Regioselective Annulation of 5-(1-Alkenyl)- and 5-Vinyl-1,3-benzodioxoles with 3-Chloro-3-cyclobutene-1,2-dione. Synthesis of 3,4-Dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-diones and Cyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-diones[1]

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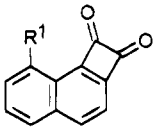
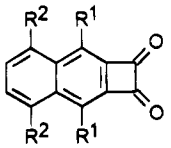
Introduction

Benzocyclobutenedione and substituted benzocyclobutenediones[2] are distinguished by their wide range of possible reactions and have been recently used as synthons as well as for the construction of complex organic molecules.[3] Several high-yield methods are available for their synthesis.[2,4] By contrast, only a small number of annulated benzocyclobutenediones (ABBDs) have been presented in the literature[1,4d,5] and there exist only a handful of reports on the reactions[5c,g–i,6] of members of this class of compounds. For example, only five benzofused benzocyclobutenediones (cyclobutanaphthalene-1,2-diones, naphthocyclobutenediones[5a]) are known. Of these, two—namely **1a**[5d] and **1b**[5g]—show angular ring fusion while the others—**2a**,[5c] **2b**,[5a] and **2c**[5h]—are condensed in a linear fashion.



1a: R^1 = H
1b: R^1 = Me



2a: $R^1 = R^2$ = H
2b: R^1 = Ph, R^2 = H
2c: R^1 = H, R^2 = Me

Cyclobuta[*a*]naphthalene-1,2-diones **1a** and **1b** were both produced by means of tedious, time consuming multistep syntheses with flash vacuum pyrolysis (FVP) as the final step. Thus, the obtained amounts of **1a** and **1b** were severely limited. The yields of the pyrolysis steps were reported to be 10 mg (20%) for **1a** and 262 mg (77%) for **1b**. Apparently for this reason the chemical reactions[6c] of the cyclobuta[*a*]naphthalene-1,2-diones have remained largely unexplored. We have recently reported on the synthesis of dihydrobenzocyclobutenediones and benzocyclobutenediones via Diels–Alder strategy, making use of 3-halo-3-cyclobutene-1,2-diones (semisquaric halides) as the dienophiles.[1,7] We will show in this communication that this may be seen as the "method of choice" for the preparation of annulated dihydrobenzocyclobutenediones and ABBDs. Our proposition is verified by the synthesis of eight substituted dihydrocyclobuta[*a*]naphthalene-1,2-diones and their dehydrogenation to the corresponding cyclobuta[*a*]naphthalene-1,2-diones. Furthermore, we will show that our method (a) may be carried out under simple and convenient experimental conditions, (b) offers satisfactory overall yields in comparison to other methods of producing ABBDs, and (c) provides access to dihydrocyclobuta[*a*]naphthalene-1,2-diones on a multigram scale, as well as cyclobuta[*a*]naphthalene-1,2-diones on a gram scale for the first time.

Results and Discussion

A solution of 3-chloro-3-cyclobutene-1,2-dione (semisquaric chloride) (**3**) and 1 equiv of 5-(1-propenyl)-1,3-benzodioxole (isosafrole) (**4a**) in dichloromethane was kept at room temperature for 3 days. During this time the solution took on a dark red color. The solvent was removed and the remaining dark brown oil subjected to column chromatography (method A). As a result one major product **A** (33%) and one minor product **B** (1%) were obtained, along with some unreacted substrate **4a**. The elemental analysis of **A** required the loss of HCl from the educts. This was confirmed by the mass spectrum which exhibited a molecular ion at *m/z* 242 (40%). Considering the reports on the reactions of isosafrole (**4a**) and (1-alkenyl)alkoxybenzenes with maleic anhydride[8] and chloromaleic anhydride,[9] and bearing in mind that, in the reaction of **3** with **4a**, ring closure may take place in the 4- or in the 6-position of isosafrole (**4a**), the structures **6a** and **6'a** came into question for compound

