Monatshefte für Chemie 129, 205–212 (1998)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Chemoselective Reactions of 2,3-Dichloro-1,4-naphthoquinone

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Summary. The reaction of 2,3-dichloro-1,4-naphthoquinone with alkoxides, primary amines, and phenols was shown to proceed chemoselectively rather to the corresponding 2-substituted 3-chloro-naphthoquinones or 2,3-disubstituted quinones than to brazanquinone derivatives. Difunctional reagents like mercaptobenzimidazole, methyl urea, or guanidine lead to the corresponding heterocyclic system. The chemoselectivity of these reactions was found to be critically dependent on the reagents and reaction conditions used. These reaction parameters can thus be used to govern the synthesis of distinct compounds.

Keywords. Quinones; Alkoxides; Chemoselective reactions; Tricyclic heterocyclic compounds.

Chemoselektive Reactionen von 2,3-Dichlor-1,4-naphthochinon

Zusammenfassung. Es wurde gezeigt, daß die Reaktion von 2,3-Dichlor-1,4-naphtho-chinon mit Alkoxiden, primären Aminen und Phenolen chemoselektiv zu den entsprechenden 2-substituierten 3-Chlornaphthochinonen und nicht zu Brazanchinonen führt. Der Einsatz von difunktionellen Reagentien wie Mercaptobenzimidazol, Methylharnstoff und Guanidin ergab die entsprechenden tricyclischen heterocyclischen Systeme. Es wurde gefunden, daß die Chemoselektivität dieser Reaktionen kritisch von den Reagentien und Reaktionsbedingungen abhängt. Diese Reaktions-parameter können verwendet werden, um die Synthese bestimmter Verbindungen zu steuern.

Introduction

Quinones play an important role in our life, and interest in their biological functions has stimulated basic chemical research in several areas. The use of quinones, in fact, dates to antiquity, and the history of these compounds is perhaps longer than that of any other group of naturally occurring substances. They are important not only as a pigments but also as a drugs [1a–d].

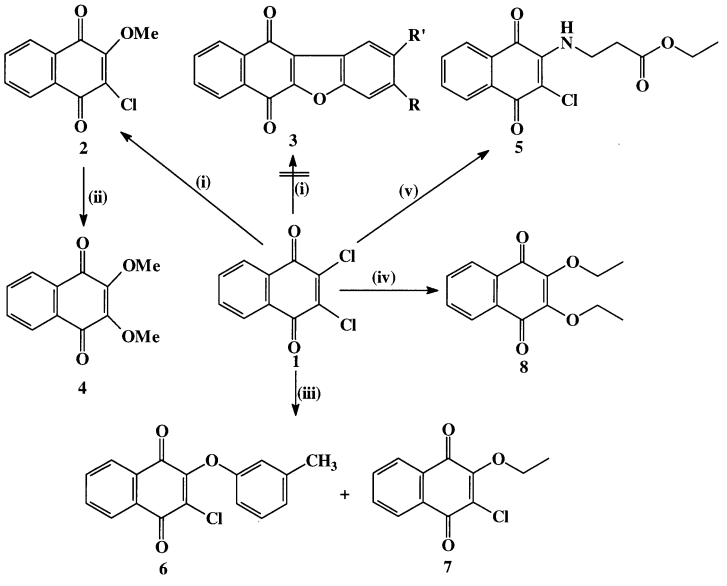
2,3-Dichloro-1,4-naphthoquinone (**1**) is known as a key synthetic intermediate in organic, medicinal, and industrial chemistry [2, 3]. The reactions of **1** with a variety of alkoxides and mercaptanes to form 2,3-dialkoxy-1,4-naphthoquinones and 2,3-dialkylthio-1,4-naphthoquinones [4a–d] have been studied in some detail. A variety of 2-amino-3-alkylseleno-1,4-naphthoquinones [5] have also been prepared from **1** in good yields. Cyclization involving the halogen derivatives of 2,3-dihalo-1,4-naphthoquinone have yielded three- to six-membered heterocyclic

rings [6a–g]. A number of such 1,4-naphthoquinones have been shown to be metabolite antagonists [6b] and to display fungicide activity [7]. Naphthoquinone derivatives have been reported to inhibit *in vitro* the anaerobic glycolysis of *Schistosoma mansoni* [4a], to influence the synthesis of prothrombin and the respiratory enzymes of malaria parasites as well as enzymes associated with glycolysis, esterification, and the functioning of the tubercle bacillus [4b], and some show antitubercular activity and antimalarial effects [4c]. Following these leads it seemed to be important to further exploit the general reactivity of **1** towards nucleophiles.

