

Tomás Torres, S. V. Eswaran, Wolfram Schäfer\*

Max-Planck-Institut für Biochemie,  
D-8033 Martinsried bei München, West Germany  
Received September 20, 1984

3-Methoxy[2,1]benzoxazole-4,7-quinones **1** and naphth[2,3-c]isoxazole-4,9-quinone **4** react with dimethyl sulfoxides to give sulfoximidoquinones **2** and **5**, sulfimidoquinones **8** and **11** respectively as major products.

*J. Heterocyclic Chem.*, **22**, 701 (1985).

We have developed before various methods for the preparation of substituted arylamino- and alkylaminobenzo- and naphthoquinones [1,2,3] and related *N*-heterocyclic quinones, such as quinazolinequinones [4], quinolinequinones [5], indazolequinones [6], [2,1]benzoxazole-4,7-quinones and naphth[2,3-c]isoxazole-4,9-quinones [7,9]. The present paper describes the synthesis of 2-dialkylsulfoximido- and 2-dialkylsulfimido-3-carbomethoxy-1,4-benzoquinone and naphthoquinone derivatives. During a study on the rearrangement of [2,1]benzoxazolequinones [9] in dimethylsulfoxide we have found that the reaction of **1** and **4** with sulfoxides and sulfides in an appropriate non polar solvent provides an interesting method for the preparation of sulfoximido- and sulfimidoquinones respectively. To our knowledge, no examples of such compounds have been described in the literature [10,11,12].

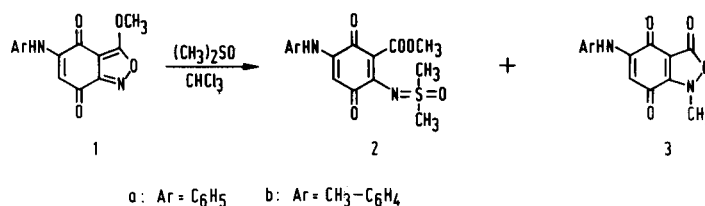
The reaction of **1** with dimethyl sulfoxide, molar ratio 1:400, in a diluted chloroform solution, during about 20 days at room temperature led to the sulfoximidoquinones

**2** in about 70% yield. As by-products (2-3% yield) isoxazolone quinones **3** were isolated as consequence of a rearrangement reaction of **1** [9].

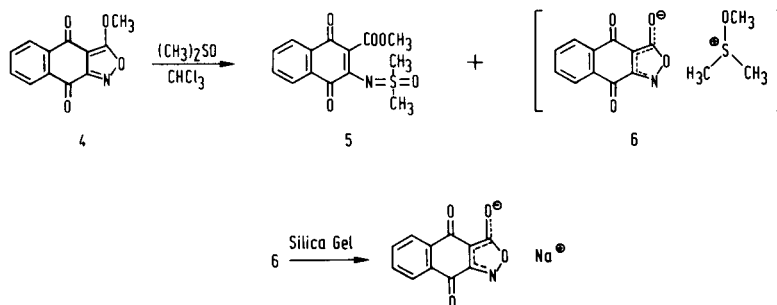
Thermolysis or photolysis of 3-methoxybenzoxazoles [13] lead to the cleavage of the N-O bond and the formation of aryl nitrenes [14,15]. The formation of **2** suggests a similar mechanism, in which a vinylogous carbomethoxy-nitrene form of **1** attacks the unshared electron pair on the sulfur atom of dimethylsulfoxide [10,12,16]. This intramolecular stabilized nitrenoid [14,15] may be favored by the presence of the electron withdrawing quinone system.

The long reaction time could not be reduced by increasing the temperature, because of the thermal instability of the isoxazolequinones of type **1** [8]. Also an increase in the concentration of **1** and dimethyl sulfoxide with the concomitant increase of the polarity of the reaction mixture led to by-products formation and yields of **2** decreased drastically. The reaction could not be carried out in more apolar solvents than chloroform because of the low solubility of **1**.