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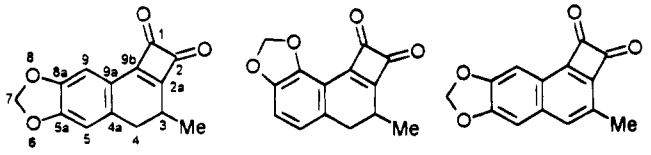
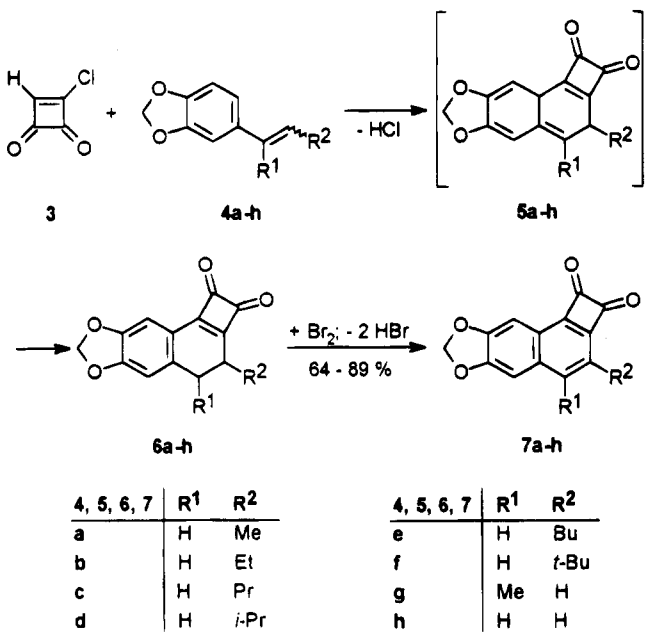


6a 6'a 7a

A. The ^{1}H NMR spectrum provided an unambiguous identification. Two singlet signals at δ 6.82 and 7.16 correspond to two protons in the para positions of a benzene ring, thus requiring that structure **6a** be attributed to compound **A**.

Following the structure elucidation of **A**, compound **B**—exhibiting a molecular ion at *m/z* 240 (11%)—was readily shown to be cyclobuta[5,6]naphthodioxoledione **7a**. It is obvious that **7a** results from dehydrogenation of 3,4-dihydrocyclobuta[5,6]naphthodioxoledione **6a** under the experimental conditions given, indicating the relative ease of this aromatization process. The aforementioned findings, together with the results obtained from the reactions of semisquaric chloride (**3**) with further 5-(1-alkenyl)-1,3-benzodioxoles **4b**–**g** and 5-vinyl-1,3-benzodioxole (**4h**), are illustrated in Scheme 1 and summarized in Table 1.

Scheme 1



3 4a-h 5a-h

6a-h 7a-h

4, 5, 6, 7	R^1	R^2
a	H	Me
b	H	Et
c	H	Pr
d	H	*i*-Pr

4, 5, 6, 7	R^1	R^2
e	H	Bu
f	H	*t*-Bu
g	Me	H
h	H	H

Table 1 shows that the reaction of semisquaric chloride (**3**) with 5-(1-alkenyl)- and 5-vinyl-1,3-benzodioxoles **4a**–**h** affords the 3,4-dihydrocyclobuta[5,6]naphthodioxole-1,2-diones **6a**–**h** according to method A with yields ranging from 15–49% (Table 1, entries 1, 3, 5, 7, 9, 11, 13, 15). Compounds **6a**–**f** may also be obtained in somewhat lower yields (19–28%), yet much more conveniently, by carrying out the reactions without a solvent at elevated temperature and working up the reaction mixtures by repeated recrystallization from ethanol (method B; Table 1, entries 2, 4, 6, 8, 10, 12). In the cases of 5-(1-isopropenyl)-1,3-benzodioxole (pseudosafrole) (**4g**) and 5-vinyl-1,3-benzodioxole (4,5-(methylenedioxy)styrene) (**4h**), reactions with semisquaric chloride (**3**) without a solvent were extremely vigorous. Decomposition took place and no products could be isolated (Table 1, entries 14 and 16). However, these reactions were carried out successfully

Table 1. Yields of 3,4-Dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-diones (6a–h) Obtained from the Reaction of Semisquaric Chloride (3) with 5-(1-Alkenyl)- and 5-Vinyl-1,3-benzodioxoles (4a–h)

entry	aliphatic-aromatic diene	method[a]	yields (%) of **6**
1	**4a**	A	**6a** 33[b,c]
2	**4a**	B	**6a** 22;[c,d] 28[d,e]
3	**4b**	A	**6b** 36[b,c]
4	**4b**	B	**6b** 25;[c,d] 24[d,f]
5	**4c**	A	**6c** 49[b,c]
6	**4c**	B	**6c** 20[c,d]
7	**4d**	A	**6d** 37[b,c]
8	**4d**	B	**6d** 20;[c,d] 26[d,f]
9	**4e**	A	**6e** 45[b,c]
10	**4e**	B	**6e** 24;[c,d] 23[d,f]
11	**4f**	A	**6f** 25[b,c]
12	**4f**	B	**6f** 19[c,d]
13	**4g**	A	**6g** 15[b,c]
14	**4g**	B	**6g** 0
15	**4h**	A	**6h** 21[b,c]
16	**4h**	B	**6h** 0