Results and Discussion

The work presented here focuses upon chemoselective reactions of **1** towards a variety of phenol derivatives in the presence of alkoxides. Thus, the reaction of **1** with 3,4-dimethylphenol or 3,5-dihydroxybenzoic acid in refluxing methanol containing CH_3ONa resulted chemoselectively in 2-chloro-3-methoxy-1,4-naphthoquinone (**2**) in very good yield rather than in the formation of benzo[*b*]naphto-[2,3-*d*]furan-6,11-dione derivatives (**3**) which have been previously prepared using phenols in refluxing pyridine [6c] or with C_2H_5ONa as catalyst [6e].

Interestingly enough, reaction of **2** with $NaNH_2$/MeOH at room temperature afforded 2,3-dimethoxy-1,4-naphthoquinone (**4**) in 70% yield, Of course, $NaNH_2$ should produce methanolate under these conditions, leading to the disubstituted



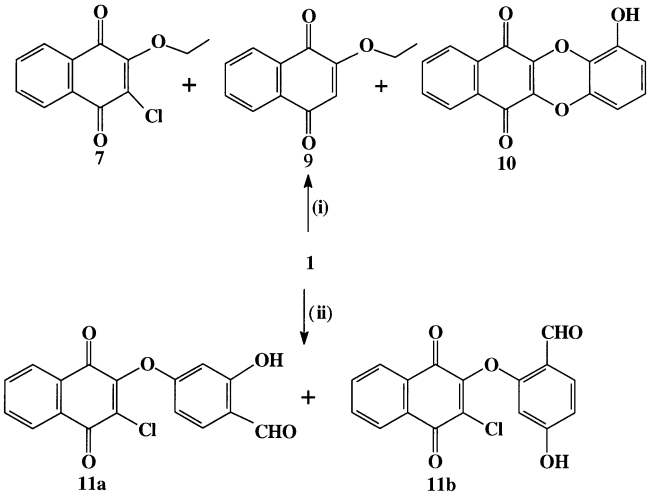
(ia) 3,4-Dimethylphenol/MeONa/MeOH, reflux/N_2, 8 h, **2** (96%)
(ib) 3,4-Dihydroxybenzoic acid/MeONa/MeOH, reflux, 8 h, **2** (77%)
(ii) $NaNH_2/CH_3OH$, room temp., 5 min, **4** (70%)
(iii) m-Cresol/*t*-BuOK/C_2H_5OH, reflux, 6 h, **6** (82%) and **7** (5%)
(iv) 3,4-Dimethylphenol/*t*-BuOK/C_2H_5OH, reflux, 6 h, **8** (37%)
(v) $H_2N(CH_2)_2COOC_2H_5$/*DMF*, room temperature, 12 h (70%)

Scheme 1

derivative **4**. However, using this condition afforded the disubstituted product **4** which was not produced under the much more vigorous conditions employed to prepare the monosubstituted derivative **2**. Using *β*-alanine ethyl ester in *DMF* at room temperature afforded the corresponding N-substitued derivative **5** in 70% yield. In addition, upon reacting **1** with *m*-cresol using *t*-BuOK as a non-nucleophilic base in refluxing ethanol, 2-aryloxy-3-chloro-1,4-naphthoquinone (**6**) was formed in 82% yield besides a trace of the 2-ethoxy derivative **7** (5%). On the other hand, the reaction of **1** with *m*-cresol/*t*-BuOK using methanol as solvent instead of ethanol produced **2** in 66% yield, and only 1% of the cresoxy derivative **6**. Moreover, if the reaction of **1** was conducted with 3,4-dimethylphenol/*t*-BuOK in hot ethanol, 2,3-diethoxy-1,4-naphthoquinone (**8**) was obtained in 37% yield. Thus, the chemoselective substitution critically depends on the reagents and reaction conditions used.

