General Synthetic Entry to Linearly-Fused Dihydrobenzocyclobutene-1,2-diones and Benzocyclobutene-1,2-diones via Annulation of 1,2-Bis(methylene)carbocycles with 3-Chloro-3-cyclobutene-1,2-dione[1]

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The tandem Diels−Alder/dehydrochlorination reaction of semisquaric chloride (**1**) with the 1,2-bis(methylene)cycloalkanes **2a**−**c** and 1,2-bis(methylene)-4-cyclohexene (**9**) affords the linearly-fused cycloalkanodihydrobenzocyclobutene-1,2-diones **3a**−**c** and 3,4,7,8-tetrahydrocyclobuta[*b*]-naphthalene-1,2-dione (**10**), respectively. On treatment with MnO_2, **3a**−**c** are dehydrogenated to the respective carbocycle-fused benzocyclobutene-1,2-diones **4a**−**c** in good yields. **3a** and **3b** react with bromine to give the addition products **5a**,**b**, which, on treatment with silver trifluoroacetate, afford the benzocyclobutene-1,2-diones **4a**,**b**. For preparative purposes, the sequence **3** → **5** → **4** can be performed advantageously as a "one-pot procedure". Double-condensation reactions of **4a**,**b** with α,α′-biscyano-*o*-xylene and *o*-phenylenediamine afford the pentacyclic biphenylenes **7a**,**b** and the cyclobutahetarenes **8a**,**b**, respectively. These cyclobutenediones suggest themselves as building blocks for the construction of extended linearly-fused polycyclic compounds with novel ring sequences. *o*-Quinodimethanes **12a**−**g** generated in situ by the thermal decomposition of the respective 1,4-dihydro-2,3-benzoxathiin-3-oxides (sultines) **11a**−**g** react with semisquaric chloride (**1**) to afford the 3,8-dihydronaphtho[*b*]cyclobutene-1,2-diones **13a**−**g**. These, on dehydrogenation with bromine and/or MnO_2, furnish the naphtho[*b*]cyclobutene-1,2-diones **14a**−**g** in fair to good yields. As described for **4a**,**b** the naphtho[*b*]cyclobutene-1,2-diones **14a**−**c** are condensed with α,α′-biscyano-*o*-xylene and *o*-phenylenediamine to furnish the pentacyclic biphenylenes **15a**−**c** and the pentacyclic cyclobutahetarenes **16a**−**c**.

Introduction

Benzocyclobutene-1,2-dione and substituted benzocyclobutene-1,2-diones[2] have recently attracted much attention as synthons as well as in the construction of complex organic molecules.[3] By contrast, only a limited number of angularly-fused benzocyclobutenediones[1,4] have been presented in the literature, and only three linearly-fused benzocyclobutenediones[5−7] have come to our attention. Moreover, linearly-fused hydrogenated benzocyclobutenediones, such as 3,8-dihydronaphtho[*b*]-cyclobutene-1,2-diones, represent an unknown class of compounds.

Recently,[1,4d−f] we have reported that (1-alkenyl)arenes readily undergo Diels−Alder reactions with 3-chlorocyclobutene-1,2-dione (semisquaric chloride) (**1**)[8] to give angularly fused dihydrobenzocyclobutenediones, which can subsequently be dehydrogenated to yield angularly fused benzocyclobutenediones. For potential wider applicability, we have now extended this procedure, developing a simple, straightforward synthesis of linearly-fused dihydrobenzocyclobutenediones **C** (Scheme 1).

Scheme 1 outlines the Diels−Alder reaction of a 1,2-bis(methylene)carbocycle **A** with semisquaric chloride (**1**) to give **B**, followed by regiospecific elimination of hydrogen chloride to furnish **C**. Dehydrogenation of **C** then affords the desired linearly-fused benzocyclobutenedione **D**.

(1) Oxocarbons and Related compounds. 29. Part 28: Schmidt, A. H.; Kircher, G.; Zylla, J.; Veit, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 409.

(2) For reviews, see: (a) Schmidt, A. H.; Ried, W. *Synthesis* **1978**, 869. (b) Butenschön, H. In *Houben-Weyl, Methods of Organic Chemistry*; de Meijere, A., Ed.; Georg Thieme Verlag: Stuttgart, New York, 1997; Vol. E 17f; pp 972 and 1027.

(3) For leading references, see: (a) Staab, H. A.; Ipaktschi, J. *Tetrahedron Lett.* **1966**, 583. (b) Staab, H. A.; Ipaktschi, *J. Chem. Ber.* **1968**, *101*, 1457. (c) Jung, M. E.; Lowe, J. A. *J. Org. Chem.* **1977**, *42*, 2371. (d) Spangler, L. A.; Swenton, J. S. *J. Org. Chem.* **1984**, *49*, 1800 and references therein. (e) Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351. (f) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Iyer, S.; Leeds, J. P. *Tetrahedron* **1985**, *41*, 5839 and references therein. (g) Spangler, L. A.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1986**, 828. (h) Liebeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065. (i) Petri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067. (j) Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1987**, *52*, 1174. (k) Liebeskind, L. S.; Chidambaram, R.; Mitchell, D.; Foster, B. S. *Pure Appl. Chem.* **1988**, *60*, 27. (l) Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989. (m) Liebeskind, L. S. *Tetrahedron* **1989**, *44*, 3053. (n) Mitchell, D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 291.

(4) (a) Gould, K. J.; Hacker, N. P.; McOmie, J. F. W.; Perry, D. H.; *J. Chem. Soc., Perkin, Trans. 1* **1980**, 1834. (b) Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Saminathan, S. *Aust. J. Chem.* **1987**, *40*, 107. (c) Schmidt, A. H.; Künz, C.; Malmbak, M.; Zylla, J. *Synthesis* **1994**, 422. (d) Schmidt, A. H.; Kircher, G.; Künz, C.; Wahl, S.; Hendriok, M. W. *J. Org. Chem.* **1995**, *60*, 3890. (e) Schmidt, A. H.; Lechler, K. O.; Pretz, T.; Franz, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 497. (f) Schmidt, A. H.; Kircher, G.; Spring, M.; Hendriok, M. W.; Künz, C. *J. Prakt. Chem./Chem.-Ztg.* **1997**, *339*, 564.

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(7) Brown, R. F. C.; Browne, N. R.; Coulston, K. J.; Eastwood. F. W. *Aust. J. Chem.* **1990**, *43*, 1935.