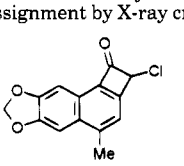
[a] Method A: In CH_2Cl_2; rt for 72 h and then removal of solvent and heating to 80 °C. Product isolated by column chromatography. Method B: Neat, rt to 80 °C within 4 h. Product obtained by repeated crystallization of the reaction mixture from ethanol. [b] Yields of pure isolated products, based on (diene **4** used–diene **4** recovered). [c] Reaction on a 0.01 molar scale. [d] Yields of pure isolated products based on diene **4** used, taking its purity into account. See Table 2. [e] Reaction on a 0.1 molar scale. [f] Reaction on a 0.02 molar scale.

when dichloromethane was used as a solvent (Table 1, entries 13 and 15). The low yield of **6g** may be explained by the isolation of an additional compound **C** ($C_{14}H_9ClO_3$)[10] from the reaction mixture with an 8% yield. The high value of this methodology for the preparation of 3,4-dihydrocyclobuta[5,6]naphthodioxole-1,2-diones **6** was further supported by a test run on a multigram scale: Thus, semisquaric chloride (**3**) (11.65 g; 0.1 mol) and isosafrole (**4a**) (16.22 g; 0.1 mol) were brought to reaction without solvent. Repeated crystallization of the crude reaction mixture afforded 6.44 g (28%) 3-methyl-2,4-dihydrocyclobuta[5,6]naphthodioxole-1,2-dione **6a** (Table 1, entry 2).

In earlier work, we have demonstrated that Diels–Alder reactions of semisquaric chloride (**3**) with aliphatic[7] and cycloaliphatic[1] dienes afforded 1,4-dihydrocyclobutenediones. We assume that the reactions of semisquaric chloride (**3**) with the aliphatic-aromatic dienes[11] **4** also lead, primarily, to 1,4-dihydrobenzocyclobutenediones **5** (Scheme 1). However, these 1,4-dihydrobenzocyclobutenediones **5** are not isolated, since an energetically favorable subsequent reaction—aromatization of the 1,3-cyclohexadiene moiety with the formation of **6**[12]—exists for them.

The 3,4-dihydrocyclobuta[5,6]naphthodioxole-1,2-diones **6** readily underwent dehydrogenation. Thus, treat-

(10) The exact structure is not clear because of low solubility and insufficient tendency to crystallize. We believe that **C** has the structure shown below. After the submission of this manuscript, strong support of this structure was obtained from the reactions of cycloaliphatic-aromatic dienes with semisquaric chloride (**3**). One of the condensation products obtained in these reactions crystallized nicely and allowed unambiguous structure assignment by X-ray crystal structure analysis.



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ment of **6a–h** with 1.2 equiv of bromine in boiling tetrachloromethane gave the corresponding cyclobuta-[5,6]naphthodioxole-1,2-diones **7a–h** in good yields (Scheme 1).

It is of note that the fully aromatized compounds **7a–h** exhibit melting points much higher than the dihydroaromatics **6a–h** (melting point difference 28–107 °C). The former compounds are also noticeably lighter in color than the latter ones (e.g. **7a**: pale-yellow; **6a**: orange).

In summary, the reaction of semisquaric chloride (**3**) with 5-(1-alkenyl)- and 5-vinyl-1,3-benzodioxoles **4** provides a facile and efficient synthesis of substituted dihydrocyclobuta[*a*]naphthalene-1,2-diones **6** and cyclobuta[*a*]naphthalenediones **7**. The synthesis is amenable to multigram scale preparation. Generalization of this methodology, as well as its application to the preparation of polycyclic and heterocyclic annulated dihydrobenzocyclobutenediones and benzocyclobutenediones, is currently under investigation.