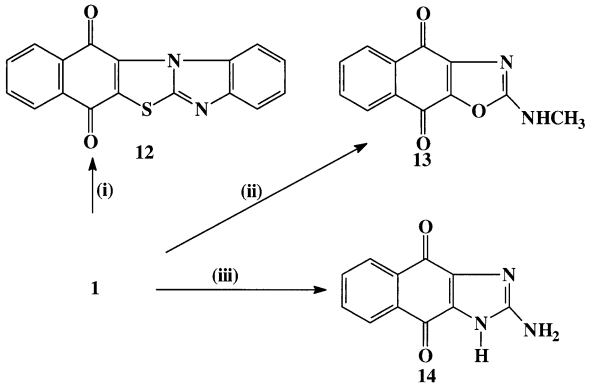
To extend these studies to diphenolic or other difunctional reagents, **1** was reacted with pyrrogallol/*t*-BuOK in refluxing ethanol. This afforded a mixture of 2-chloro-3-ethoxy-1,4-naphthoquinone (**7**, 43%), 2-ethoxy-1,4-naphthoquinone (**9**, 9.5%), and 1-hydroxybenzo[*b*]naphtho[2,3-*e*][1,4]dioxin-9,11-quinone (**10**, 5%). Formation of the reduced product **9** could be attributed to the reducing properties of pyrrogallol. As in the former cases, the choices of reagents and reaction conditions critically influenced the course of the reaction. This might be used to direct the synthesis of defined products properly, as was demonstrated by conducting the reaction of **1** with 2,4-dihydroxybenzaldehyde in acetone containing K_2CO_3 at room temperature, resulting in the isomers **11a–b** which could be easily distinguished by their ^{1}H NMR spectra in 81% overall yield (see Experimental).

To test for difunctional heterofunctional reagents, **1** was reacted with 2-mercaptobenzimidazole in refluxing pyridine, resulting in **12** in 92% yield (compare Ref. [6h]), whereas reaction of **1** with methylurea gave 2-methyl-



(i) Pyrogallol/*t*-BuOK/C_2H_5OH, reflux, 6 h, **7** (43%), **9** (9.5%), **10** (5%)
(ii) 2,4-Dihydroxybenzaldehyde/acetone/K_2CO_3, room temperature; **11a** (12%), **11b** (69%)

Scheme 2



(i) 2-Mercaptobenzimidazole/pyridine, reflux 5 h, **12** (92%)
(ii) a) $(H_3C)_2NCONH_2$/neat, 30 min, b) C_2H_5OH, reflux, 2 h (62%)
(iii) Guanidine/*DMF*, room temperature, 48 h (68%)

Scheme 3

aminonaphtho[2,3-*d*]oxazole-4,9-dione (**13**) in 62% yield. On reaction of **1** with guanidine in dimethylformamide at room temperature, the cyclized product **14** was obtained in 68% yield.

In conclusion, we found that the reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with different alkoxides under a variety of basic conditions afforded 2- or 2,3-disubstituted 1,4-naphthoquinones chemoselectively, depending critically on the reaction conditions and the reagents used.

Experimental

Melting points were determined on a Büchi apparatus and are uncorrected. IR spectra were measured using an Electrophotometer 580 and an FT spectrometer 1710, Perkin-Elmer. ^{1}H NMR and ^{13}C NMR spectra were determined using WP 200 SY and AM 300 instruments (Bruker). APT (attached proton test): spin echo based selection of multiplicities of ^{13}C signals; quaternary C and CH_2 carbons: positive signals (+), CH and CH_3 carbons: negative signals (−). MS: MAT 312 Finnigan spectrometer of the Spectral unit, Department of Organic Chemistry, Hannover University, D-30167 Hannover, Germany. Microanalyses were carried out in the laboratory of the Chemistry Department, Assiut University; the results agreed favorably with the calculated data. Column chromatography (silica gel, 0.02–0.63 mm, Merck) was carried out under weak positive pressure.

2-Chloro-3-methoxy-1,4-naphthoquinone (**2**; $C_{11}H_7ClO_3$)

Method A: A mixture of 1.14 g (5 mmol) **1**, 0.6 g 3,4-dimethylphenol (5 mmol), and 0.37 g sodium methoxide (10 mmol) was refluxed in 20 ml methanol for 8 h. The resulting yellow precipitate was collected by filtration and recrystallized from ethanol to give **2**; yield: 96%; m.p.: 140°C.

Method B: Like A, but using 3,5-dihydroxybenzoic acid instead of 3,4-dimethylphenol; 77% yield.