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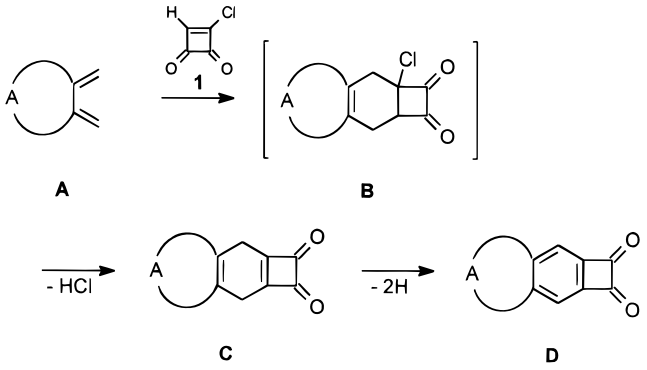
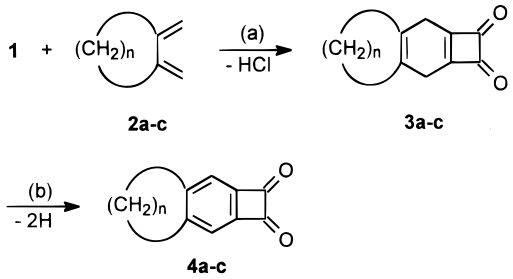
Scheme 1



Results and Discussion

We began by examining the reaction of semisquaric chloride (**1**) with the 1,2-bis(methylene)cycloalkanes **2a**−**c**, which were prepared by treatment of the respective 2-methylcycloalkanone with KO-*t*-Bu following literature procedures.[9] On combining **1** with 1,2-bis(methylene)-cyclohexane (**2a**) in dichloromethane, the solution immediately took on a deep-red color and began to boil gently. The red oil crystallized at 80 °C under reduced pressure and furnished 3,4,5,6,7,8-hexahydrocyclobuta-[*b*]naphthalene-1,2-dione (**3a**) in 53% yield. The higher homologues **3b** and **3c** were obtained with similar yields (59%; 51%) under the same reaction conditions (Scheme 2).

Scheme 2[a]



compound	n
2a, 3a, 4a,	4
2b, 3b, 4b,	5
2c, 3c, 4c,	6

[a] Reaction conditions: (a) in CH_2Cl_2; rt for 12 h, then heating to 80 °C for 4 h; (b) MnO_2 in benzene; reflux for 4 h.

It was found that dehydrogenation of the dihydrobenzocyclobutenediones **3a**−**c** was conveniently accomplished by means of activated MnO_2. The desired cycloalkanobenzocyclobutenediones **4a**−**c** were thus obtained with high purity and good yields (Scheme 2 and Table 1).

Dehydrogenation of **3a**−**c** was attempted, in analogy to well-established procedures,[4c−f] by treatment with bromine. While **3c** afforded the desired hexahydrocyclobutabenzocyclooctene-1,2-dione **4c** in 92% yield (Table 1, entry 9), dehydrogenation of **3a** and **3b** was, surprisingly, not observed under such conditions. Instead, addition of bromine to the central C=C double bond took place[10] and the dibromo adducts **5a**,**b** were obtained (Scheme 3).

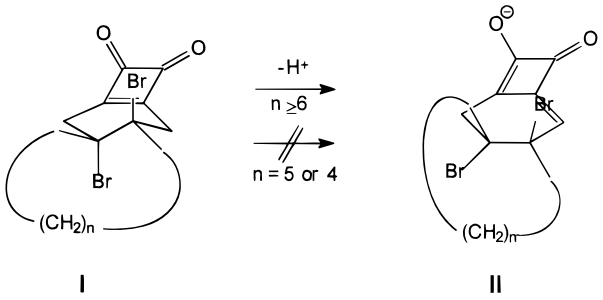
(9) Arenz, T.; Vostell, M.; Frauenrath, H. *Synlett* **1991**, 23.

Table 1. Yields of Cycloalkano-Annulated Benzocyclobutene-1,2-diones 4a−c Obtained by Dehydrogenation of the Dihydrobenzocyclobutene-1,2-diones 3a−c

entry	substrate	conditions	yields (%) of **4**
1	**3a**	MnO_2; benzene	**4a**, 61
2	**3a**	Br_2/$AgOCOCF_3$; EtOH	**4a**, 46
3	**3a**	H_2O_2/HCOOH	**4a**, 30
4	**3a**	I_2/AcOH	**4a**, 73
5	**3a**	Chloramine T; H_2O/EtOH	**4a**, 66
6	**3b**	MnO_2; benzene	**4b**, 63
7	**3b**	Br_2/$AgOCOCF_3$; EtOH	**4b**, 53
8	**3c**	MnO_2; benzene	**4c**, 78
9	**3c**	Br_2; EtOH	**4c**, 92

Treatment of the dibromo-adduct **5a** with Bu_3SnH was expected to yield the octahydronaphthocyclobutene-1,2-dione **6**. Yet, hexahydronaphthocyclobutene-1,2-dione **3a** was the only product obtained. We finally succeeded in the generation of **6** by the addition of HBr to **3a** and successive treatment of the reaction mixture with Bu_3SnH. In this way, **6** was obtained with 39% yield.

We assume that the action of bromine on **3a**−**c** leads to the *trans* adducts **I** ($n = 4-6$). The elimination of HBr occurs via deprotonation of a CH_2 group in the cyclohexene ring and subsequent formation of the anions **II**.



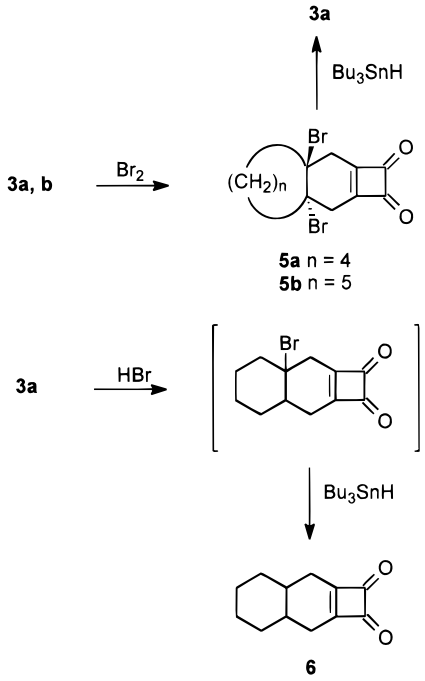
The delocalization of **II** requires a nearly flat conformation of the cyclohexene ring. The dihedral angle between both carbons at the ends of the cycloalkane ring increases from approximately 60° (staggered conformation) to approximately 120° (eclipsed conformation). A similar large dihedral angle is not possible for the cyclohexane ring (**II**: $n = 4$) and leads to a large internal ring strain for the cycloheptane ring (**II**: $n = 5$). However, for all rings with $n \geq 6$ (cyclooctane and above) this dihedral angle is not a limiting factor. The observed reaction behavior, therefore, agrees with the *trans* conformation of the dibromides **I**. In contrast, one would expect that the three conformeric *cis*-dibromides (with $n = 4-6$) would all be easily dehydrobrominated.

Structure **6** forms by a radical exchange of a bromine atom with a hydrogen atom via tributyltin hydride (Bu_3SnH). A mixture of cis and *trans* conformations should result. Experiments to separate the conformers have so far failed.

As outlined in Scheme 4, treatment of **5a**,**b** with 2 equiv of silver trifluoroacetate resulted in smooth elimination of AgBr and trifluoroacetic acid to give the desired cycloalkanobenzocyclobutene-1,2-diones **4a**,**b**. The sequence **3** → **5** → **4** could also be performed as a "one-pot

(10) Similar behavior has been reported for 3,6-dihydrobenzocyclobutene-1,2-dione which, on treatment with bromine, afforded a dibromo addition product: Carpino, L. A.; Tsao, J.-H. *J. Org. Chem.* **1979**, *44*, 2387.

