c**),[7] in which an electron-withdrawing methylsulfonyl group is located at the 1-position, would undergo an inverse-electron-demand Diels–Alder reaction. In fact, the reaction of **6c** with **3a**, **b**, and **3d** at 120 °C for 10 min resulted in the formation of the corresponding aromatized (methylsulfonyl)naphthalenes **10a**, **b**, and **10d**, respectively. The reaction with **3f** gave



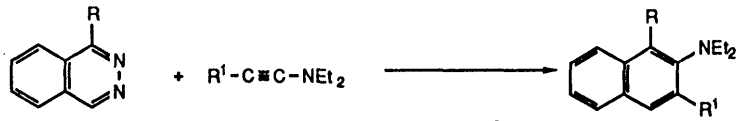
6	R	reaction conditions (temperature, time)	12	yield (%)	^{1}H-NMR($CDCl_3$) C^4-H
6d[8]	OMe	160°C, 5 h	12d	-	8.95
6e[9]	SMe	160°C, 3 h	12e	33	9.12
6f[10]	Ph	140°C, 3 h	12f[14]	48	9.35
6g[11]	Me	140°C, 3 h	12g[16]	47	9.37
6h[8]	Cl	130°C, 1 h	12h	54	9.48
6a	H	130°C, 1 h	12a[18]	49	9.51
6b[6]	CN	120°C, 10 min	7a[6a]	86	9.52
6c[7]	SO_2Me	120°C, 10 min	10a	79	9.59

Chart 4



14 13 E 15

Chart 5



6	R	9	R^1	reaction conditions (temperature, time)	product	yield (%)
6b	CN	9a	Me	25°C, 10 min	16a	90
6b	CN	9b	Et	25°C, 10 min	16b	89
6c	SO_2Me	9a	Me	65°C, 10 min	17a	70
6c	SO_2Me	9b	Et	65°C, 10 min	17b	65

Chart 6

the dihydro-1-(methylsulfonyl)naphthalene **11f**. Under the same reaction conditions, no reaction occurred between **6c** and **3e** or **3g**, resulting in the recovery of the starting **6c**. These results are summarized in Chart 2.

In order to examine the generality of the inverse-electron-demand Diels–Alder reaction of the phthalazine ring system, the 1-substituted phthalazines **6a** and **6d—h** were subjected to the reaction with **3a**. Except for 1-methoxyphthalazine (**6d**), under the conditions described in Chart 4, the 1-substituted phthalazines **6a** and **6e—h** gave the corresponding 4-substituted dihydrobenz[*f*]indenes **12a** and **12e—h**, *i.e.*, even the 1-substituted phthalazines **6e—g** having an electron-donating substituent reacted successfully. As shown in Chart 4, a stronger electron-donating substituent, which exhibits a higher chemical shift of the proton at the 4-position of **6**, requires both a higher reaction temperature and a longer reaction time, and gives the product **12** in lower yield.

Since it seems that indole is an electron-rich enamine, an inverse-electron-demand Diels–Alder reaction between 1-phthalazinecarbonitrile **6b** and *N*-methyl-1*H*-indole (**13**) was attempted, but no reaction took place, and the starting **6b** was recovered. However, the more electron-poor 1,4-phthalazinedicarbonitrile (**14**)[6b] could undergo inverse-electron-demand Diels–Alder reaction with **13** to afford 5-methyl-5*H*-benz[*b*]carbazole-6,11-dicarbonitrile **15** in 21% yield. The formation of compound **15** presumably involves sequential cycloaddition of **13**, elimination of nitrogen and ready oxidation of the resultant intermediate, the dihydro-5*H*-benzo[*b*]carbazoledicarbonitrile (E), as shown in Chart 5.

Since the ynamines **9**, like the enamines **3**, are well known to be electron-rich dienophiles,[8] it was expected that an inverse-electron-demand Diels–Alder reaction of **6** with **9** would take place. When **6b** reacted with the ynamine **9a** or **9b** at 25 °C for 10 min, the expected reaction proceeded smoothly, and the 1-naphthonitrile **16a** or **16b** was obtained in good yield. Similarly, **6c** reacted with **9a** and **9b** to give

the 1-(methylsulfonyl)naphthalenes, **17a** and **17b**.

The assigned structures for the compounds newly obtained in this paper were consistent with their elemental analyses and spectral data, as described in the experimental section. However, we have not determined the stereochemistry of **8** and **11**, and it is not clear why the reaction in the case of **8i** did not proceed to full aromatization by elimination of morpholine, giving a product like **7**.