^{1}H NMR ($CDCl_3$): $\delta = 4.32$ (s, 3H, OCH_3), 7.7–7.8 (m, 2H, Ar-H), 8.02–8.15 (m, 2H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 61.86$ (−, OCH_3, 126.83, 126.91 (−, Ar-CH), 128.2 (+, C-2), 130.75, 130.97 (+, C-4a, C-8a), 133.91, 134.33 (−, Ar-CH), 156.73 (+, C-3), 178.50, 179.89 (+, C-1, C-4) ppm; MS: *m/z* (%) = 223 [M^{+1}] (13), 222 [M^+] (85), 209 (3), 193 (23), 187 (12), 176 (4), 165

(7), 157 (100), 151 (22), 129 (39), 123 (39), 113 (2), 104 (24), 101 (19), 99 (11), 88 (11), 77 (11), 76 (43), 69 (3), 65 (2).

2,3-Dimethoxy-1,4-naphthoquinone (**4**; $C_{12}H_{10}O_4$)

A mixture of 0.3 g (1.3 mmol) **2** and 0.1 g $NaNH_2$ (2.7 mmol) was stirred in 15 ml methanol at room temperature for 5 min. The reaction mixture was diluted with water, and the resulting precipitate was collected by filtration and chromatographed on silica gel (ether/cyclohexane = 1:4) to give **4** in 70% yield; m.p.: 114–115°C, Ref. [4b]: m.p.: 114–115°C.

^{1}H NMR ($CDCl_3$): $\delta = 4.12$ (s, 6H, $2OCH_3$), 7.7 (m, 2H, Ar-H), 8.05 (m, 2H, Ar-H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 61.432$ (+, 2 OCH3), 126.215 (−, Ar-CH), 130.793 (+, C-4a, C-8a), 133.734 (−, Ar-CH), 147.499 (+, C-2, C-3), 181.945 (+, 2 C=O, C-1, C-4) ppm; MS: *m/z* (%) = 218 [M^+] (74), 209 (5), 204 (33), 203 (100), 189 (19), 180 (2), 175 (23), 173 (74), 161 (9), 157 (10), 147 (36), 133 (14), 117 (4), 105 (54), 104 (82), 101 (6), 97 (4), 89 (28), 83 (3), 77 (29), 76 (85), 66 (12).

2-Ethoxycarbonylamino-3-chloro-1,4-naphthoquinone (**5**; $C_{15}H_{14}NClO_4$)

A solution of 0.55 g (2.5 mmol) **1** in 10 ml *DMF* was stirred at room temperature, and a solution of 0.34 g *ß*-alanine ethyl ester (2.6 mmol) in 10 ml *DMF* was added dropwise over a period of 10 min. The reaction mixture was stirred at room temperature for 12 h and then diluted with water. The resulting red crystals were collected by filtration and recrystallized from ethanol to give **5** in 70% yield, m.p.: 119°C.

^{1}H NMR ($CDCl_3$): $\delta = 1.35$ (t, $J = 7$ Hz, 3H, CH_3), 2.8 (t, 2H, CH_2), 4.3 (m, 4H, (2H, OCH_2, 2H, $NHCH_2$), 6.5 (m, 1H, NH), 7.8 (m, 2H, Ar-H), 8.2 (m, 2H, Ar-H)ppm.

2-Aryloxy-3-chloro-1,4-naphthoquinone (**6**; $C_{17}H_{11}ClO_3$) *and 2-chloro-3-ethoxy-1,4-naphthoquinone* (**7**; $C_{12}H_9ClO_3$)

A mixture of 1.14 g (5 mmol) **1**, 0.54 g *m*-cresol (5 mmol) and 1.0 g *t*-BuOK (9 mmol) was refluxed in 20 ml ethanol for 6 h. The reaction mixture was concentrated to dryness and washed several times with KOH solution to remove the excess of *m*-cresol. The residue was dissolved in $CHCl_3$, dried ($MgSO_4$), and filtered. The combined filtrate was concentrated and chromatographed on silica gel (ether/cyclohexane = 1:6) to give **7** in 5% yield, m.p.: 97–98°C (Ref. [4a]: m.p.: 97–98°C), in the first fraction, followed by **6** (82% yield, m.p.: 126°C, deep yellow crystals) in the next fraction.