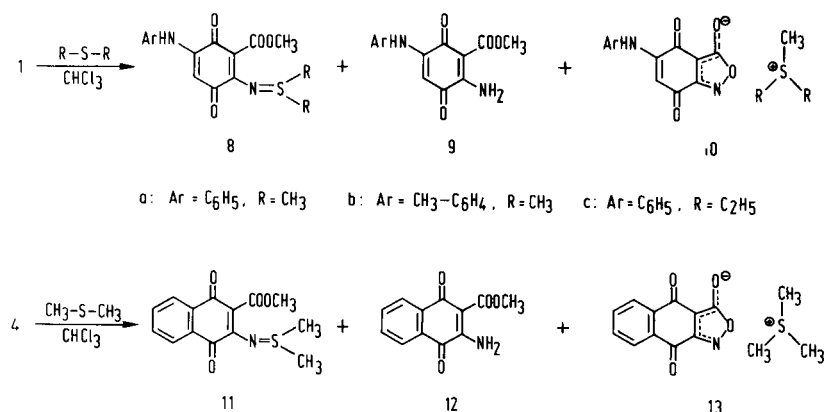
Scheme I



Scheme II



## Scheme III



The naphthisoazolequinone **4** reacted also with dimethyl sulfoxide at room temperature to give the sulfoximidoquinone **5**, but the reactions proceeded very much slower than with **1** (after 120 days the conversion was of about 50%). In this case, the reaction could be done at reflux temperature, because **4** is thermally stable under these conditions. By this way, **5** was obtained in 42% yield after about 90 hours. In this case the quinone **7** was obtained as minor product; it could be formed by cation exchange of an initially formed dimethylmethoxysulfoxonium salt **6** (not isolated) by treatment with silica gel (particle size < 0.063 mm, about 30% sodium). The salt **6** could be originated by methylation of dimethyl sulfoxide by **4**. Evidence of the behaviour of 3-methoxyisoxazolequinones of type **1** and **4** as methylating agents, as well as the formation of dimethylmethoxysulfonium salts of type **6** was obtained by <sup>1</sup>H-nmr and <sup>13</sup>C-nmr spectroscopy using deuterated compounds as substrates [9].

The structures of the sulfoximidoquinones **2** and **5** and the isoxazolonequinones **3** were established by ir, nmr and ms. In detail <sup>1</sup>H-nmr signals in **2** and **5** at  $\delta$  3.9 (singlet, 3H) and 3.4 (singlet, 6H) confirmed the presence of the methoxycarbonyl- and dimethylsulfoximido substituents respectively. Quinones **3** show two characteristic ir absorption bands in the 1800-1770 cm<sup>-1</sup> range, which are associated with stretching vibrations of the C-3 carbonyl group. The presence of a N-methyl group was established by the nmr signal at 4.1 ppm. In addition, **3** on reductive ring opening and oxidation of the intermediate hydroquinones gave 5-aryl-amino-2-methylamino-3-carboxy-1,4-benzoquinones.

Under similar reaction conditions as described above, sulfoximidoquinones **8** and **11** were isolated by the reaction of **1** and **4** with dialkylsulfides, possibly through the same mechanism mentioned above [11,17,18]. Here the reaction times were much smaller than in the reaction with dimethyl

yl sulfoxide, probably due to the enhanced nucleophilic character of the sulfur atom in alkyl sulfides.

So, **1** and dimethyl- or diethylsulfide, molar ratio 1:600, in a diluted chloroform solution formed **8** at room temperature within 30 hours in about 70% yield. The corresponding trialkylsulfonium salt **10** and the aminoquinone **9** were isolated as minor components. Starting with **4**, quinones **11**, **12** and **13** were formed under the same conditions. The main reaction product after 170 hours was in this case **13** (45% yield) whereas the sulfoximidoquinone **11** was isolated in only 22% yield.

Sulfoximidoquinones **8** and **11** are very sensitive to acidic media; with 1*N* hydrochloric acid they suffer hydrolysis to give **9** and **12**, respectively.

Sulfoximidoquinones **8** and **11** as well as the trialkylsulfonium salts **10** and **13** were characterized by their ir, nmr and ms; in addition **9** and **12** were also identified by comparison with authentic samples [1,8].

## EXPERIMENTAL

For melting points, spectroscopic apparatus and analysis, please see the preceding paper.

5-Anilino-3-carbomethoxy-2-dimethylsulfoximido-1,4-benzoquinone (**2a**).