We concluded that the inverse-electron-demand Diels–Alder reaction between the electron-poor 1-substituted phthalazines and electron-rich enamines or ynamines provides a useful method for the systhesis of the 1-substituted naphthalenes.

Experimental

All melting points are uncorrected. Infrared (IR) absorption spectra were recorded on a Jasco A-102 diffrection grating IR spectrometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured at 60 MHz on a Hitachi R-24B high-resolution NMR spectrometer. Chemical shifts are quoted in parts per million (ppm) with tetramethylsilane as an internal standard, and coupling constants (J) are given in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, and br s = broad singlet. Mass spectra (MS) were recorded on a JEOL JMS D-100 mass spectrometer. Samples were vaporized in a direct inlet system. Column chromatography was carried out on SiO_2, Wakogel C-200 (200 mesh).

Reaction of 1-Phthalazinecarbonitrile (6b)[6] with Enamines (3a—i). General Method A mixture of **6b** (1.28 mmol, 200 mg) and an enamine **3** (0.5 ml) was heated at 120 °C for 10 min. After cooling, the reaction mixture was diluted with H_2O (10 ml), acidified with aqueous AcOH, and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4, concentrated, and chromatographed on a column of SiO_2. The first fraction eluted with $CHCl_3$ gave the 1-naphthonitrile **7** or the 2,3-dihydro-1-naphthonitrile **8**.

From the reaction with 1-cyclopentenylpiperidine (**3a**), 2,3-dihydro-1*H*-benz[*f*]indene-4-carbonitrile (**7a**) was obtained as colorless needles from petroleum benzin, mp 75 °C, in 86% yield (212 mg). Compound **7a** was identified by comparison with an authentic specimen prepared by another route.[6a]

From 1-cyclohexenylpiperidine (**3b**), 1,2,3,4-tetrahydro-5-anthracenecarbonitrile (**7b**) was obtained as colorless needles from petroleum benzin, mp 86.5 °C, in 82% yield (215 mg). Compound **7b** was identified by comparison with an authentic specimen prepared by another route.[9]

From 1-(1-phenylethylenyl)piperidine (**3c**), 2-phenyl-1-naphthonitrile (**7c**) was obtained as colorless needles from petroleum benzin, mp 119 °C, in 76% yield (224 mg). Compound **7c** was identified by comparison with an authentic specimen prepared by another route.[10]

From 1-(2-phenylethylenyl)piperidine (**3d**), 3-phenyl-1-naphthonitrile (**7d**) was obtained as colorless needles from petroleum benzin, mp 129 °C, in 77% yield (225 mg). *Anal.* Calcd for $C_{17}H_{11}N$: C, 89.05: H, 4.84; N, 6.11. Found: C, 89.19; H, 4.92; N, 6.10. MS *m/z*: 229 (M^+) IR ν_{max}^{KBr} cm^{-1}: 2218 (CN). ^{1}H-NMR ($CDCl_3$): 8.38—7.47 (11H, m, aromatic H).

From *N*-(4-methyl-1-penten-2-yl)morpholine (**3e**), 2-(2-methylpropyl)-1-naphthonitrile (**7e**) was obtained as an oil in 69% yield (186 mg). MS *m/z*: 209 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$): 8.10 (1H, m, C^8-H), 7.78 (1H, d, J = 8.0 Hz, C^4-H), 7.7—7.35 (3H, m, aromatic H), 7.20 (1H, d, J = 8.0 Hz, C^3-H), 2.85 (2H, d, J = 7.0 Hz, CH_2CHMe_2), 2.02 (1H, m, CH_2CHMe_2), 0.98 (6H, d, J = 7.0 Hz, $CH(CH_3)_2$).

From *N*-(2-methyl-1-propenyl)morpholine (**3f**), 2,3-dihydro-3,3-dimethyl-2-morpholino-1-naphthonitrile (**8f**) was obtained as colorless needles from MeOH, mp 93.5 °C, in 74% yield (254 mg). *Anal.* Calcd for $C_{17}H_{20}N_2O$: C, 76.08; H, 7.51; N, 10.44. Found: C, 76.17; H, 7.59; N, 10.36. MS *m/z*: 268 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$): 7.55—6.82 (4H, m, aromatic H), 6.54 (1H, s, C^4-H), 3.66—3.45 (4H, m, 2 × OCH_2), 3.19 (1H, s, C^2-H), 2.70—1.87 (4H, m, 2 × NCH_2), 1.94 (3H, s, CH_3), 1.30 (3H, s, CH_3).