6: ^{1}H NMR ($CDCl_3$): $\delta = 2.32$ (s, 3H, CH_3), 6.8 (m, 2H, Ar-H), 6.95 (m, 1H, Ar-H), 7.2 (m, 1H, Ar-H), 7.7–7.85 (m, 2H, Ar-H), 8.05 (m, 1H, Ar-H), 8.2 (m, 1H, Ar-H)ppm; ^{13}C NMR ($CDCl_3$): $\delta = 21.391$ (−, CH_3), 113.465, 117.141, 124.850, 127.196, 127.305, 129.448, 134.387, 134.487 (−, Ar-H), 130.624, 131.171, 133.703 (+, C-4a, C-8a, C-3′), 140.101 (+, C-2), 153.564 (+, C-1′), 156.356 (+, C-3), 177.972, 178.394 (+, C-1, C-4)ppm; MS: *m/z* (%) = 299 [M^{+2}] (33), 298 [M^{+1}] (12), 297 [M^+] (43), 285 (7), 283 (7), 263 (55), 235 (20), 228 (7), 221 (12), 210 (22), 207 (15), 201 (9), 194 (10), 189 (8), 180 (23), 176 (23), 173 (23), 165 (14), 163 (19), 159 (14), 157 (17), 149 (19), 147 (11), 139 (12), 133 (18), 123 (26), 119 (23), 117 (20), 109 (39), 107 (76), 99 (24), 97 (60), 89 (26), 83 (63), 81 (89), 77 (66), 76 (26), 77 (100), 65 (57).

7: ^{1}H NMR ($CDCl_3$): $\delta = 1.45$ (t, $J = 7$ Hz, 3H, CH_3), 4.62 (q, $J = 7$ Hz, 2H, OCH_2), 7.75 (m, 2H, Ar-H), 8.05–8.20 (m, 2H, Ar-H)ppm; ^{13}C NMR ($CDCl_3$): $\delta = 16.025$ (−, CH_3), 70.7.25 (+, OCH_2), 126.864, 126.956 (−, Ar-H), 129.215 (+, C-2), 130.807, 131.110 (+, C-4a, C-8a), 133.886, 134.278 (−, Ar-CH), 156.603 (+, C-3), 178.666, 179.765 (+, 2 C=O, C-1, C-4)ppm; MS: *m/z* (%) = 236 [M^+] (44), 223 (18), 221 (48), 214 (2), 208 (33), 201 (24), 194 (17), 192 (18), 180 (100), 173 (42), 163 (5), 157 (78), 145 (18), 135 (8), 129 (19), 123 (24), 117 (10), 105 (45), 101 (14), 99 (10), 89 (26), 77 (20), 76 (36), 65 (1).

2,3-Diethoxy-1,4-naphthoquinone (**8**; $C_{14}H_{14}O_4$)

A mixture of 0.55 g (2.5 mmol) **1**, 0.31 g 3,4-dimethylphenol (2.5 mmol), and 0.5 g *t*-BuOK was stirred in ethanol for 6h. The reaction mixture was worked up as mentioned above and chromatographed (silica gel, ether/cyclohexane = 1:6) to give **8** in 37% yield, m.p.: 80°C.

^{1}H NMR ($CDCl_3$): $\delta = 1.45$ (t, $J = 7$ Hz, 6H, $2CH_3$), 4.4 (q, $J = 7$ Hz, 4H, 2 OCH_2), 7.7 (m, 2H, Ar-H), 8.05 (m, 2H, Ar-H)ppm; ^{13}C NMR ($CDCl_3$): $\delta = 15.599$ (−, 2 CH_3), 69.651 (+, 2 OCH_2-2,3), 126.061 (−, Ar-CH), 130.720 (+, C-4a, C-8a), 133.982 (−, Ar-CH), 147.397 (+, C-2, C-3), 182.100 (+, 2 C=O, C-1, C-4)ppm; MS: *m/z* (%) = 246 [M^+] (35), 231 (4), 218 (34), 217 (77), 211 (9), 203 (18), 191 (13), 174 (17), 162 (100), 146 (30), 133 (18), 122 (25), 107 (34), 105 (47), 91 (7), 89 (15), 88 (23), 77 (33), 76 (31), 65 (4).