Experimental Section

Melting points were measured in capillary tubes and are uncorrected. IR spectra were recorded as solids in KBr pellets on a Perkin-Elmer 1310 spectrometer and UV spectra on a Perkin-Elmer Lambda 2 spectrometer. Mass spectra were determined on a Varian CH 7A spectrometer at an ionizing voltage of 70 eV by electron impact. NMR spectra were obtained on a Bruker AM 400 spectrometer. ^{1}H NMR spectra were recorded at 100.6 MHz using $CDCl_3$ or DMSO-d_6 as solvent and as internal standard (δ = 76.99 and δ = 39.50, respectively) unless otherwise stated. Elemental analyses were performed by the Institute of Chemistry, University of Mainz. GC/MS spectra were recorded on a Hewlett-Packard 5890, Series II. Injection temperature was 260 °C; column temperature: 60 °C at the beginning, gradient 10 °C/min to 250 °C, and then 250 °C isothermal for 15 min; capillary column DB 624, J&W (30 m × 0.25 mm × 0.25 μm) with He as carrier gas. Analytical thin layer chromatography was performed on precoated sheets of silica gel (silica gel 60, F 254, layer thickness 0.2 mm; Riedel de Haen, Seelze). Column chromatography was performed with silica gel (silica gel 60, 70–230 mesh; Merck, Darmstadt).

Starting Materials. Semisquaric chloride (**3**) was obtained by reacting semisquaric acid[13] with oxalic dichloride[1] or with phosgene.[14] Isosafrole (**4a**) was obtained from Merck, Darmstadt. According to information provided by the manufacturer it has the following composition: (*E*/*Z*)-**4a** > 95%; (*E*)-**4a**:(*Z*)-**4a** = 85:15. The 5-(1-alkenyl)-1,3-benzodioxoles **4b–g** and 5-vinyl-1,3-benzodioxole (**4h**) were produced by means of the Grignard reaction of 5-formyl-1,3-benzodioxole (piperonal) from Janssen Chimica, Brüggen, with the appropriate alkylmagnesium halide and subsequent thermal dehydration of the resulting alcohol.

5-(1-Alkenyl)-1,3-benzodioxoles 4b–g and 5-Vinyl-1,3-benzodioxole (4h). General procedure. The appropriate alcohol (0.25 mol) was heated on an oil bath to 180 °C while being stirred magnetically. The water released was continuously distilled off over a period of 1–2 h. The remaining liquid was vacuum distilled twice. The yields and the compositions of the aliphatic-aromatic dienes **4b–h** thus obtained are summarized in Table 2.

Table 2. Yields and Physical Properties of 5-(1-Alkenyl)-1,3-benzodioxoles 4b–g and 5-Vinyl-1,3-benzodioxole (4h)

compd	bp (°C/*p*)	yield (%)	purity (*E*/*Z*)-**4** (%)	ratio (*E*)-**4**:(*Z*)-**4**
4b	130–132 / 12 mm (130–131 / 14 mm)[15]	59	93	94:6
4c	140 / 12 mm (90–92 / 0.3 mm)[16]	60	92	95:5
4d	140 / 12 mm	77	84	98:2
4e	154 / 12 mm (95–97 / 0.15 mm)[16]	89	96	96:4
4f	140 / 0.05 mbar	57	91	100:0
4g	70 / 0.02 mbar 135 / 20 mm)[17]	59	98	–
4h	60 / 0.05 mbar (107–108 / 5 mm)[18]	48	98	–

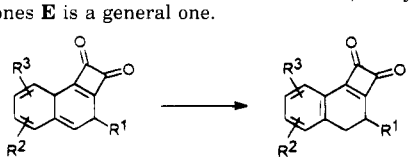
3-Methyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]-dioxole-1,2-dione (6a). Method A: A solution of semisquaric chloride (**3**) (1.16 g, 10 mmol) and isosafrole (**4a**) (1.62 g, 10 mmol) in CH_2Cl_2 (30 mL) was stirred magnetically at rt for 72 h. The solvent was removed under reduced pressure, and the reaction mixture was kept *in vacuo* at 80 °C until its color changed from dark red to brown and no further HCl was released (ca 60 min). The reaction mixture was subjected to column chromatography (silica gel 500 g) using CH_2Cl_2 as eluent to give the components according to the following order of elution: unreacted isosafrole (**4a**): 0.46 g (28%), **7a**: 0.02 g (1%); mp 246–247 °C. **6a**: Orange crystals; mp 139–140 °C (EtOH); yield 0.58 g (33%); IR 1770–1750 (vs, br), 1610 (w), 1560 (m) (C=O; C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 3H; J = 9.9 Hz), 2.76 (dd, 1H, J = 10.3 Hz, J = 16.5 Hz), 3.09 (dd, 1H, J = 7.7 Hz), 3.31 (m, 1H), 6.04 (s, 2H), 6.82 (s, 1H), 7.16 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.74, 29.35, 36.34, 102.07, 106.77, 109.86, 118.92, 133.96, 147.18, 152.59, 191.64, 194.36, 194.51, 198.85; UV (CH_3OH) λ_{max} (log ϵ) 201 nm (4.39), 246 (4.05), 288 (3.91); MS *m*/*z* (relative intensity) 242 (M^+, 40), 214 (47), 186 (52), 155 (27), 128 (100). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.30; H, 4.05.

