Oxocarbons and related compounds. Part 28.[1] Polycycle-fused dihydrobenzocyclobutenediones and benzocyclobutenediones. Synthesis of cyclobuta[*c*]- and cyclobuta[*a*]-phenanthrene-1,2-diones and cyclobuta[*a*]triphenylene-11,12-dione

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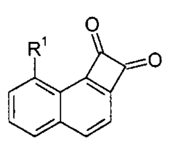
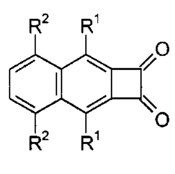
The Diels–Alder reaction of semisquaric chloride **5** with 1-(alk-1-enyl)naphthalenes, 2-(alk-1-enyl)naphthalenes and 9-vinylphenanthrene is used to prepare dihydrocyclobuta[*c*]phenanthrene-1,2-diones **8a–c**, dihydrocyclobuta[*a*]phenanthrene-1,2-diones **12a–c**, and dihydrocyclobuta[*a*]triphenylene-11,12-dione **18**, respectively. Treatment of the dihydrocyclobutaarenediones with bromine effects aromatization and opens up a route for the synthesis of cyclobuta[*c*]phenanthrene-1,2-diones **9a–c**, cyclobuta[*a*]phenanthrene-1,2-diones **13a–c** and cyclobuta[*a*]triphenylene-11,12-dione **19**. The range of Diels–Alder reactions with semisquaric chloride **5** is extended to the use of 4-(prop-1-enyl)-1,2-dihydronaphthalene **14**. Tetrahydrocyclobuta[*a*]phenanthrene-1,2-dione **15** is obtained in 69% yield, which can be oxidized, stepwise or at once, to give cyclobuta[*a*]phenanthrene-1,2-dione **13b** in good yields.

Introduction

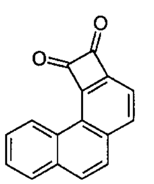
Benzocyclobutene-1,2-dione (BBD) and substituted benzocyclobutenediones[2] have become useful intermediates[3] in organic synthesis. They are furthermore used as synthons[4] for the construction of complex organic compounds.[5] Several efficient methods have been developed for their synthesis[2,6] and have given access to their preparation on a gram scale. By contrast, only a small number of carbocycle-fused benzocyclobutene-1,2-diones (higher analogs of BBD) have been described so far. At the outset of our work two general routes existed for their preparation: The 'pyrolytic procedure' developed by Rees[7] and McOmie[8] which has been used for the preparation of the naphtho[*a*]cyclobutene-1,2-diones **1a**[9] and **1b**,[10] the naphtho[*b*]cyclobutene-1,2-dione **2c**,[11] and the phenanthro[*c*]cyclobutene-1,2-dione **3**,[12] while the naphtho[*b*]cyclobutene-1,2-diones **2a**[13] and **2b**[14] and phenanthro[*l*]cyclobutene-1,2-dione **4**[15] were obtained by Cava's 'hydrolysis of annulated tetrahalogenated cyclobutenes'.



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 = Ph



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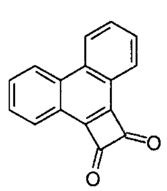

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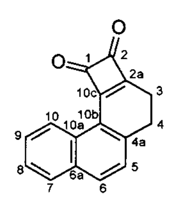
Recently we have introduced[6e] and established[16] the use of 3-chlorocyclobut-3-ene-1,2-dione (semisquaric chloride) in Diels–Alder reactions for the construction of dihydrobenzocyclobutenediones and benzocyclobutenediones. Application of this methodology to 5-(alk-1-enyl)benzodioxoles and 1,2-dialkoxy-4-(alk-1-enyl)benzenes provided a simple and efficient route to cyclobuta[5,6]naphtho[2,3-*d*][1,3]dioxole-1,2-diones[17] and 6,7-dialkoxycyclobuta[*a*]naphthalene-1,2-diones.[1] In the following we report on the extension of this method for the preparation of cyclobuta[*c*]- and cyclobuta[*a*]-phenanthrene-1,2-diones as well as cyclobuta[*a*]triphenylene-11,12-dione, the first pentacyclic representative of this type.