2-Ethoxy-1,4-naphthoquinone (**9**; $C_{12}H_{10}O_3$) *and 1-hydroxybenzo[b]-naphtho-[2,3-e]dioxine-6,11-quinone* (**10**; $C_{16}H_8O_5$)

A mixture of 1.14 g (5 mmol) **1**, 1.0 g pyrrogallol (7.9 mmol), and 1.0 g *t*-BuOK was refluxed in 20 ml ethanol for 6 h. The reaction mixture was concentrated to dryness and washed several times with water to remove the excess of pyrrogallol and of course *t*-BuOK. The residue was dissolved in $CHCl_3$, dried ($MgSO_4$), and filtered. The combined filtrate was concentrated and chromatographed on silica gel (ether/cyclohexane = 1:1) to give yellow crystals of **7** (43%) in the first fraction followed by **9** (9.5%) in the second fraction. The final fractions separated from the flash column gave 5% of the corresponding 1-hydroxybenzo[*b*]naphtho[2,3-*e*]dioxine-6,11-quinone (**10**).

9: M.p.: 91°C; ^{1}H NMR ($CDCl_3$): $\delta = 1.55$ (t, $J = 7$Hz, 3H, CH_3), 4.1 (q, $J = 7$ Hz, 2H, OCH_2), 6.15 (s, 1H-3), 7.65–7.8 (m, 2H, Ar-H), 8.05–8.15 (m, 1H, Ar-H), 8.2 (m, 1H, Ar-H)ppm; MS: *m/z* (%) = 202 [M^+] (100), 187 (15), 180 (2), 173 (20), 167 (2), 160 (31), 158 (79), 146 (31), 135 (3), 130 (32), 118 (7), 105 (83), 102 (40), 89 (44), 77 (30), 76 (27), 69 (16), 65 (2).

10: M.p.: 268–270°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 6.5$ (dd, $J = 1$ Hz, $J = 9$ Hz, 1H, Ar-H), 6.62 (dd, $J = 1$ Hz, $J = 9$ Hz, 1H, Ar-H), 6.83 (dd like t, $J = 0.0$ Hz, $J = 9$ Hz, 1H, Ar-H), 7.85 (m, 2H, Ar-H), 8.0 (m, 2H, Ar-H), 10.22 (s, 1H, OH)ppm; ^{13}C NMR (*DMSO*-d_6) $\delta = 107.384$, 114.404, 125.208, 125.857 (−, Ar-CH), 129.037, 129.912, 129.954 (+, Ar-C), 134.452 (−, Ar-CH), 138.948, 139.392, 141.394, 146.476 (+, Ar-C), 177.182, 177.212, (+, C=O, C-1, C-4)ppm; MS: *m/z* (%) = 280 [M^+] (100), 251 (8), 223 (6), 210 (2), 196 (9), 180 (2), 173 (30), 168 (11), 152 (3), 149 (3), 139 (12), 128 (4), 120 (3), 112 (5), 108 (38), 104 (10), 97 (3), 89 (10), 77 (8), 76 (19), 65 (2).

2-(3′-Hydroxy-4′-aldehydophenoxy)-3-chloro-1,4-naphthoquinone (**11a;** $C_{17}H_9ClO_5$) *and 2-(3′-Hydroxy-5′-aldehydophenoxy)-3-chloro-1,4-naphthoquinone* (**11b;** $C_{17}H_9ClO_5$)

A mixture of 1.14 g (5 mmol) **1** , 0.4 g 2,4-dihydroxybenzaldehyde (5 mmol), and 0.5 g K_2CO_3 was stirred in 20 ml acetone for 3 h. The reaction mixture was concentrated to dryness and washed several times with water. The residue was dissolved in $CHCl_3$, dried ($MgSO_4$), and filtered. The combined filtrate was concentrated and chromatographed on silica gel (ether/cyclohexane = 1:2) to give yellow crystals of a mixture of **11a** and **11b** in 81% overall yield. From this mixture, only **11b** could be purified sufficiently by further chromatography. **11a**: ^{1}H NMR ($CDCl_3$): $\delta = 6.5$–8.2 (m, 7H, Ar-H), 9.7 (s, 1H, CHO), 11.38 (s, 1H, OH)ppm; MS: *m/z* (%) = 329 [M^{+1}] (2), 328 [M^+] (2), 293 (2), 265 (2), 241 (1), 234 (3), 225 (1), 209 (2), 195 (1), 184 (3), 171 (1), 167 (2), 156 (2), 149 (3), 138 (82), 137 (100), 129 (2), 120 (4), 109 (12), 97 (4), 92 (9), 81 (30), 77 (4), 65 (5).