Method B: Semisquaric chloride (**3**) (1.16 g, 10 mmol) and isosafrole (**4a**) (1.62 g, 10 mmol) were combined, and the mixture was heated with magnetical stirring as follows: at 40 °C for 1 h; at 50 °C for 2 h; at 80 °C for 1 h. The red color of the reaction mixture increased in intensity up to 50 °C. Beginning at ca 60 °C, HCl was released and removed *in vacuo*. The color changed slowly to brown and the viscosity of the reaction mixture increased. Heating was stopped when no further HCl was released. The reaction mixture was triturated with hexane (3 × 30 mL). The solid obtained was recrystallized three times from ethanol (90 mL each time), the second time with the aid of charcoal, to give pure **6a**. Yield 0.51 g (22%).

Preparation on a multigram scale: **3** (11.65 g, 0.1 mol) and **4a** (16.22 g, 0.1 mol) were mixed together, and the mixture was heated with magnetical stirring as follows: at 40 °C for 1.5 h; at 50 °C for 6 h; at 60 °C for ca. another 1 h. Released HCl was removed *in vacuo*. When no more HCl was set free, the brown, viscous oil was triturated with hot hexane (10 × 50 mL). The resulting solid was recrystallized from ethanol (3 × 600 mL); the second time with the aid of charcoal to give pure **6a**. Yield 6.44 g (28%).

3-Ethyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]-dioxole-1,2-dione (6b). Method A: Prepared as described for **6a**; unreacted **4b**: 0.53 g (30%). **7b**: 0.02 g (1%), mp 182–183 °C. **6b**: Orange crystals; mp 150–151 °C (EtOH); yield 0.64 g (36%); IR 1770–1740 (vs, br), 1600 (w), 1560 (m) (C=O; C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, 3H, J = 7.4 Hz), 1.57–1.86 (m, 2H), 2.84 (dd, 1H, J = 8.6 Hz, J = 16.1 Hz), 3.06–3.21 (m, 2H), 6.04 (s, 2H), 6.82 (s, 1H), 7.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 11.73, 25.25, 34.08, 36.58, 102.05, 106.85, 109.83, 119.05, 134.24, 147.16, 152.60, 191.98, 194.41, 194.52, 198.77; UV (CH_3OH) λ_{max}

(12) Unpublished work from our group clearly demonstrates that the transformation of 1,3-cyclohexadieno-annulated 1,4-dihydrobenzocyclobutenediones **D** into benzo-annulated 1,2-dihydrobenzocyclobutenediones **E** is a general one.



D **E**

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(log ϵ) 202 nm (4.31), 247 (4.25), 286 (4.00); MS *m/z* (relative intensity) 256 (M^+, 71), 228 (64), 200 (68), 185 (100), 172 (40). Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.27; H, 4.88.

Method B: prepared as described for **6a**; yield 0.59 g (25%).

3-*n*-Propyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]-dioxole-1,2-dione (6c). Method A: Prepared as described for **6a**; unreacted **4c**: 0.55 g (29%). **7c**: none. **6c**: Orange crystals; mp 114–115 °C (EtOH); yield 0.94 g (49%); IR 1770–1740 (vs, br), 1600 (w), 1560 (m) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, 3H, J = 7.2 Hz), 1.47–1.79 (m, 4H), 2.83 (dd, 1H, J = 8.4 Hz, J = 16.5 Hz), 3.10 (dd, 1H, J = 7.8 Hz), 6.04 (s, 2H), 6.82 (s, 1H), 7.22 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.92, 20.38, 34.25, 34.39, 34.70, 102.96, 106.88, 109.87, 119.10, 134.16, 147.21, 152.61, 191.84, 194.48, 194.60, 199.03; UV (CH_3OH) λ_{max} (log ϵ) 202 nm (4.31), 247 (4.23), 287 (4.01); MS *m/z* (relative intensity) 270 (M^+, 44), 242 (25), 214 (8), 186 (100), 127 (23). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.92; H, 5.03.

Method B: prepared as described for **6a**; yield 0.49 g (20%).