Scheme 3



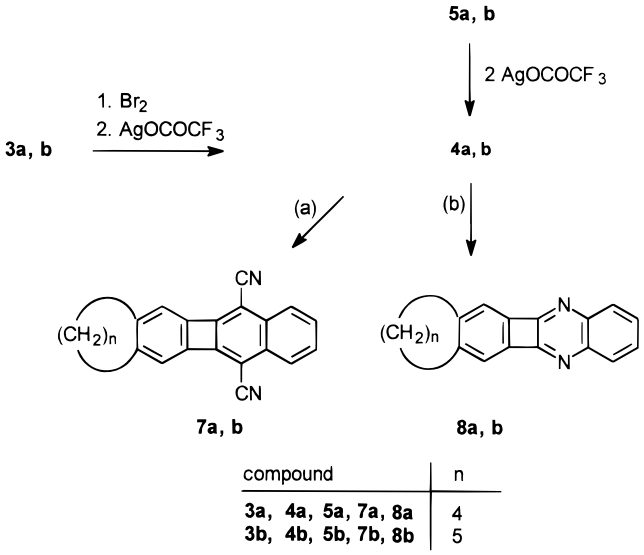
procedure". Yields are given in Table 1, entries 2 and 7. It is interesting to note that treatment of **3a** with double-bond reagents such as H_2O_2/formic acid, I_2/acetic acid, and chloramine T did not furnish addition products but resulted in aromatization of the cyclohexadiene-moiety of **3a** to give **4a**. Yields are presented in Table 1; see entries 3−5.

To test the ability of cycloalkano-annulated benzocyclobutene-1,2-diones to undergo double-condensation reactions with bisnucleophiles, **4a**,**b** were reacted with α,α′-biscyano-*o*-xylene and *o*-phenylenediamine. As expected,[11,12] the linearly fused pentacyclic cyclobutarenes **7a**,**b** and the cyclobutahetarenes **8a**,**b** were obtained (Scheme 4).

Subsequently, the reaction of **1** with 4,5-bis(methylene)cyclohexene (**9**) was performed, and it was found that the annulation proceeded even more vigorously to give 3,4,7,8-tetrahydrocyclobuta[*b*]naphthalene-1,2-dione (**10**) with 83% yield (Scheme 5). Attempts to selectively dehydrogenate **10** with Br_2, MnO_2, or DDQ proved fruitless. The experiments afforded complex mixtures of products from which single compounds could not be isolated. As indicated by MS, the crude reaction mixture obtained from the treatment of **10** with MnO_2 contained two cyclic anhydrides in addition to dehydrogenation products. The presence of the two cyclic anhydrides suggests an easy oxidation of the cyclobutenedione moiety in **10** and/or its dehydrogenation products.

On the basis of the above results, we decided to evaluate the suitability of semisquaric chloride (**1**) as a trapping reagent for 4,5-bis(methylene)-1,3-cyclohexadienes (*o*-quinodimethanes). *o*-Quinodimethanes act as highly reactive diene components in [4 + 2]-cycloaddition reactions, and they have proved very useful for the construction of polycyclic compounds.[13] The first procedure that we tested for the generation of *o*-quinodimethane (**12a**) was the treatment of α,α′-dibromo-*o*-xylene with powdered zinc in DMF as reported by Alder and Fremery.[14] These authors showed that under such conditions *o*-quinodimethane (**12a**) is generated in good yield and can be trapped with dienophiles (maleic anhydride, acrylonitrile, ethyl acrylate, acrolein), producing tetralin derivatives. We found, however, that on addition of zinc dust to a solution of semisquaric chloride (**1**) and α,α′-dibromo-*o*-xylene in DMF the solution became black. Workup of the reaction mixture yielded only resinous products. A control experiment investigating the stability of semisquaric chloride (**1**) in DMF verified that **1** suffers rapid decomposition in this solvent (almost complete destruction within 20 min at room temperature). From a great number of further procedures that we tested for the generation of *o*-quinodimethanes and their subsequent trapping with semisquaric chloride (**1**) in vain, two further methods deserve special mention as they are commonly found in the literature: (a) the reaction of α,α′-dibromo-*o*-xylene with Zn in dioxane under ultrasound sonication[15] and (b) the reaction of α,α,α′-tribromo-*o*-xylene with NaH in THF.[16] Finally, we turned to a thermal extrusion procedure for the generation of *o*-quinodimethane (**12a**) under mild and neutral conditions.

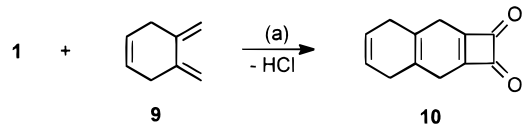
Scheme 4[a]



compound	n
3a, 4a, 5a, 7a, 8a	4
3b, 4b, 5b, 7b, 8b	5

[a] Reaction conditions: (a) α,α′-biscyano-*o*-xylene, DBU cat., CH_3CN, reflux for 5 min; (b) *o*-phenylenediamine, AcOH cat., EtOH, reflux for 30 min.

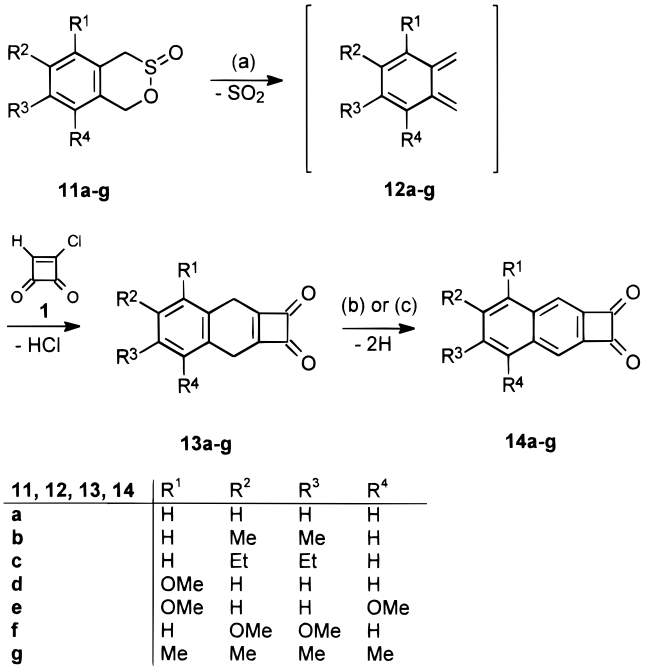
Scheme 5[a]



[a] Reaction conditions: (a) in CH_2Cl_2; rt for 36 h, then heating to 80 °C for 30 min.