To a stirred solution of 600 mg (2.22 mmoles) of **1a** in 600 ml of chloroform 60 ml (66 g, 0.85 mole) of dimethylsulfoxide was added. According to tlc (silica gel, chloroform-acetone 10:1), the starting material had disappeared after about 25 days. The solution was washed with water, dried, the solvent was evaporated and finally the residue was chromatographed on silica gel using chloroform as eluent. The second, dark violet zone gave 561 mg (72%) of **2a**, recrystallizing from ethyl acetate as black violet crystals, mp 199-200°; ir (potassium bromide): 3245 cm<sup>-1</sup> (NH), 1925, 1708, 1632, 1608, 1588, 1514; uv (ethanol):  $\lambda$  250 nm (log  $\epsilon$  4.14), 359 (4.26), 531 (3.13); nmr (deuteriochloroform):  $\delta$  3.39 (s, SOCH<sub>3</sub>, 6H), 3.88 (s, COOCH<sub>3</sub>, 3H), 6.01 (s, quinone-H, 1H), 7.1-7.6 (m, aromatic, 5H), 7.8 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 348 (M<sup>+</sup>, 20), 316 (M-32, 22), 144 (100).

Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>S: C, 55.16; H, 4.63; N, 8.04; S, 9.20. Found: C, 55.15; H, 4.66; N, 7.92; S, 9.27.

5-Anilino-1-methyl[2,1]benzoxazole-3(1*H*)-one-4,7-quinone (**3a**).

The first, red colored zone of the above mentioned chromatography gave 18 mg (3%) of **3a**, recrystallizing from benzene as red crystals, mp 212° dec; ir (potassium bromide): 3200 cm<sup>-1</sup> (NH), 1785, 1774, 1656, 1619, 1589, 1565, 1490; uv (ethanol): λ 245 nm (log ε 4.11), 273 sh (3.88), 361 (4.16), 492 (3.47); nmr (deuteriochloroform): δ 4.12 (s, N-CH<sub>3</sub>, 3H), 6.12 (s, quinone-H, 1H), 7.1-7.6 (m, aromatic, 5H), 8.2 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 270 (M<sup>+</sup>, 40), 144 (100).

Anal. Calcd. for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 62.23; H, 3.73; N, 10.37. Found: C, 62.00; H, 3.80; N, 10.29.

3-Carbomethoxy-2-dimethylsulfoximido-5-toluidino-1,4-benzoquinone (**2b**).

According to the method described above for the preparation of **2a** 400 mg (1.4 mmoles) of **1b**, 40 ml of dimethylsulfoxide in 400 ml of chloroform gave 354 mg (69%) of **2b** as black violet crystals, mp 224-225° dec; ir (potassium bromide): 3250 cm<sup>-1</sup> (NH), 2930, 1713, 1634, 1613, 1592, 1519; uv (ethanol): λ 249 nm (log ε 4.12), 360 (4.16), 530 (3.22); nmr (deuteriochloroform): δ 2.35 (s, CH<sub>3</sub>-Ar, 3H), 3.38 (s, SOCH<sub>3</sub>, 6H), 3.88 (s, COOCH<sub>3</sub>, 3H), 5.95 (s, quinone-H, 1H), 7.0-7.4 (m, aromatic, 4H), 7.74 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 362 (M<sup>+</sup>, 36), 330 (M-32, 37), 158 (100).

Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sub>5</sub>S: C, 56.34; H, 5.01; N, 7.73; S, 8.85. Found: C, 56.37; H, 5.18; N, 7.72; S, 8.61.

1-Methyl-5-toluidino[2,1]benzoxazole-3(1*H*)-one-4,7-quinone (**3b**).

The red colored zone from the chromatography of the above described reaction gave 10 mg (2%) of **3b** as red needles from acetone, mp 217-219°; ir (potassium bromide): 3255 cm<sup>-1</sup> (NH), 1800, 1772, 1658, 1622, 1560, 1507; uv (ethanol): λ 247 nm (log ε 4.17), 273 sh (3.92), 362 (4.17), 497 (3.56); nmr (deuteriochloroform): δ 2.39 (s, CH<sub>3</sub>-Ar, 3H), 4.13 (s, N-CH<sub>3</sub>, 3H), 6.08 (s, quinone-H, 1H), 7.0-7.5 (m, aromatic, 4H), 8.16 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 284 (M<sup>+</sup>, 59), 158 (100).

Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 63.38; H, 4.26; N, 9.85. Found: C, 63.52; H, 4.30; N, 9.82.

3-Carbomethoxy-2-dimethylsulfoximido-1,4-naphthoquinone (**5**).

To a stirred solution of 200 mg (0.87 mmole) of **4** in 250 ml of chloroform 25 ml (27.5 g, 0.35 mole) of dimethyl sulfoxide were added. After refluxing the solution for 4 days, according to the silica gel, chloroform-acetone 10:1, starting material had disappeared. The solution was washed with water, dried, evaporated and the residue was purified by chromatography on silica gel with chloroform as eluent to give 115 mg (43%) of **5**, which recrystallized from ethanol/hexane as yellow crystals, mp 177-178°; ir (potassium bromide): 1730 cm<sup>-1</sup>, 1676, 1635, 1590, 1553; uv (ethanol): λ 222 nm (log ε 4.09), 258 (4.26), 294 (3.95), 335 sh (3.46), 420 (3.53); nmr: δ 3.41 (s, SOCH<sub>3</sub>, 6H), 3.92 (s, COOCH<sub>3</sub>, 3H), 7.5-8.3 (m, aromatic, 4H); ms: 307 (M<sup>+</sup>, 35), 276 (M-31, 15), 78 (100).

Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>NO<sub>5</sub>S: C, 54.72; H, 4.26; N, 4.56; S, 10.43. Found: C, 54.67; H, 4.25; N, 4.46; S, 10.22.

3-Hydroxynaphth[2,3-*c*]isoxazole-4,9-quinone, Sodium Salt (**7**).

The aqueous extract of the above reaction was evaporated, the resulting dimethyl sulfoxide solution was diluted with chloroform and shaken with 10 g of silica gel (Woelm, Eschwege, BRD, below 0.063 mm, containing about 30% sodium, deactivated with 10% water). After filtration the solid material was washed with chloroform and then with acetone until the eluent was colorless. The acetone solution was concentrated to a volume of 5 ml. On addition of chloroform 21 mg (10%) of **7** separated as a yellow solid which was recrystallized from acetone, mp > 360°; ir (potassium bromide): 1695 cm<sup>-1</sup>, 1678, 1600, 1581, 1556; uv (ethanol): λ 235 nm (log ε 4.36), 286 (4.17), 428 (3.53); nmr (deuteriodimethylformamide): δ 7.6-7.9 (m, aromatic H-6/7, 2H), 8.0-8.3 (m, aromatic H-5/8, 2H).

Anal. Calcd. for C<sub>11</sub>H<sub>4</sub>NO<sub>4</sub>Na: C, 55.71; H, 1.70; N, 5.91. Found: C, 55.82; H, 1.88; N, 6.00.

5-Anilino-3-carbomethoxy-2-dimethylsulfinido-1,4-benzoquinone **8a**.

To a stirred solution of 300 mg (1.11 moles) of **1a** in 300 ml of chloroform, 50 ml (4.23 g, 0.68 mole) dimethyl sulfide was added. According to the control, starting material had disappeared after 30 hours. After evaporation of the solvent the residue was dissolved in 50 ml of dichloromethane, the solution was extracted with 25 ml of water and the organic phase was again evaporated to dryness. The dark residue on treatment with 15 ml of acetonitrile yielded undissolved 25 mg (8%) of 2-amino-5-anilino-3-carbomethoxy-1,4-benzoquinone **9a** [1]. From the acetonitrile solution after evaporation 244 mg (66%) of **8a** were isolated, crystallizing from ethyl acetate/*n*-hexane as black needles, mp 177°; ir (potassium bromide): 3200 cm<sup>-1</sup>, 1722, 1600, 1565; uv (ethanol): λ 251 nm sh (log ε 4.13), 283 sh (3.84), 369 (4.21), 522 (3.03); nmr (deuteriochloroform): δ 2.82 (s, S-CH<sub>3</sub>, 6H), 3.88 (s, COOCH<sub>3</sub>, 3H), 5.94 (s, quinone-H, 1H), 7.1-7.6 (m, aromatic, 5H), 8.6 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 332 (M<sup>+</sup>, 18), 300 (M-32, 22), 144 (100).

Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S: C, 57.82; H, 4.85; N, 8.43; S, 9.65. Found: C, 57.97; H, 4.88; N, 8.37; S, 9.57.

5-Anilino-3-hydroxy[2,1]benzoxazole-4,7-quinone, Trimethylsulfonium Salt **10a**.

The yellow aqueous solution obtained above on evaporation without heating gave 47 mg (13%) of **10a** which crystallized from acetonitrile/ether as yellow crystals, mp 154° dec; ir (potassium bromide): 3290 cm<sup>-1</sup>, 1711, 1698, 1632, 1581, 1560, 1510; uv (ethanol): λ 243 nm sh (4.11), 256 sh (4.18), 271 sh (4.04), 370 (4.18), 457 sh (3.35); nmr (deuteriodimethyl sulfoxide): δ 2.85 (s, S-CH<sub>3</sub>, 9H), 5.69 (s, quinone-H, 1H), 7.1-7.6 (m, aromatic, 5H), 8.9 (broad, exchangeable by deuterium oxide, NH, 1H); ms: decomposition to **3a**, m/e 270 (M<sup>+</sup>) and dimethyl sulfide m/e 62 (M<sup>+</sup>).

Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S: C, 57.82; H, 4.85; N, 8.43; S, 9.65. Found: C, 57.92; H, 4.78; N, 8.41; S, 9.25.

3-Carbomethoxy-2-dimethylsulfinido-5-toluidino-1,4-benzoquinone (**8b**).

From 150 mg (0.53 mmole) of **1b**, 25 ml (21.1 g, 0.34 mole) of dimethyl sulfide and 150 ml of chloroform according to the described procedure for the preparation of **8a**, 14 mg (9%) of **9b** [1] and 125 mg (68%) of **8b** were isolated; **8b** was recrystallized from ethyl acetate/*n*-hexane to give dark red crystals, mp 176-178° dec; ir (potassium bromide): 3200 cm<sup>-1</sup>, 1712, 1625, 1609, 1565; uv (ethanol): λ 252 nm sh (4.12), 2.84 sh (3.86), 370 (4.20), 523 (3.06); nmr (deuteriochloroform): δ 2.36 (s, CH<sub>3</sub>-Ar, 3H), 2.82 (s, S-CH<sub>3</sub>, 6H), 3.88 (s, COOCH<sub>3</sub>, 3H), 5.89 (s, quinone-H, 1H), 7.0-7.3 (m, aromatic, 4H), 8.5 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 346 (M<sup>+</sup>, 11), 314 (M-32, 18), 158 (100).

Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub>S: C, 58.94; H, 5.24; N, 8.09; S, 9.26. Found: C, 58.66; H, 5.38; N, 7.90; S, 9.16.

3-Hydroxy-5-toluidino[2,1]benzoxazole-4,7-quinone, Trimethylsulfonium Salt (**10b**).

From the yellow aqueous solution proceeding from the preparation of **8b** after evaporation, 23 mg (12%) of **10b** was obtained as yellow crystals, mp 162-164° dec from acetonitrile/ether; ir (potassium bromide): 3295 cm<sup>-1</sup>, 3010, 1710, 1628, 1614, 1580, 1560; uv (ethanol): λ 243 nm sh (log ε 4.15), 256 (4.18), 270 sh (4.04), 370 (4.14), 457 sh (3.37); nmr (deuteriodimethyl sulfoxide): δ 2.30 (s, CH<sub>3</sub>-Ar, 3H), 2.85 (s, SCH<sub>3</sub>, 9H), 5.63 (s, quinone-H, 1H), 7.21 (s, aromatic, 4H), 8.9 (broad, exchangeable by deuterium oxide, NH, 1H); ms: decomposition to **3b**, m/e 284 (M<sup>+</sup>) and dimethylsulfide, m/e 62 (M<sup>+</sup>).

Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub>S: C, 58.94; H, 5.24; N, 8.09; S, 9.26. Found: C, 58.76; H, 5.31; N, 8.01; S, 8.97.