3-*i*-Propyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-d][1,3]-dioxole-1,2-dione (6d). Method A: Prepared as described for **6a**; unreacted **4d**: 0.45 g (24%). **7d**: 0.12 g (6%), mp 248–249 °C. **6d**: Orange crystals; mp 190–191 °C (EtOH); yield (0.76 g (37%); IR 1780–1750 (vs, br), 1600 (w), 1565 (m) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, 3H, J = 6.8 Hz), 1.10 (d, 3H, J = 6.8 Hz), 2.00–2.08 (m, 1H), 2.92–3.14 (m, 3H), 6.04 (s, 2H), 6.82 (s, 1H), 7.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.80, 20.59, 30.66, 31.87, 42.15, 102.04, 106.81, 109.64, 119.06, 134.75, 147.11, 152.64, 192.59, 194.44, 194.51, 198.44; UV (CH_3OH) λ_{max} (log ϵ) 203 nm (4.30), 248 (4.24), 288 (4.07); MS *m/z* (relative intensity) 270 (M^+, 67); 242 (48); 214 (18); 199 (100); 172 (70); 141 (45); 115 (35). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.90; H, 5.11.

Method B: prepared as described for **6a**; yield 0.46 g (20%).

3-*n*-Butyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]-dioxole-1,2-dione (6e). Method A: Prepared as described for **6a**; unreacted **4e**: 0.61 g (30%). **7e**: none. **6e**: Orange crystals; mp 100–101 °C (EtOH); yield 0.89 g (45%); IR 1770–1750 (vs, br), 1605 (w), 1565 (m) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J = 7.2 Hz), 1.27–1.80 (m, 6H), 2.79–2.85 (dd, 1H, J = 8.4 Hz, J = 16.4 Hz), 3.06–3.12 (dd, 1H, J = 7.8 Hz), 6.02 (s, 2H), 6.80 (s, 1H), 7.17 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.76, 22.48, 29.16, 31.69, 34.28, 34.81, 102.03, 106.67, 109.83, 118.91, 134.16, 147.09, 152.55, 191.68, 194.44, 194.50, 198.97; UV (CH_3OH) λ_{max} (log ϵ) 203 nm (4.31), 247 (4.23), 287 (4.02); MS *m/z* (relative intensity) 284 (M^+, 64), 256 (25), 228 (10), 213 (100), 141 (28). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.81; H, 5.67. Found: C, 71.63; H, 5.73.

Method B: prepared as described for **6a**; yield 0.66 g (24%).

3-*tert*-Butyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]-dioxole-1,2-dione (6f). Method A: Prepared as described for **6a**; unreacted **4f**: 0.96 g (47%). **7f**: none. **6f**: Orange crystals; mp 222–224 °C (EtOH); yield 0.37 g (25%); IR 1775–1755 (vs, br), 1600 (w), 1560 (m) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 9H), 2.95–3.02 (m, 3H), 6.03 (s, 2H), 6.82 (s, 1H), 7.20 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.86, 30.54, 34.07, 47.10, 102.03, 106.65, 109.47, 118.87, 135.29, 147.09, 152.70, 192.68, 194.09, 194.55, 198.57; UV (CH_3OH) λ_{max} (log ϵ) 202 nm (4.29), 248 (4.19), 289 (4.08); MS *m/z* (relative intensity) 284 (M^+, 57), 256 (34), 228 (5), 172 (100), 141 (18). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.81; H, 5.67. Found: C, 71.53; H, 5.52.

Method B: prepared as described for **6a**; yield 0.48 g (19%).

4-Methyl-3,4-dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]-dioxole-1,2-dione (6g). Method A: Prepared as described for **6a** with the exception that heating at 80 °C was omitted; unreacted **4g**; 0.36 g (22%). Compound **C**: 0.16 g (8%) mp 231–232 °C (toluene). Anal. Calcd for $C_{14}H_9ClO_3$: C, 64.51; H, 3.48; Cl 13.60. Found: C, 64.22; H, 3.41; Cl, 13.31. **7f**: 0.1 g (5%) mp 275–277 °C. **6f**: Orange crystals; mp 183–184 °C (EtOH); yield 0.28 g (15%); IR 1790–1750 (vs, br), 1605 (w), 1570 (m) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, 3H, J = 7.1 Hz), 2.90 (dd, 1H, J = 4.8 Hz, J = 19.0 Hz), 3.10 (dd, 1H, J = 7.6 Hz), 3.22 (m, 1H), 6.04 (s, 2H), 6.85 (s, 1H), 7.20 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.83, 29.66, 33.47, 102.11, 106.96, 108.92, 118.19, 140.11, 147.07, 152.86, 191.99, 194.19, 194.77, 195.15; UV (CH_3OH) λ_{max} (log ϵ) 210 nm (4.34), 253 (4.21), 294 (4.02); MS *m/z* (relative intensity) 242 (M^+, 65), 214 (96), 186 (51), 128 (100). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.41; H, 4.10.