(11) Buckland, P. R.; Hacker, N. P.; McOmie, J. F. W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1443.
(12) Abou-Teim, O.; Hacker, N. P.; Jansen, R. B.; McOmie, J. F. W.; Perry, D. H. J *J. Chem. Soc., Perkin Trans. 1* **1981**, 988.
(13) For reviews, see: (a) Oppolzer, W. *Synthesis* **1978**, 793. (b) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. (c) Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3. (d) Charlton, J. L.; Alauddin, M. N. *Tetrahedron* **1987**, *43*, 2873.
(14) Alder, K.; Fremery, M. *Tetrahedron* **1961**, *14*, 190.
(15) Han, B. H.; Boudjouk, P. *J. Org. Chem.* **1982**, *47*, 751.
(16) Becker, C. L.; McLaughlin, M. L. *Synlett* **1991**, 642.

Scheme 6[a]



11, 12, 13, 14	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	Me	Me	H
c	H	Et	Et	H
d	OMe	H	H	H
e	OMe	H	H	OMe
f	H	OMe	OMe	H
g	Me	Me	Me	Me

[a] Reaction conditions: (a) in benzene; reflux for 2 h, then evaporating and heating to 70 °C for 15 min; (b) Br_2 in AcOH; reflux for 2.5 h; (c) MnO_2 in benzene; reflux for 45 min.

Table 2. Yields of 3,8-Dihydronaphtho[*b*]cyclobutene-1,2-diones 13a−g Obtained from the Reaction of Semisquaric Chloride (1) with *o*-Quinodimethanes 12a−g Generated in Situ by the Thermal Decomposition of the Sultines 11a−g

entry	sultine	[substrate]	solvent	yields (%) of **13**
1	**11a**	[**12a**]	benzene	**13a**, 51
2	**11b**	[**12b**]	benzene	**13b**, 58
3	**11c**	[**12c**]	benzene	**13c**, 48
4	**11d**	[**12d**]	benzene	**13d**, 48
5	**11e**	[**12e**]	benzene	**13e**, 75
6	**11f**	[**12f**]	benzene	**13f**, 12
7	**11f**	[**12f**]	$CHCl_3$	**13f**, 43
8	**11g**	[**12g**]	benzene	**13g**, 44

Durst[17] and co-workers showed that 1,4-dihydro-2,3-benzoxathiin-3-oxide (**11a**) decomposes smoothly in refluxing benzene to give the *o*-quinodimethane (**12a**) and sulfur dioxide. Here, maleic anhydride was used successfully as the trapping reagent. Using this procedure, we succeeded in the generation of *o*-quinodimethane (**12a**) and its trapping with semisquaric chloride (**1**). Recrystallization of the crude reaction product provided 3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (**13a**) with 51% yield. Treatment of **13a** with bromine resulted in a clean aromatization affording naphtho[*b*]cyclobutene-1,2-dione (**14a**) with 94% yield (Scheme 6). The aforementioned findings, together with the results obtained from the reactions of semisquaric chloride (**1**) with the substituted *o*-quinodimethanes **12b**−**g** obtained *in situ* by the thermal decomposition of the respective sultines **11b**−**g** are illustrated in Scheme 6. Yields of products are summarized in the Tables 2 and 3.

Table 2 shows that the reactions of semisquaric chloride (**1**) with the *o*-quinodimethanes **12a**−**g** afford the 3,8-dihydronaphtho[*b*]cyclobutene-1,2-diones in fair to good yields (entries 1−5) with the exception of 5,6-dimethoxy-3,8-didydronaphtho[*b*]cyclobutene-1,2-dione (**13f**). Following the typical preparation procedure (entry 6), **13f** was only obtained in 12% yield. In a modified procedure, the thermal instability of the sultine **12f** was taken into account. $CHCl_3$ was used as the solvent, and a cooled solution of **12f** was added into the boiling solution of semisquaric chloride (**1**) dropwise. Thus, the yield of the 3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione **13f** could be enhanced to a satisfactory 43% (entry 7). It should be noted that 5,8-diacetoxy-1,4-dihydro-2,3-benzoxathiin-3-oxide, in the presence of semisquaric chloride (**1**), is thermally stable in boiling benzene. Black tarry products were obtained, however, when the controlled thermal extrusion of SO_2 in boiling xylene in the presence of semisquaric chloride was attempted.

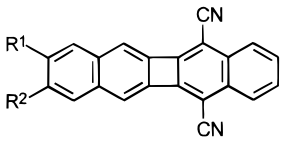
Table 3. Yields of Naphtho[*b*]cyclobutene-1,2-diones 14a−g Obtained by the Dehydrogenation of the 3,8-Dihydronaphtho[*b*]cyclobutene-1,2-diones 13a−g

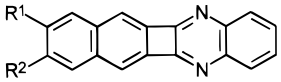
entry	substrate	conditions	yields (%) of **14**
1	**13a**	Br_2/AcOH	**14a**, 94
2	**13b**	Br_2/AcOH	**14b**, 83
3	**13c**	Br_2/AcOH	**14c**, 84
4	**13d**	MnO_2/benzene	**14d**, 86
5	**13e**	Br_2/AcOH	**14e**, 38
6	**13e**	MnO_2/benzene	**14e**, 45
7	**13f**	Br_2/AcOH	**14f**, 91
8	**13g**	Br_2/AcOH	**14g**, 67

Table 3 demonstrates that aromatization of the 3,8-dihydronaphtho[*b*]cyclobutene-1,2-diones **13a**−**g** can equally well be accomplished by bromine (entries 1−3, 5, 7, and 8) and MnO_2 (entries 4 and 6). The use of bromine is preferred due to the homogeneity of the reaction solutions.

In conclusion, the sequence **11** → [**12**] → **13** → **14** represents a fair-yielding two-step synthesis of naphtho-[*b*]cyclobutene-1,2-diones. A notable practical feature of this methodology is that no chromatography is required at any stage and gram batches can be conveniently prepared. Thus, the procedure seems superior to both the hydrolytic[5,6] and the pyrolytic[7,18] procedure, which have been applied to the synthesis of all naphtho[*b*]cyclobutene-1,2-diones (*vide supra*) mentioned so far.

As described for the cycloalkanobenzocyclobutene-1,2-diones **4a**,**b**, the naphtho[*b*]cyclobutene-1,2-diones **14a**−**c** were reacted with α,α′-biscyano-*o*-xylene and *o*-phenylenediamine to furnish the linearly-fused pentacyclic cyclobutarenes **15a**−**c** and cyclobutahetarenes **16a**−**c**, respectively, in fair to good yields.





15a: $R^1 = R^2 = H$ (48%)
15b: $R^1 = R^2 = Me$ (52%)
15c: $R^1 = R^2 = Et$ (39%)

16a: $R^1 = R^2 = H$ (82%)
16b: $R^1 = R^2 = Me$ (85%)
16c: $R^1 = R^2 = Et$ (71%)

In summary, the reaction of semisquaric chloride (**1**) with 1,2-bis(methylene)carbocycles provides a facile and efficient synthesis of linearly-fused dihydrobenzocyclo-

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butene-1,2-diones and benzocyclobutene-1,2-diones. Application of this methodology to specially substituted 1,2-bis(methylene)carbocycles, as well as its extension to the preparation of linearly heterocycle-fused dihydrobenzocyclobutenediones, is currently under investigation.