From *N*-(3-methyl-1-buten-2-yl)morpholine (**3g**), 2-isopropyl-1-naphthonitrile (**7g**) was obtained as an oil in 75% yield (186 mg). Compound **7g** was identified by comparison with an authentic specimen prepared by another route.[11]

From *N*-(1-phenyl-1-propenyl)morpholine (**3h**), 3-methyl-2-phenyl-1-naphthonitrile (**7h**) was obtained as colorless needles from petroleum benzin, mp 102—104 °C, in 78% yield (243 mg). *Anal.* Calcd for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.79; H, 5.41; N, 5.73. MS *m/z*: 243 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2223 (CN). ^{1}H-NMR ($CDCl_3$): 8.15 (1H, m, C^8-H), 7.95—7.20 (9H, m, aromatic H), 2.25 (3H, s, CH_3).

From *N*-(2-penten-3-yl)morpholine (**3i**), 2-ethyl-2,3-dihydro-3-methyl-2-morpholino-1-naphthonitrile (**8i**) was obtained as colorless plates from MeOH, mp 120 °C, in 70% yield (506 mg). *Anal.* Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.43; H, 7.82; N, 9.87, MS *m/z*: 282 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2226 (CN). ^{1}H-NMR ($CDCl_3$); 7.58—6.80 (5H, m, aromatic H and C^4-H), 3.56 (4H, m, 2 × OCH_2), 3.00—2.20 (7H, m, C^3-H, 2 × NCH_2, and CH_2Me), 1.28 (3H, t, J = 7.0 Hz, CH_2CH_3), 0.98 (3H, d, J = 7.0 Hz, C^3-CH_3).

Reaction of 6b with Cyclopentanone Catalyzed by Piperidine A mixture of **6b** (200 mg, 0.71 mmol), cyclopentanone (60 mg, 0.71 mmol), piperidine (15 mg, 0.18 mmol), and K_2CO_3 (20 mg) in xylene (1 ml) was refluxed for 24 h. After cooling, the reaction mixture was concentrated under reduced pressure, diluted with H_2O (5 ml), acidified with AcOH, and extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4, and concentrated to dryness. The residue was chromatographed on a column of SiO_2. The first fraction eluted with $CHCl_3$ gave **7a** in 40% yield (99 mg).

Reaction of 1-(Methylsulfonyl)phthalazine (6c)[7] with Enamines (3). General Method A mixture of **6c** (1.0 mmol, 200 mg) and an enamine **3** (1 ml) was heated at 120 °C for 10 min. The same work-up of the reaction mixture as described for the reaction of **6b** with **3** gave the 1-(methylsulfonyl)naphthalene (**10**) or the 2,3-dihydro-1-(methylsulfonyl)-naphthalene **11**.

From the reaction of **6c** with **3a**, 2,3-dihydro-4-(methylsulfonyl)-1*H*-benz[*f*]indene (**10a**) was obtained as colorless needles from benzene–petroleum benzin, mp 105—107 °C, in 79% yield (195 mg). *Anal.* Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73. Found: C, 68.11; H, 5.75. MS *m/z*: 246 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1300, 1135 (SO_2). ^{1}H-NMR ($CDCl_3$): 8.75 (1H, m, C^5-H), 7.85—7.30 (4H, m, aromatic H), 3.53 (2H, t, J = 8.0 Hz, C^3-H_2), 3.12 (3H, s, SO_2CH_3), 3.02 (2H, t, J = 8.0 Hz, C^1-H_2), 2.05 (2H, m, C^2-H_2).

From **3b**, 5-(methylsulfonyl)-1,2,3,4-tetrahydroanthracene (**10b**) was obtained as colorless needles from benzene–petroleum benzin, mp 110—112 °C, in 71% yield (185 mg). *Anal.* Calcd for $C_{15}H_{16}O_2S$: C, 69,20; H, 6.19. Found: C, 69.06; H, 6.16. MS *m/z*: 260 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1295, 1139 (SO_2). ^{1}H-NMR ($CDCl_3$): 8.78 (1H, m, C^8-H), 7.80—7.20 (4H, m, aromatic H), 3.70—2.70 (4H, m, C^1-H_2 and C^4-H_2), 3.15 (3H, s, SO_2CH_3), 2.10—1.55 (4H, C^2-H_2 and C^3-H_2).