Method B: Semisquaric chloride (**3**) (1.16 g, 10 mmol) and pseudosafrole (**4g**) (1.62 g, 10 mmol) were combined and left at rt. The reaction mixture heated up very strongly over a period of ca. 5 min. Then a vigorous reaction took place with the evolution of gases. The remaining black solid was unsoluble in common organic solvents.

3,4-Dihydrocyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (6h). Method A: Prepared as described for **6a**; unreacted **4h**: 0.25 g (17%). **7h**: none. **6h**: Orange crystals; mp 215–216 °C (EtOAc); yield 0.40 g (21%); IR 1790–1750 (vs, br), 1605 (w), 1565 (m) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06 (t, 4H, J = 2.9 Hz), 6.06 (s, 2H), 6.87 (s, 1H), 7.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.27, 27.95, 102.73, 107.03, 110.13, 119.59, 134.88, 147.62, 153.03, 193.09, 194.84, 194.91, 196.30; UV (CH_3OH) λ_{max} (log ϵ) 210 nm (4.32), 253 (4.18), 293 (3.94); MS *m/z* (relative intensity) 228 (M^+, 49), 200 (82), 172 (100). Anal. Calcd for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found: C, 67.87; H, 3.56.

Method B: As described for **6g**.

Aromatization of 3,4-Dihydrocyclobuta[5,6]naphtho-dioxole-1,2-diones. Generation of Cyclobuta[5,6]naphtho-dioxole-1,2-diones 7a–h. General Procedure. To the suspension of 3,4-dihydrocyclobuta[5,6]naphthodioxole-1,2-dione **6a–h** (1.2 mmol) in CCl_4 (30 mL) was added bromine (0.23 g, 1.4 mmol) in one portion. The mixture was stirred magnetically and heated at reflux until no further HBr was generated (ca. 3–4 h). On cooling to −15 °C the product precipitated. It was collected by vacuum filtration and recrystallized.

3-Methylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7a): yellow crystals; mp 246–247 °C (MeCN); yield 0.22 g (76%); IR 1800, 1770, 1780–1740 (vs, br), 1605 (m) (C=O; C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.57 (s, 3H), 6.30 (s, 2H), 7.53 (s, 1H), 7.58 (s, 1H), 7.93 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 16.70, 101.48; 102.66, 105.15, 120.02, 127.69, 134.11, 135.84, 150.03, 151.80, 172.02, 172.45, 193.74; UV (CH_3OH) λ_{max} (log ϵ) 202 nm (4.32), 223 (4.29), 259 (4.09), 289 (4.67); MS *m/z* (relative intensity 240 (M^+, 11), 212 (28), 184 (100), 126 (85), 76 (30). Anal. Calcd for $C_{14}H_8O_4$: C, 70.00; H, 3.35. Found: C, 69.86; H, 3.43.

Preparation on a Gram Scale. A suspension of **6a** (2.00 g, 8.3 mmol) in CCl_4 (200 mL) was heated to reflux. Then a solution of bromine (1.92 g, 12.0 mmol) in CCl_4 (40 mL) was added over 10 min. The reaction mixture was heated at reflux for 3 h. The solvent was removed *in vacuo*, and the remaining solid was recrystallized from MeCN to give pure **7a**. Yield 1.27 g (64%).

3-Ethylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7b): yellow crystals; mp 182–183 °C (acetone); yield 0.22 g (72%); IR 1780–1740 (vs, br), 1605 (m), 1550 (w) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3H, J = 7.5 Hz), 2.97 (q, 2H, J = 7.5 Hz), 6.18 (s, 2H), 7.24 (s, 1H), 7.63 (s, 1H), 7.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.28, 25.68, 102.42, 102.98, 105.18, 121.05, 134.11, 134.51, 135.46, 150.22, 152.21, 173.52, 173.66, 193.81, 194.33; UV (CH_3OH) λ_{max} (log ϵ) 201 nm (4.38), 223 (4.24), 260 (4.04), 289 (4.64); MS *m/z* (relative intensity) 254 (M^+, 52), 226, (40), 198 (100), 170 (19), 139 (59). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 70.80; H, 4.12.