Experimental Section

For general experimental techniques, see our previous paper.[19] In extension, the NMR spectra of several of the newly prepared compounds were recorded on a Bruker AMX 500 spectrometer (^{1}H NMR, 500 MHz; ^{13}C NMR, 125 MHz).

Starting Materials. Semisquaric chloride (**1**) was obtained by reacting semisquaric acid[20] with phosgene[8] or with oxalic dichloride.[4c] 1,2-Bis(methylene)cycloalkanes **2a**−**c**[9] and 4,5-bis(methylene)cyclohexene (**9**)[21] were prepared according to literature procedures. The sultines **11a**−**g** were obtained by the reaction of the respective α,α′-dibromo-*o*-xylene with sodium hydroxymethane sulfinate·2H_2O (rongalite) following the experimental directions given by Hoey and Dittmer.[22] Details and modifications of the preparation procedures of **11a**−**g**, 5,8-diacetoxy-1,4-dihydro-2,3-benzoxathiin-3-oxide, and further differently substituted sultines as well as observations concerning their thermal stability (rearrangement to 1,3-dihydrobenzo[*c*]thiopene-2,2-dioxides) will be published elsewhere. Activated MnO_2 was purchased from Aldrich.

3,4,5,6,7,8-Hexahydrocyclobuta[*b*]naphthalene-1,2-dione (3a). Typical Procedure. To a solution of the diene **2a** (1.08 g, 10 mmol) in CH_2Cl_2 (20 mL) was added semisquaric chloride (**1**) (1.16 g, 10 mmol) in the same solvent (5 mL). The solution turned red immediately and heated gently. It was kept at room temperature for 12 h. The solvent was then removed *in vacuo*, and the resulting oil was kept at 70−80 °C for 4 h. HCl evolved, and the oil solidified. The solid was dissolved and submitted to column chromatography (silica gel; CH_2Cl_2/acetone; 50/1 as eluent): pale yellow crystals; mp 130−131 °C (EtOH); yield 1.00 g (53%); IR 1790−1755 (vs), 1660 (w), 1590 (s) (C═O, C═C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63−1.66 (m, 4H), 1.97−2.00 (m, 4H), 3.19 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.68, 29.90, 30.22, 124.14, 196.81, 201.22; UV (MeOH) λ_{max} (log ϵ) 205 nm (4.33); MS *m*/*z* (relative intensity) 188 (M^+, 50), 160 (12), 159 (31), 132 (18), 131 (49), 117 (36), 104 (100), 91 (57). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.39; H, 6.47.

4,5,6,7,8,9-Hexahydro-1*H*-cyclobuta[4,5]benzo[1,2]cycloheptene-1,2(3*H*)-dione (3b). Prepared as described for compound **3a**: pale yellow crystals; mp 131−132 °C (EtOH); yield (59%). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.25; H, 7.02.

3,4,5,6,7,8,9,10-Octahydrocyclobuta[4,5]benzo[1,2]cyclooctene-1,2-dione (3c): pale yellow crystals; mp 145−147 °C (EtOH); yield (51%). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.91; H, 7.57.

4,5,6,7-Tetrahydrocyclobuta[*b*]naphthalene-1,2-dione (4a). Dehydrogenation of 3a with MnO_2. Typical Procedure. To a solution of **3a** (0.40 g, 2.1 mmol) in benzene (20 mL) was added MnO_2 (2.60 g, 30 mmol). The suspension was stirred and heated to reflux for 4 h. It was filtrated and the solvent removed *in vacuo*. The solid was crystallized from EtOH to give **4a** as yellow crystals: mp 150−151 °C (EtOH); yield 0.24 g (61%); 1790−1770 (vs), 1600 (w), 1570 (m) (C═O, C═C) cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 1.82−1.86 (m, 4H), 2.91−2.94 (t, 4H, J = 6.3 Hz), 7.67 (s, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 21.91, 30.81, 121.77, 147.97, 170.90, 194.40; UV (MeOH) λ_{max} (log ϵ) 195 nm (4.38), 236 (4.65), 310 (3.93), 320 (3.92); MS *m*/*z* (relative intensity) 186 (M^+, 13), 158 (100), 130 (14), 129 (31), 115 (33). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.53; H, 5.36.

Dehydrogenation of 3a with Bromine/Silver Trifluoroacetate. To a solution of **3a** (0.60 g, 3.18 mmol) in EtOH (25 mL) was added bromine (0.56 g, 3.5 mmol) in the same solvent (5 mL). It was heated until the brown color had completely disappeared (ca. 5 min) before a solution of silver trifluoroacetate (1.55 g, 7.0 mmol) in EtOH (10 mL) was added. The reaction mixture was heated to reflux for 1.5 h and filtrated from precipitated AgBr and the solvent removed *in vacuo*. Upon cooling, the solid crystallized to give **4a**: yellow crystals; mp 140−150 °C (EtOH); yield 0.27 g (46%).

Treatment of 5a with Silver Trifluoroacetate. To a boiling solution of *trans*-3a,7a-dibromooctahydrocyclobuta[*b*]naphthalene-1,2-dione **5a** (0.80 g, 2.3 mmol) in EtOH (20 mL) was added a solution of silver trifluoroacetate (1.07 g, 4.8 mmol) in EtOH (10 mL). The reaction mixture was heated to reflux for 1 h and filtered while hot. The filtrate was evaporated to dryness, and the resulting solid was crystallized from EtOH to give **4a** as yellow crystals: mp 149−151 °C; yield 0.19 g (44%).

Dehydrogenation of 3a with H_2O_2/HCOOH. To a solution of H_2O_2 (0.3 g, 35% in H_2O) in HCOOH (10 mL) was added **3a** (0.40 g, 2.1 mmol) under stirring. The reaction mixture was heated to 75 °C for 2 h and then evaporated to dryness. The residue was treated with HCl (18%, 40 mL) and the mixture heated to 100 °C for 1 h. The mixture was then extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried ($MgSO_4$) and evaporated to dryness. The resulting solid was crystallized from EtOH to give **4a**: yellow crystals; mp 148−150 °C; yield 0.12 g (30%).

Dehydrogenation of 3a with I_2/AcOH. To a solution of **3a** (0.40 g, 2.1 mmol) in AcOH (20 mL) was added iodine (0.55 g, 2.2 mmol). The solution was kept at room temperature for 24 h before it was heated to reflux for 3 h and subsequently poured into a solution of $Na_2S_2O_3$ (3 g) in water (200 mL) with vigorous stirring. After extraction with CH_2Cl_2 and the usual workup, the residue was crystallized from EtOH to give **4a**: yellow crystals; mp 149−151 °C; yield 0.29 g (73%).

Dehydrogenation of 3a with Chloramine T. To a solution of **3a** (0.20 g, 1.05 mmol) in water (5 mL), EtOH (15 mL), and AcOH (0.5 mL) was added chloramine T·3H_2O (0.6 g, 2.1 mmol). It was heated to reflux for 1 h then cooled to room temperature. The precipitate was collected by filtration to give **4a**: yellow crystals; mp 148−149 °C (EtOH); yield 0.13 g (66%).