Results and discussion

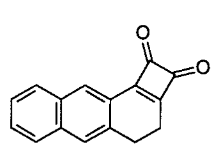
Cyclobuta[*c*]phenanthrene-1,2-diones

A solution of semisquaric chloride **5** and 1 equiv. of 2-vinylnaphthalene **6a** in dichloromethane was kept at room temperature for 24 h. During this time the solution took on a dark red colour. The solvent was removed and the remaining oil was kept at 70–80 °C at reduced pressure until the colour of the highly viscous oil turned to brown (method A). It was then subjected to column chromatography. As a result one major product **A** and one minor product **B** were obtained along with some unreacted starting material **6a**. The elemental analysis of **A** required the loss of HCl from the educts. This was confirmed by the mass spectrum which showed a molecular ion at *m*/*z* 234. Since ring closure with semisquaric chloride **5** might take place in the 1- or 3- position of 2-vinylnaphthalene **6a** the two structures **8a** and **8′a** came into question for compound **A**.

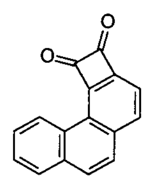
The ^{1}H NMR spectrum provided unambiguous identification. The appearance of four doublet signals and two triplet



8a



8′a

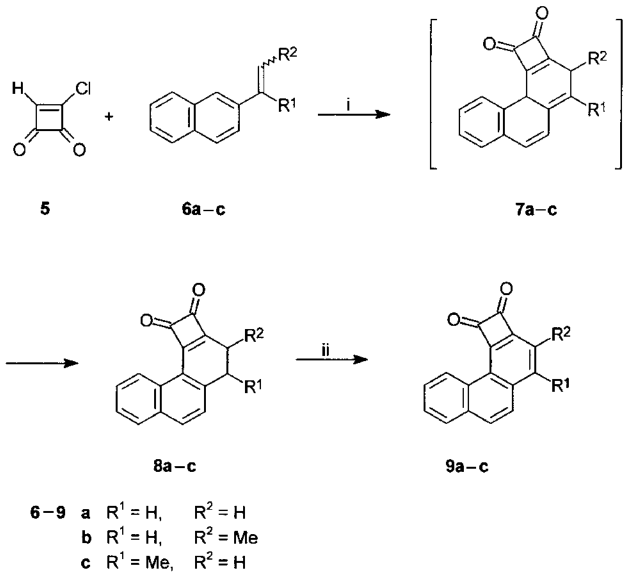


9a

signals in the aromatic region is in accordance with the aromatic proton pattern of 3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-dione **8a**† but not with that of **8′a**. This finding is in agreement with reports on the reactions of 2-vinylnaphthalene **6a** and 2-(alk-1-enyl)naphthalenes with maleic anhydride[18,19] and 4-acetoxycyclopent-2-enone[20] which also led to the formation of phenanthrene systems.

On the basis of the structure elucidation of **A**, compound **B**—exhibiting a molecular ion at *m*/*z* 232—was readily shown to be cyclobuta[*c*]phenanthrene-1,2-dione **9a** (≡**3**).‡,[12] It is apparent that **9a** results from dehydrogenation of 3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-dione **8a** under the experimental conditions applied.

In extension of the before mentioned results semisquaric chloride **5** was reacted with 2-(prop-1-enyl)naphthalene **6b** and 2-(isopropenyl)naphthalene **6c** without a solvent at elevated temperature (method B). The expected alkyl-3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-diones **8b**,**c** were obtained, accompanied by small amounts of the corresponding dehydrogenated products **9b**,**c**. The results are illustrated and summarized in Scheme 1.