3-*n*-Propylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7c): yellow crystals; mp 168–170 °C (acetone); yield 0.23 g (71%); IR 1780–1740 (vs, br), 1600 (m), 1560 (w) (C=O; C=C) cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$) δ 0.93 (t, 3H, J = 7.3 Hz), 1.72–1.82 (m, 2H), 2.85 (t, 2H, J = 7.4 Hz), 6.26 (s, 2H), 7.50 (s, 1H), 7.51 (s, 1H), 7.87 (s, 1H); ^{13}C NMR (DMSO-d_6/$CDCl_3$) δ 13.24, 22.55, 33.58, 101.62, 102.56, 105.22, 120.28, 132.77, 134.14, 135.08, 150.05, 151.86, 172.48, 172.59, 193.42, 193.71; UV (CH_3OH) λ_{max} (log ϵ) 202 nm (4.35), 222 (4.32), 260 (4.10), 289 (4.71); MS *m/z* (relative intensity) 268 (M^+, 91), 240 (46), 212 (100), 184 (95), 128 (11). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.28; H, 4.40.

3-Isopropylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7d): yellow crystals; mp 248–249 °C (acetone); yield 0.23 g (71%); IR 1780–1740 (vs, br), 1600 (m), 1555 (w) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (d, 6H, J = 6.9 Hz), 3.22–3.29 (m, 1H), 6.19 (s, 2H), 7.27 (s, 1H), 7.68 (s, 1H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.83, 32.40, 102.45, 103.11, 105.37, 121.20, 132.52, 134.69, 140.94, 150.31, 152.32, 173.46, 174.03, 193.42, 194.43; UV (CH_3OH) λ_{max} (log ϵ) 202 nm (4.37), 222 (4.29), 259 (4.08), 289 (4.67); MS *m/z* (relative intensity) 268 (M^+, 65), 240

(40), 225 (52), 212 (100), 197 (24), 170 (23), 153 (29), 139 (75). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.26; H, 4.52.

3-*n*-Butylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7e): yellow crystals; mp 155–156 °C (EtOH); yield 0.23 g (68%); IR 1780–1740 (vs, br), 1600 (m), 1560 (w) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3H, J = 7.4 Hz), 1.35–1.40 (m, 2H), 1.73–1.80 (m, 2H), 2.93 (t, 2H, J = 7.6 Hz), 6.18 (s, 2H), 7.24 (s, 1H), 7.63 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.76, 22.25, 29.21, 32.14, 102.48, 103.03, 105.23, 121.12, 134.27, 134.52, 134.84, 150.28, 152.25, 173.66, 173.73, 193.93, 194.46; UV (CH_3OH) λ_{max} (log ϵ) 203 nm (4.36) 223 (4.34), 260 (4.13), 289 (4.75); MS *m/z* (relative intensity) 282 (M^+, 49), 254 (24), 226 (16), 184 (100). Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 4.99. Found: C, 71.96; H, 4.84.

3-*tert*-Butylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7f): yellow crystals; mp 250–251 °C (*n*-PrOH); yield 0.26 g (77%); IR 1780–1740 (vs, br), 1600 (m), 1560 (w) (C=O; C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (s, 9H), 6.19 (s, 2H), 7.29 (s, 1H), 7.69 (s, 1H), 7.72 (s, 1H); ^{13} C NMR ($CDCl_3$) δ 30.05, 34.85, 102.44, 102.99, 105.62, 120.83, 130.81, 134.67, 144.34, 150.36, 152.38, 174.09, 174.24, 192.92, 194.44; UV (CH_3OH) λ_{max} (log ϵ) 211 nm (4.35), 230 (4.36), 266 (4.13), 296 (4.72); MS *m/z* (relative intensity) 282 (M^+, 51); 254 (21); 226 (100); 153 (46). Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 4.99. Found: C, 72.05; H, 4.89.

4-Methylcyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7g): yellow crystals; mp 275–277 °C (*n*-BuOH); yield 0.26 g (90%); IR 1785–1755 (vs, br), 1605 (m) (C=O; C=C) cm^{-1}; MS *m/z* (relative intensity) 240 (M^+, 34); 212 (59); 184 (100); 126 (25). Anal. Calcd for $C_{14}H_8O_4$: C, 70.00; H, 3.36. Found: C, 69.60; H, 3.51.

Cyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (7h): yellow crystals; mp 294–296 °C (xylene, *n*-BuOH); yield 0.26 g (96%); IR 1790–1740 (vs, br), 1620 (w), 1600 (w); MS *m/z* (relative intensity) 226 (M^+, 39); 198 (69); 170 (100); 112 (15). Anal. Calcd for $C_{13}H_6O_4$: C, 69.03; H, 2.67. Found: C, 69.08, H, 2.67.

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