5,6,7,8-Tetrahydro-1*H*-cyclobuta[4,5]benzo[1,2]cycloheptene-1,2(4*H*)-dione (4b). Dehydrogenation of 3b with MnO_2. Prepared as described for **4a**: yellow crystals; mp 142−144 °C (EtOH); yield (63%). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.78; H, 6.02.

Dehydrogenation of 3b with Bromine/Silver Trifluoroactetate. Prepared as described for **4a**: yellow crystals; mp 140−142 °C (EtOH); yield (53%).

Treatment of 5b with Silver Trifluoroacetate. Prepared as described for **4a**: yield of **4b** 51%.

4,5,6,7,8,9-Hexahydrocyclobuta[4,5]benzo[1,2]cyclooctene-1,2-dione (4c). Dehydrogenation of 3c with MnO_2. Prepared as described for **4a**: yellow crystals; mp 182−184 °C (EtOH); yield (78%). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.18; H, 6.51.

Dehydrogenation of 3c with Bromine. A solution of **3c** (0.12 g, 0.55 mmol) in EtOH (10 mL) was heated to reflux, and bromine (0.10 g, 0.61 mmol) in EtOH (5 mL) was added with stirring. After 5 min, the brown color had disappeared. Subsequently, half of the solvent was evaporated *in vacuo*. When the remaining solution was cooled to −15 °C, **4c** crystallized: yield 0.10 g (84%); mp 181−183 °C.

***trans*-3a,7a-Dibromo-3,3a,4,5,6,7,7a,8-octahydrocyclobuta[*b*]naphthalene-1,2-dione (5a).** To a boiling solution of **3a** (0.60 g, 3.2 mmol) in EtOH (20 mL) was added bromine (0.56 g, 3.5 mmol) in the same solvent (5 mL). The brown color faded within 5 min. It was then heated to reflux for 5 min. On cooling to −15 °C, **5a** crystallized from the solution: white crystals; mp 137 °C (EtOH); yield 0.80 g (72%); 1800, 1780

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(vs), 1600 (s) (C═O, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.64−1.82 (m, 2H), 1.89−2.02 (m, 2H), 2.06−2.10 (m, 2H), 2.19−2.26 (m, 2H), 3.46−3.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.78, 37.56, 41.74, 71.18, 195.61, 198.95; UV (MeOH) λ_{max} (log ϵ) 231 nm (4.29), 310 (3.51), 320 (3.46); MS *m/z* (relative intensity) 350 (M^+, 5), 348 (M^+, 11), 346 (M^+, 5), 322 (5), 320 (11), 318 (5) 159 (100). Anal. Calcd for $C_{12}H_{12}Br_2O_2$: C, 41.41; H, 3.48; Br 45.92. Found: C, 41.57; H, 3.52; Br 45.56.

***trans*-3a,8a-Dibromo-3a,4,5,6,7,8,8a,9-octahydro-1*H*-cyclobuta[4,5]benzo[1,2]cycloheptene-1,2(3*H*)-dione (5b).** Prepared as described for **5a**: white crystals; mp 120−121 °C (EtOH); yield (64%). Anal. Calcd for $C_{13}H_{14}Br_2O_2$: C, 43.13; H, 3.90; Br 44.14. Found: C, 43.35; H, 3.89; Br 44.01.

3,3a,4,5,6,7,7a,8-Octahydrocyclobuta[*b*]naphthalene-1,2-dione (6). A solution of **3a** (1.00 g, 5.3 mmol) in HBr (30 mL, 36% in AcOH) was stirred at room temperature overnight. It was then poured onto water (150 mL) and the mixture extracted with CH_2Cl_2 (3 × 50 mL). The organic phase was washed with water (3 × 50 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The residue was kept *in vacuo* (3 × 10^{-3} mm) for 30 min and then dissolved in benzene (20 mL). To this solution were added Bu_3SnH (1.9 g, 6.5 mmol) and AIBN (catalytic amount), and the reaction mixture was refluxed for 1 h. The solvent was evaporated, and the residue was subjected to column chromatography (silica gel 60) using CH_2Cl_2/acetone (50:1 vol/vol) as eluent. **6** was obtained as pale yellow crystals: mp 68−69 °C (*n*-heptane); yield 0.39 g (39%); IR 1780 (vs), 1600 (s) (C═O, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05−1.13 (m, 2H), 1.20−1.25 (m, 2H), 1.32−1.43 (m, 2H), 1.72−1.78 (m, 2H), 1.87−1.90 (m, 2H), 2.14−2.23 (m, 2H), 2.83−2.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.18, 30.92, 33.65, 37.71, 197.31, 204.00; UV (MeOH) λ_{max} (log ϵ) 217 nm (4.16); MS *m/z* (relative intensity) 190 (M^+, 68), 162 (100), 134 (8), 119 (29), 105 (51), 92 (85). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.64; H, 7.36.

7,8,9,10-Tetrahydrodibenzo[*b*,*h*]biphenylene-5,12-dicarbonitrile (7a). A solution of α,α′-dicyano-*o*-xylene (0.30 g, 1.9 mmol) and DBU (three drops) in acetonitrile (10 mL) was heated to reflux. Within 10 min, a solution of the cyclobutene-1,2-dione **4a** (0.30 g, 1.6 mmol) in the same solvent (15 mL) was added dropwise. The reaction mixture was heated to reflux for 5 min and cooled to room temperature, and the precipitate collected by filtration: yellow crystals; mp 251−252 °C (toluene); yield 0.32 g (62%); IR 2230 (m), 1600 (w), (C≡N, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.74−1.77 (m, 4H), 2.66 (s, 4H), 6.78 (s, 2H), 7.42−7.46 (m, 2H), 7.69−7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.39, 30.53, 99.02, 114.04, 122.53, 126.23, 128.96, 130.67, 143.55, 143.90, 153.43; UV (MeOH) λ_{max} (log ϵ) 201 nm (4.85), 262 (4.67), 285 (4.68), 304 (4.60), 382 (4.02), 403 (4.32), 428 (4.48); MS *m/z* (relative intensity) 306 (M^+, 100), 279 (41), 265 (11). Anal. Calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61; N 9.14. Found: C, 86.09; H, 4.58; N 9.07.

8,9,10,11-Tetrahydro-7*H*-benzo[*b*]cyclohepta[*h*]biphenylene-5,13-dicarbonitrile (7b). Prepared as described for compound **7a**: yellow crystals; mp 235−236 °C (*n*-BuOH); yield 58%. Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N 8.74. Found: C, 86.11; H, 4.98; N 8.77.