11b: M.p.: 168–169°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 6.8$–6.9 (m, 2H, Ar-H), 7.67–8.15 (m, 5H, Ar-H), 10.1 (s, 1H, CHO), 11.1 (s, 1H, OH)ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 104.222$, 108.432, 126.756, 126.919, 132.392, 134.740. 131.917, (−, Ar-CH), 118.701, 130.707, 131.670, 134.584, 151.737, 162.094, 162.781, (+, Ar-C), 177.684, 178.159, (+, 2C=O, C-1, C-4,), 191.230 (−, CHO)ppm; MS: *m/z* (%) = 329 [M^{+1}] (9), 328 [M^+] (28) 327 [M^{-1}] (100), 310 (2), 301 (7), 299 (17), 293 (58), 282

(3), 265 (58), 258 (9), 247 (7), 237 (25), 230 (8), 223 (4), 209 (27), 191 (11), 181 (14), 173 (6), 163 (31), 151 (13), 135 (29), 123 (22), 109 (7), 105 (13), 99 (32), 92 (9), 88 (15), 81 (7), 77 (13), 76 (29), 65 (54).

Naphtho[2,3-d]thiazolo[2,3-a]benzimidazol-7,12-dione (**12;** $C_{17}H_8N_2O_2S$)

A mixture of 1.14 g (5 mmol) **1** and 0.75 g 2-mercaptobenzimidazole (5 mmol) was refluxed in 20 ml pyridine for 5 h. The reaction mixture was cooled, and the precipitate formed was collected by filtration and crystallized from pyridine to give **12** as brown red crystals in 92% yield, m.p: 258°C (Ref. [6d,h]: m.p.: 265°C).

^{1}H NMR (CD_2Cl_2): $\delta = 7.45$ (m, 2H, Ar-H), 7.75–7.90 (m, 3H, ArH), 8.2–8.35 (m, 2H, Ar-H), 8.95 (d, $J = 7$ Hz, 1H, Ar-H)ppm; MS: *m/z* (%) = 304 [M^+] (21), 303 [M^{-1}] (100), 277 (2), 276 (9), 248 (5), 235 (1), 221 (1), 215 (3), 204 (4), 190 (4), 176 (9), 165 (2), 152 (5), 146 (7), 132 (7), 120 (10), 114 (3), 104 (18), 97 (2), 90 (8), 81 (4), 76 (34), 65 (2).

2-Methylaminonaphtho[2,3-d]oxazole-4,9-dione (**13;** $C_{12}H_8N_2O_3$)

A mixture of 1.14 g (5 mmol) **1** and 2.0 g methylurea (27 mmol) was heated to 200–220°C for 0.5 h. The reaction mixture was cooled and then refluxed in 20 ml ethanol for another 2 h. The solvent was removed, and the residue was washed with water several times and recrystallized from ethanol to give the oxazole derivative **13** in 62% yield, m.p.: 142–143°C.

^{1}H NMR ($CDCl_3$): $\delta = 3.4$ (d, 3H, $NHCH_3$, 6.1 (m, 1H, NH), 7.75 (m, 2H, Ar-H), 8.0 (m, 2H, Ar-H)ppm.

2-Aminonaphtho[2,3-d]imidazole-4,9-dione (**14**; $C_{11}H_7N_3O_2$)

A mixture of 0.55 g (2.5 mmol) **1** and 0.5 g guanidine was stirred in 10 ml *DMF* for 48 h. The reaction mixture was diluted with water, and the resulting precipitate was collected by filtration and recrystallized from ethanol to give red crystals of **14** in 68% yield, m.p.: 152–154°C. ^{1}H NMR (*DMSO*-d_6): $\delta = 7.45$ (s, 2H, NH_2, exchangeable with D_2O), 7.6–8.2 (m, 5H, 4H, Ar-H, 1H, NH)ppm.

Acknowledgments

We thank Prof. *H. Falk*, Institut für Chemie, Johannes-Kepler-Universität Linz, A-4040 Linz, Austria, for helpful discussions.

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Received July 8, 1997. Accepted August 8, 1997