From **3d**, 1-(methylsulfonyl)-3-phenylnaphthalene (**10d**) was obtained as colorless plates from benzene–petroleum benzin, mp 133—136 °C, in 59% yield (167 mg). *Anal.* Calcd for $C_{17}H_{14}O_2S$: C, 72.33; H, 5.00. Found: C, 72.38; H, 5.04, MS *m/z*: 282 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1299, 1128 (SO_2). ^{1}H-NMR ($CDCl_3$): 8.82—7.20 (11H, m, aromatic H), 3.19 (3H, s, SO_2CH_3).

From **3f**, 2,3-dihydro-3,3-dimethyl-1-(methylsulfonyl)-2-morpholinonaphthalene (**11f**) was obtained as colorless plates from EtOH, mp 180–185 °C, in 63% yield (202 mg). *Anal.* Calcd for $C_{17}H_{23}NO_3S$: C, 63.52; H, 7.21; N, 4.36. Found: C, 63.25; H, 7.15; N, 4.31. MS *m/z*: 321 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1300, 1110 (SO_2). ^{1}H-NMR ($CDCl_3$): 8.10 (1H, m, C^8-H), 7.51—6.90 (3H, m, aromatic H), 6.94 (1H, s, C^4-H), 3.51 (4H, t, J = 8.0 Hz, 2 × OCH_2), 3.21 (3H, s, SO_2CH_3), 2.93 (1H, s, C^2-H), 2.70—2.00 (4H, m, 2 × NCH_2), 1.35 (3H, s, CH_3), 0.98 (3H, s, CH_3).

Reaction of the 1-Substituted Phthalazines 6 with 3a. General Method A mixture of **6** (300 mg) and **3a** (1 ml) was heated under the reaction conditions described in Chart 4. Work-up of the reaction mixture as described for the reaction of **6b** with **3a** gave the 4-substituted 2,3-dihydro-1*H*-benz[*f*]indene **12**.

Thus, reaction of 1-(methylthio)phthalazine (**6e**)[12] gave 2,3-dihydro-4-(methylthio)-1*H*-benz[*f*]indene (**12e**) as a yellow oil in 33% yield (120 mg). MS *m/z*: 214. ^{1}H-NMR ($CDCl_3$): 8.45 (1H, m, C^5-H), 7.85—7.05 (4H, m, aromatic H), 3.40—2.94 (4H, m, C^1-H_2 and C^3-H_2), 2.30 (3H, s, SCH_3), 2.20—1.90 (2H, m, C^2-H_2).

1-Phenylphthalazine (**6f**)[13] gave 2,3-dihydro-4-phenyl-1*H*-benz[*f*]indene (**12f**) as colorless needles from EtOH, mp 80—82 °C, in 48% yield (171 mg). Compound **12f** was identified by comparison with an authentic specimen prepared by another route.[14]

1-Methylphthalazine (**6g**)[15] gave 2,3-dihydro-4-methyl-1*H*-benz[*f*]indene (**12g**) as a slightly yellow oil in 47% yield (180 mg). Compound **12g** was identified by comparison with an authentic specimen prepared by another route.[16]

1-Chlorophthalazine (**6h**)[17] gave 4-chloro-2,3-dihydro-1*H*-benz[*f*]indene (**12h**) as a slightly yellow oil in 54% yield (196 mg). MS *m/z*: 202 (M^+). ^{1}H-NMR ($CDCl_3$): 8.05 (1H, m, C^5-H), 7.70—7.20 (4H, m, aromatic

H), 3.23—2.92 (4H, m, C^1H_2 and C^3-H_2), 2.29—1.76 (2H, m, C^2-H_2).