7,8,9,10-Tetrahydronaphtho[2′,3′:3,4]cyclobuta[1,2-*b*]-quinoxaline (8a). To a solution of the cyclobutene-1,2-dione **4a** (0.13 g, 0.7 mmol) and AcOH (three drops) in EtOH (10 mL) was added a solution of *o*-phenylenediamine (0.09 g, 0.7 mmol) in the same solvent (3 mL). The reaction mixture was heated to reflux for 30 min and cooled to room temperature and the precipitate collected by filtration: yellow-green crystals; mp 218−220 °C (ethylene glycol monomethyl ether); yield 0.14 g (72%); IR 1640 (m), 1580 (m), (C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.74−1.77 (m, 4H), 2.71−2.74 (t, 4H, J = 6.2 Hz), 7.09 (s, 2H), 7.33−7.35 (m, 2H), 7.57−7.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.43, 30.59, 122.96, 128.09, 128.90, 142.39, 143.88, 151.49, 168.78; UV (MeOH) λ_{max} (log ϵ) 201 nm (4.66), 223 (4.40), 232 (4.38), 240 (4.41), 270 (4.68), 296 (4.17), 364 (4.16), 380 (4.41), 401 (4.44); MS *m/z* (relative intensity) 258 (M^+, 100), 230 (20), 129 (12), 115 (12). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.79; H, 5.36; N, 10.77.

8,9,10,11-Tetrahydro-7H-cyclohepta[4′,5′]benzo[1′,2′:3,4]cyclobuta[1,2-*b*]quinoxaline (8b). Prepared as described for compound **8a**: yellow-green crystals; mp 273−275 °C (ethylene glycol monomethyl ether); yield 56%. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.61; H, 5.94; N, 10.16.

3,4,7,8-Tetrahydrocyclobuta[*b*]naphthalene-1,2-dione (10). To a solution of the diene **9** (2.12 g, 20 mmol) in CH_2Cl_2 (20 mL) was added semisquaric chloride (**1**) (2.32 g, 20 mmol) in the same solvent (10 mL). The reaction mixture began to reflux vigorously and took on a deep red color. It was kept at room temperature for 36 h. The solvent was then removed in vacuo and the resulting oil kept at 80 °C for 30 min. While at 80 °C the oil solidified. This solid was triturated with EtOH, filtered, and crystallized from toluene: white crystals; mp 178−181 °C dec (toluene); yield 3.10 g (83%); IR 1800−1755 (vs), 1660 (m), 1620−1590 (s) (C═O, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 4H), 3.23 (s, 4H), 5.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.26, 31.24, 121.96, 123.56, 196.51, 200.84; UV (MeOH) λ_{max} (log ϵ) 211 nm (4.18); MS *m/z* (relative intensity) 186 (M^+, 66), 158 (25), 130 (30), 129 (100), 115 (74). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.53; H, 5.36.

3,8-Dihydronaphtho[*b*]cyclobutene-1,2-dione (13a). Typical Procedure. A solution of semisquaric chloride (**1**) (2.5 g, 21.5 mmol) and 1,4-dihydro-2,3-benzoxathiin-3-oxide (**11a**) (4.4 g, 26 mmol) in benzene (40 mL) was heated to reflux for 2 h. The solution took on a dark red color. HCl was released, and a white solid precipitated. The solvent was removed, and the residue was kept under reduced pressure at 60−70 °C for 15 min. The solid was triturated with boiling EtOH and then recrystallized from EtOAc to afford **13a**: white crystals; mp 191−194 °C dec (toluene); yield 2.02 g (51%); IR 1800−1770 (vs), 1640 (m), 1620 (s), 1570 (m) (C═O, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.12 (s, 4H), 7.28 (s, 4H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 28.88, 128.36, 129.97, 130.33, 196.69, 201.19; UV (MeOH) λ_{max} (log ϵ) 209 nm (4.38); MS *m/z* (relative intensity) 184 (M^+, 37), 156 (11), 128 (100), 102 (15). Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.31; H, 4.36.

5,6-Dimethyl-3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (13b). Prepared as described for compound **13a**: white crystals; mp 234−235 °C (toluene); yield (58%). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.69. Found: C, 79.17; H, 5.61.

5,6-Diethyl-3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (13c). Prepared as described for compound **13a**: white crystals; mp 166−167 °C (EtOAc); yield 48%. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.87; H, 6.84.

4-Methoxy-3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (13d). Prepared as described for compound **13a**: white crystals; mp 190−191 °C dec (EtOAc); yield 48%. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.55; H, 4.66.

4,7-Dimethoxy-3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (13e). Prepared as described for compound **13a**. The crude product was purified by filtration over silica gel using CH_2Cl_2/acetone (50/1) as eluent: slightly red crystals; mp 244−245 °C dec ($CHCl_3$); yield 75%. Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.79; H, 5.03.

5,6-Dimethoxy-3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (13f). Following the typical preparation procedure for **13a**, a mixture of products was obtained. The mixture was submitted to column chromatography (CH_2Cl_2/acetone (50/1) as eluent), and components were obtained in the following order of elution. **13f**: slightly yellow powder; mp 277−278 °C (ethylene glycol monomethyl ether); yield 12%; IR 1785 (vs), 1740 (s), 1610 (s), 1570 (m) (C═O, C═C) cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 202 nm (4.40), 286 (3.34); MS *m/z* (relative intensity). 244 (M^+, 100), 216 (56), 188 (22), 145 (44), 115 (41). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.74; H, 5.01. 1,3-Dihydro-5,6-dimethoxybenzo[*c*]thiophene-2,2-dioxide: white crystals; mp 181−182 °C (acetone); yield 1,48 g (65%); ^1H NMR ($CDCl_3$) δ 3.83 (s, 6H), 4.26 (s, 4H), 6.73 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 56.16, 57.17, 108.67, 123.01, 149.90; MS *m/z* (relative intensity) 208 (M^+, 10), 164 (100). Anal. Calcd

for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.30; S, 14.05. Found: C, 52.52; H, 5.70; S, 14.17.

Modified Procedure. The sultine **11f** (1.0 g, 4.4 mmol) was dissolved in precooled $CHCl_3$ (−15 °C, 20 mL). This solution was added dropwise to a boiling solution of **1** (0.61 g, 5.2 mmol) in the same solvent (15 mL) while being stirred magnetically. Addition was finished after ca. 15 min. The reaction mixture was heated to reflux for 2 h; the solvent was then removed *in vacuo* and the residue kept at 80 °C for 15 min. The crystalline mass was triturated with boiling acetone (2 × 10 mL) to remove side products (e.g., 1,3-dihydro-5,6-dimethoxybenzo-[*c*]thiophene-2,2-dioxide, 0.25 g (25%)) and then crystallized from ethylene glycol monomethyl ether. **13f** was obtained as slightly yellow powder: mp 277−279 °C; yield 0.46 g (43%).

4,5,6,7-Tetramethyl-3,8-dihydronaphtho[*b*]cyclobutene-1,2-dione (13g). Prepared as described for compound **13a**. The crude product was purified by filtration over silica gel using CH_2Cl_2 as eluent: pale yellow crystals; mp 255−256 °C dec; yield 44%. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.55; H, 6.89.