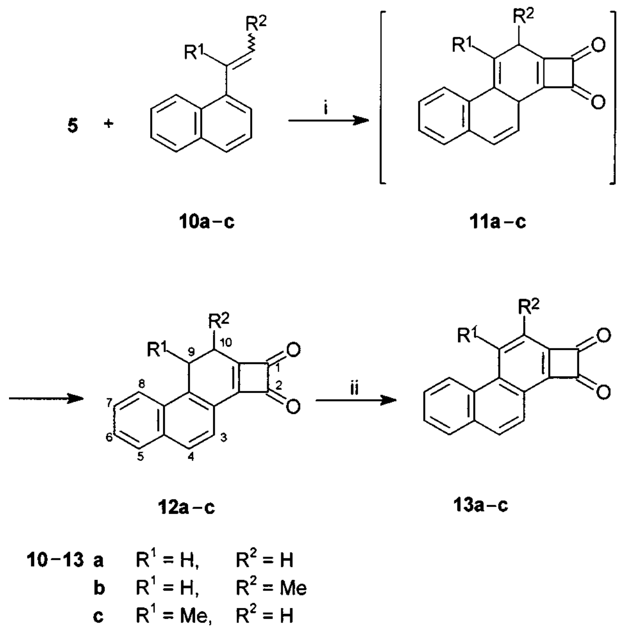


Scheme 1 *Reagents and conditions*: i, method A: CH_2Cl_2, room temp. for 24 h, then heating to *ca*. 75 °C; method B: neat, room temp. to 70 °C within 6 h; ii, CCl_4, Br_2, reflux, 3 h.

According to Scheme 1 the primary cycloadducts from semisquaric chloride **5** and 2-(alk-1-enyl)naphthalenes **6** suffer elimination of HCl to give the intermediates **7**. The aromatic naphthalene moiety of **8** is then derived from the rapid double bond isomerization in the tetracyclic intermediates **7**. The 3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-diones **8** readily underwent dehydrogenation. Thus, treatment of **8a**–**c** with 1.2 equiv. of bromine in boiling tetrachloromethane gave the corresponding cyclobuta[*c*]phenanthrene-1,2-diones **9a**–**c** in good yields (Scheme 1).

Cyclobuta[*a*]phenanthrene-1,2-diones

At the outset of our work cyclobuta[*a*]phenanthrene-1,2-diones were unknown. They seemed of special interest since their four rings are arranged in the same manner as in the steroidal skeleton. Reaction of semisquaric chloride **5** with 1-vinylnaphthalene **10a** under the conditions of method A afforded the 9,10-dihydrocyclobuta[*a*]phenanthrene-1,2-dione **12a** in 29% yield as the only product. 1-(Prop-1-enyl)naphthalene **10b** and **5** were allowed to react according to method B and afforded 10-methyl-9,10-dihydrocyclobuta[*a*]phenanthrene-1,2-dione **12b** in slightly higher yield (32%). For reasons of comparison 1-(isopropenyl)naphthalene **10c** and semisquaric chloride **5** were allowed to react using both methods. Method A afforded a mixture of the 9,10-dihydrocyclobuta[*a*]phenanthrene-1,2-dione **12c** (9%) and the dehydrogenation product **13c** (8%). Following method B the same products were obtained with 15 and 22% yield, respectively. The results are summarized in Scheme 2. Furthermore it shows that the reaction pathway



Scheme 2 *Reagents and conditions*: i, method A: CH_2Cl_2, room temp. for 24 h, then heating to *ca*. 75 °C; method B: neat, room temp. to 70 °C within 6 h; ii, CCl_4, Br_2, reflux, 3 h.

leading to **12a**–**c** is completely analogous to that for the generation of cyclobuta[*c*]phenanthrene-1,2-diones.

The dihydrocyclobuta[*a*]phenanthrene-1,2-diones **12a**–**c** were readily dehydrogenated by treatment with 1.2 equiv. of bromine and gave the cyclobuta[*a*]phenanthrene-1,2-diones **13a**–**c** in good yields.