Phthalazine (**6a**) gave 2,3-dihydro-1*H*-benz[*f*]indene (**12a**) as colorless needles from petroleum benzin, mp 94 °C, in 49% yield (189 mg). Compound **12a** was identified by comparison with an authentic specimen prepared by another route.[18]

Reaction of 1,4-Phthalazinedicarbonitrile (14)[6b] with 1-Methyl-1*H*-indole (13) A mixture of **14** (300 mg, 1.67 mmol) and **13** (2 ml) was heated at 140 °C for 3 h. Work-up of the reaction mixture as described for the reaction of **6b** with **3** gave 5-methyl-5*H*-benzo[*b*]carbazole-6,11-dicarbonitrile (**15**) as a pale yellow powder, mp 263 °C, in 21% yield (96 mg). *Anal.* Calcd for $C_{19}H_{11}N_3$: C, 81.12; H, 3.94; N, 14.94. Found: C, 81.01; H, 3.95; N, 14.44. MS *m/z*: 281 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2209, 2210 (CN). ^{1}H-NMR ($CDCl_3$): 8.70—7.20 (2H, m, aromatic H), 7.80—7.20 (6H, m, aromatic H), 4.18 (3H, s, NCH_3).

Reaction of the 1-Substituted Phthalazines 6 with the Ynamines 9. General Method A mixture of **6** (200 mg) and **9** (1 ml) was stirred under the reaction conditions described in Chart 6. Work-up of the reaction mixture as described for the reaction of **6b** with **3** gave the 1-substituted naphthalene.

Thus, reaction of **6b** with 1-(*N*,*N*-diethylamino)-1-propyne (**9a**) gave 2-(*N*,*N*-diethylamino)-3-methyl-1-naphthonitrile (**16a**) as a pale yellow oil in 90% yield (275 mg). MS *m/z*: 238 (M^+). IR ν_{max}^{neat} cm^{-1}: 2220 (CN). ^{1}H-NMR ($CDCl_3$): 7.90 (1H, m, C^8-H), 7.71—6.90 (4H, m, aromatic H), 3.33 (4H, q, J=7.0 Hz, 2×$\underline{CH_2}$Me), 2.38 (3H, s, CH_3), 1.10 (6H, t, J=7.0 Hz, 2×$CH_2\underline{CH_3}$).

Reaction of **6b** with 1-(*N*, *N*-diethylamino)-1-butyne (**9b**) gave 2-(*N*,*N*-diethylamino)-3-ethyl-1-naphthonitrile (**16b**) as a pale yellow oil in 89% yield (288 mg). MS *m/z*: 252 (M^+). IR ν_{max}^{neat} cm^{-1}: 2210 (CN). ^{1}H-NMR ($CDCl_3$): 8.00 (1H, m, C^8-H), 7.79—7.10 (4H, m, aromatic H), 3.37 (4H, q, J=7.0 Hz, 2×$\underline{CH_2}$Me), 2.79 (2H, q, J=7.0 Hz, $\underline{CH_2}$Me), 1.30 (3H, t, J=7.0 Hz, $CH_2\underline{CH_3}$), 1.09 (6H, t, J=7.0 Hz, $CH_2\underline{CH_3}$).

Reaction of **6c** with **9a** gave 2-(*N*,*N*-diethylamino)-3-methyl-1-(methylsulfonyl)naphthalene (**17a**) as a pale yellow oil in 70% yield (205 mg). MS *m/z*: 291 (M^+). IR ν_{max}^{neat} cm^{-1}: 1292, 1125 (SO_2). ^{1}H-NMR ($CDCl_3$): 8.87 (1H, m, C^8-H). 7.82—7.30 (4H, m, aromatic H), 3.62—3.02 (4H, m, 2×$N\underline{CH_2}$Me), 3.23 (3H, s, SO_2CH_3), 2.45 (3H, s, CH_3), 1.11 (6H, t, J=7.0 Hz, 2×$CH_2\underline{CH_3}$).

Reaction of **6c** with **9b** gave 2-(*N*,*N*-diethylamino)-3-ethyl-1-(methylsulfonyl)naphthalene (**17b**) as a pale yellow oil in 65% yield (200 mg). MS *m/z*: 305 (M^+). IR ν_{max}^{neat} cm^{-1}: 1294, 1127 (SO_2). ^{1}H-NMR ($CDCl_3$): 8.78 (1H, m, C^8-H), 7.80—7.20 (4H, m, aromatic H), 3.22 (3H, s, SO_2CH_3), 3.26 (4H, q, J=7.0 Hz, 2×$N\underline{CH_2}$Me), 2.78 (2H, q, J=7.0 Hz, $\underline{CH_2}$Me) 1.30 (3H, t, J=7.0 Hz, $CH_2\underline{CH_3}$), 1.04 (6H, t, J=7 Hz, 2×$CH_2\underline{CH_3}$).

Acknowledgement The authors are greatly indebted to the staff of the central analysis room of the University of Shizuoka for the elemental analyses and MS measurements.

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