5-Anilino-3-carbomethoxy-2-diethylsulfinido-1,4-benzoquinones (**8c**).

From 200 mg (0.74 mmole) of **1a** and 49 ml (41 g, 0.45 mole) of diethyl sulfide in 200 ml of chloroform according to the above described procedure for the preparation of **8a** besides 6 mg (3%) of **9a** [1], 184 mg (69%) of **8c** was obtained as dark red crystals, mp 159-160° dec from ethyl acet-

ate/hexane; ir: 3216  $\text{cm}^{-1}$ , 1717, 1622, 1600, 1570; uv (ethanol):  $\lambda$  252 nm sh (4.15), 283 sh (3.85), 370 (4.24), 523 (3.11); nmr (deuteriochloroform):  $\delta$  1.39 (t,  $\text{CH}_2\text{CH}_3$ , 6H), 3.05 (q,  $\text{CH}_2\text{CH}_3$ , 4H), 3.86 (s,  $\text{COOCH}_3$ , 3H), 5.94 (s, quinone-H, 1H), 7.1-7.6 (m, aromatic, 5H), 8.5 (broad, exchangeable by deuterium oxide, NH, 1H); ms: 360 ( $\text{M}^+$ ), 328 (M-32, 23), 144 (100).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ : C, 59.98; H, 5.59; N, 7.77; S, 8.90. Found: C, 60.17; H, 5.64; N, 7.77; S, 8.68.

5-Anilino-3-hydroxy[2,1]benzisoxazole-4,7-quinone, Diethylmethylsulfonium Salt (**10c**).

From the aqueous solution proceeding from the preparation of **8c** after evaporation 42 mg (16%) of **10c** were obtained as a yellow oil that could not be crystallized; ir (film): 3280  $\text{cm}^{-1}$  1715, 1630, 1587, 1560, 1510; uv (ethanol):  $\lambda$  244 nm sh (log  $\epsilon$  4.07), 257 (4.13), 272 sh (4.00), 371 (4.13), 455 sh (3.32); nmr (deuteriodimethyl sulfoxide):  $\delta$  1.34 (t, J = 7 Hz, S- $\text{CH}_2\text{-CH}_3$ , 6H), 2.85 (s, S- $\text{CH}_3$ , 3H), 3.30 (q, J = 7 Hz, S- $\text{CH}_2\text{-CH}_3$ , 4H), 5.71 (s, quinone-H, 1H), 7.1-7.6 (m, aromatic, 5H), 8.9 (broad, exchangeable by deuterium oxide, NH, 1H); ms: decomposition to **3a**, m/e 270 ( $\text{M}^+$ ) diethylsulfide, m/e 90 ( $\text{M}^+$ ) and ethylmethylsulfide, m/e 76 ( $\text{M}^+$ ). Material for elementary analysis was obtained by the following procedure: the yellow oil from four preparations, as described above, was dissolved in acetonitrile (purified for residue analysis) and centrifuged (3000 rpm). From the yellow supernatant **10c** was precipitated with absolute ether and again collected by centrifugation. The latter process was repeated three times. Purification by chromatography on silica material is impossible, because the diethylmethylsulfonium cation is substituted by a sodium cation.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ : C, 59.98; H, 5.59; N, 7.77. Found: C, 60.19; H, 5.37; N, 7.71.

3-Hydroxynaphth[2,3-c]isoxazole-4,9-quinone, Trimethylsulfonium Salt (**13**).

To a stirred solution of 200 mg (0.87 mmole) of **4** in 180 ml of chloroform 26 ml (22 g, 0.35 mole) of dimethyl sulfide were added. After seven days reaction time starting material **4** had disappeared. The solvent was evaporated. The residue was treated with chloroform giving as insoluble part after filtration 114 mg (45%) of **13** as orange crystals from acetonitrile ether, mp 175° dec; ir (potassium bromide): 3012  $\text{cm}^{-1}$ , 2920, 1704, 1672, 1609, 1590, 1560, 1505; uv (ethanol):  $\lambda$  233 nm (log  $\epsilon$  4.34), 285 (4.11), 428 (3.46); nmr (deuteriodimethyl sulfoxide):  $\delta$  2.86 (s, S- $\text{CH}_3$ , 9H), 7.5-8.2 (m, aromatic, 4H); ms: decomposition to 1-methylnaphth[2,3-c]isoxazol-3(1H)-one-4,9-quinone; ms: m/e 229 ( $\text{M}^+$ ) and dimethylsulfide, m/e 62 ( $\text{M}^+$ ).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{13}\text{NO}_4\text{S}$ : C, 57.22; H, 4.50; N, 4.81; S, 11.01. Found: C, 57.57; H, 4.56; N, 4.66; S, 11.00.