Naphtho[*b*]cyclobutene-1,2-dione (14a). Typical Procedure for the Dehydrogenation with Bromine. To a solution of the dihydro compound **13a** (1.27 g; 6.9 mmol) in boiling AcOH (40 mL) was added a solution of bromine (1.21 g, 7.6 mmol) in AcOH (5 mL), while stirring. The solution was heated to reflux for 2.5 h during which time a solid precipitated. The suspension was cooled to room temperature. The solid was then collected by filtration and recrystallized from AcOH to give **14a** as yellow crystals, yield 1.18 g (94%). On heating, the compound turned to red at ca. 240 °C. It melted at 256−259 °C (250−255 °C;[23] 256.5−258 °C[24]) and gave a red liquid which on further heating solidified to red crystals; compare ref 24: IR 1800−1790, 1760 (vs), 1590 (w) (C═O, C═C) cm^{-1}; ^1H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.74−7.76 (m, 2H), 8.04−8.06 (m, 2H), 8.47 (s, 2H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 122.33, 131.49 (2 × CH), 136.54, 163.44, 196.32; compare ref 25; UV (MeOH) λ_{max} (log ϵ) 209 nm (4.38), 272 (4.81); MS *m*/*z* (relative intensity) 182 (M^+, 12), 154 (48), 126 (100). Anal. Calcd for $C_{12}H_6O_2$: C, 79.11; H, 3.32. Found: C, 78.66; H, 3.34.

5,6-Dimethylnaphtho[*b*]cyclobutene-1,2-dione (14b). Prepared as described for compound **14a**: yellow crystals; mp 281−282 °C (toluene); yield 83%. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.73; H, 4.84.

5,6-Diethylnaphtho[*b*]cyclobutene-1,2-dione (14c). Prepared as described for compound **14a**: yellow crystals; mp 176−177 °C (EtOH); yield 84%. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.69; H, 5.92. Found: C, 80.39; H, 5.59.

4-Methoxynaphtho[*b*]cyclobutene-1,2-dione (14d). Typical Procedure for the Dehydrogenation with MnO_2. To a solution of **13d** (0.2 g, 0.93 mmol) in benzene (25 mL) was added MnO_2 (0.81 g, 9.3 mmol). It was vigorously stirred and heated to reflux for 45 min. After filtration, the solution was evaporated to dryness and the residue crystallized to give **14d**: orange crystals; mp 229−230 °C (*n*-BuOH); yield 0.17 g (86%); IR 1790 (vs), 1760 (vs), 1610 (m), 1580 (m) (C═O, C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H), 7.02−7.04 (d, 1H, J = 7.5 Hz), 7.59−7.61 (d, 1H, J = 8.4 Hz), 7.66−7.70 (m, 1H), 8.38 (s, 1H), 8.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.06, 107.68, 117.27, 120.90, 122.75, 129.12, 131.54, 137.24, 157.78, 163.36, 164.03, 195.84, 196.25; UV (MeOH) λ_{max} (log ϵ) 223 nm (4.50), 283 (4.63); MS *m*/*z* (relative intensity) 212 (M^+, 16), 184, (65), 156 (100). Anal. Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.26; H, 4.14.

4,7-Dimethoxynaphtho[*b*]cyclobutene-1,2-dione (14e). Dehydrogenation of **13e** with Bromine. Prepared as described for compound **14a**: red crystals; mp 254−256 °C (*n*-BuOH); yield 38%.

Dehydrogenation of 13e with MnO_2. Prepared as described for compound **14d**: red crystals; mp 256−259 °C (*n*-BuOH); yield 45%. Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.43; H, 4.16. Found: C, 69.48; H, 4.52.

5,6-Dimethoxynaphtho[*b*]cyclobutene-1,2-dione (14f). Prepared as described for compound **14a**: yellow crystals; mp 311−314 °C dec (xylene); yield (91%). Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.43; H, 4.16. Found: C, 69.46; H, 4.17.

4,5,6,7-Tetramethylnaphtho[*b*]cyclobutene-1,2-dione (14g). Prepared as described for compound **14a**. The crude product was purified by filtration over silica gel using CH_2Cl_2 as eluent: yellow crystals; mp 284−285 °C dec; yield 67%. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.69; H, 6.06.

Dibenzo[*b*,*h*]biphenylene-5,12-dicarbonitrile (15a). Prepared as described for **7a**: yellow crystals; mp 298−302 °C (toluene) (lit.[11] mp 305−307 °C dec); yield 48%; IR 2240 (m), 1610 (m), (C≡N, C═C) cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 215 nm (4.80), 262 (4.84), 303 (5.20), 321 (4.86), 409 (4.45), 438 (4.72); MS *m*/*z* (relative intensity) 302 (M^+, 100), 273 (5), 151 (11). Anal. Calcd for $C_{22}H_{10}N_2$: C, 87.40; H, 3.33; N, 9.72. Found: C, 87.22; H, 3.61; N, 9.54.

8,9-Dimethyldibenzo[*b*,*h*]biphenylene-5,12-dicarbonitrile (15b). Prepared as described for **7a**: yellow crystals; mp 317−319 °C (toluene); yield 52%. Anal. Calcd for $C_{24}H_{14}N_2$: C, 87.25; H, 4.27; N, 8.48; Found: C, 87.13; H, 4.35; N, 8.28.

8,9-Diethyldibenzo[*b*,*h*]biphenylene-5,12-dicarbonitrile (15c). Prepared as described for **7a**: yellow crystals; mp 306−308 °C (toluene); yield 39%. Anal. Calcd for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.01; H, 5.28; N, 7.49.

Naphtho[2′,3′:3,4]cyclobuta[1,2-*b*]quinoxaline (16a). Prepared as described for **8a** with the modification that MeOH was used as the solvent: yellow crystals; mp 280−281 °C (toluene) (lit.[12] mp 279−280 °C); yield 82%; IR 1660 (m), 1570 (w) (C═C) cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 210 nm (4.78), 232 (4.70), 241 (4.69), 248 (4.67), 287 (5.18), 311 (4.87), 394 (4.69), 419 (4.92); MS *m*/*z* (relative intensity) 254 (M^+, 100), 178 (28), 151 (10), 126 (16). Anal. Calcd for $C_{18}H_{10}N_2$: C, 85.02; H, 3.96; N, 11.02. Found: C, 85.09; H, 3.81; N, 10.92.

8,9-Dimethylnaphtho[2′,3′:3,4]cyclobuta[1,2-*b*]quinoxaline (16b). Prepared as described for **8a** but that MeOH was used as the solvent: yellow crystals; mp 339−341 °C (ethylene glycol monomethyl ether); yield 85%. Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.71; H, 4.89; N, 10.01.

8,9-Diethylnaphtho[2′,3′:3,4]cyclobuta[1,2-*b*]quinoxaline (16c). Prepared as described for **8a** with the modification that MeOH was used as the solvent: yellow crystals; mp 231−233 °C (EtOH); yield 71%. Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.11; H, 5.64; N, 8.97.

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Supporting Information Available: Spectral data (IR, ^1H, ^{13}C, mass spectra) for compounds **3b**,**c**, **4b**,**c**, **5b**, **7b**, **8b**, **13b**−**e**,**g**, **14b**,**c**,**e**−**g**, **15b**,**c**, and **16b**,**c** and UV data of some of them. This material is available free of charge via the Internet at http://pubs.acs.org.

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