3-Carbomethoxy-2-dimethylsulfimido-1,4-naphthoquinone (**11**).

The above mentioned chloroform filtered solution was evaporated to dryness and gave on recrystallization from ethylacetate/n-hexane 57 mg (22%) of **11** as dark violet needles, mp 166-167° dec; ir (potassium bromide): 1714  $\text{cm}^{-1}$ , 1668, 1586, 1562, 1505; uv (ethanol):  $\lambda$  283 nm (log  $\epsilon$  4.03), 509 (3.65); nmr (deuteriochloroform):  $\delta$  2.83 (s, S- $\text{CH}_3$ , 6H), 3.90 (s,  $\text{COOCH}_3$ , 3H), 7.4-8.3 (m, aromatic, 4H); ms: 291 ( $\text{M}^+$ , 16), 62 (100).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{13}\text{NO}_4\text{S}$ : C, 57.72; H, 4.50; N, 4.81; S, 11.01. Found: C, 57.78; H, 4.56; N, 4.67; S, 11.17.

From the mother liquor, 11 mg (5%) of **12**, which crystallized from benzene/cyclohexane as yellow crystals, mp 145° [8], was obtained.

Acknowledgements.

We are grateful to the Deutscher Akademischer Austauschdienst (D.A.A.D.) and the Max-Planck-Gesellschaft for two postdoctoral fellowships (to S. V. E. and T. T., respectively).

## REFERENCES AND NOTES

- [1] W. Schäfer and A. Aguado, *Angew. Chem.*, **83**, 441 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 405 (1971).
- [2] M. Pardo, K. Joos and W. Schäfer, *Ann. Chem.*, 99 (1982).
- [3] W. Schäfer and A. Aguado, *Tetrahedron*, **29**, 2881 (1973).
- [4] W. Schäfer and C. Falkner, *Ann. Chem.*, 1809 (1976).
- [5] W. Schäfer and C. Falkner, *Ann. Chem.*, 1445 (1977).
- [6] N. L. Agarwal, H. Bohnstengel and W. Schäfer, *J. Heterocyclic Chem.*, **21**, 825 (1984).
- [7] W. Schäfer, H. W. Moore and A. Aguado, *Synthesis*, 30 (1974).
- [8] T. Torres, S. V. Eswaran and W. Schäfer, **22**, 697 (1985).
- [9] T. Torres, S. V. Eswaran and W. Schäfer, **22**, 705 (1985).
- [10a] L. Field, *Synthesis*, 101 (1972). [b] L. Field, *Synthesis* (Review) 713 (1978). [c] A. Mancuso and D. Swern, *Synthesis*, 165 (1981).
- [11] T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, **77**, 409 (1977).
- [12] P. D. Kennewell and B. Taylor, *Chem. Soc. Rev.*, **4**, 189 (1975); *ibid.*, **9**, 477 (1980).
- [13] B. J. Wakefield and D. J. Wright, *Adv. Heterocyclic Chem.*, **25**, 180 (1979).
- [14] P. A. S. Smith, "Arylnitrenes and Formation of Nitrenes by Rupture of Heterocyclic Rings", in W. Lwowski, ed, "Nitrenes", John Wiley and Sons, New York, 1970, p 99.
- [15] V. B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Suschitzky and P. T. Gallagher, *Angew. Chem.*, **91**, 965 (1979).
- [16] W. Lwowski, "Carbonylnitrenes", in *loc. cit.* [14] p 185 and references cited therein.
- [17] L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).
- [18] W. Ando, N. Ogino and T. Migita, *Bull. Chem. Soc. Japan*, **44**, 2278 (1971).