An alternative route to cyclobuta[*a*]phenanthrene-1,2-diones is outlined in Scheme 3. Reaction of semisquaric chloride **5** with 4-(prop-1-enyl)-1,2-dihydronaphthalene **14** led to *cis*/*trans*-10-methyl-2b,3,4-10-tetrahydrocyclobuta[*a*]phenanthrene-1,2-dione **15** in good yield. On treatment of **15** with 1.1 equiv. of bromine regioselective dehydrogenation is observed to give the 3,4-dihydrocyclobuta[*a*]phenanthrene-1,2-dione **16**. This partial dehydrogenation of tetrahydrocyclobuta[*a*]phenanthrene-1,2-dione **15** can also be easily accomplished by DDQ. Subsequent reaction of **16** with one (further) equivalent of bromine led to **13b**.

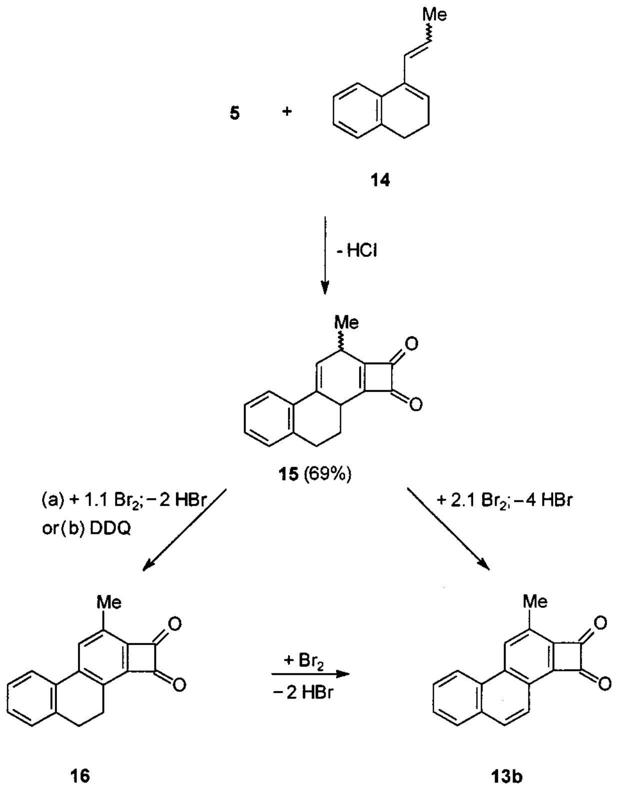
Treatment of the tetrahydro compound **15** with 2.1 equiv. of bromine allowed a one step conversion to the fully aromatized cyclobuta[*a*]phenanthrene-1,2-dione **13b**. The reaction sequence **5** + **14**→**15**→**13b** is experimentally easy to perform and works with high yields (69 and 91%). Thus it represents the method of choice for the preparation of cyclobuta[*a*]phenanthrene-1,2-diones.

Cyclobuta[*a*]triphenylene-11,12-dione

9-Vinylphenanthrene **17** reacts analogously, in the diene synthesis, to vinylnaphthalenes.[21] Its reaction with semisquaric

† The ^1H and ^{13}C chemical shift assignments (see Experimental) were achieved from 2D ^1H–^1H, ^1H–^{13}C connectivities (COSY and HETCOR experiments).

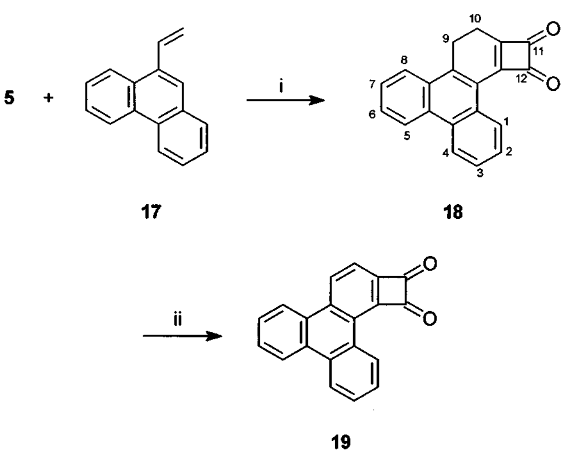
‡ **9a** prepared by the ‘pyrolytic procedure’ was reported to have mp 277–278 °C (decomp.) (ethyl acetate–light petroleum).[12] This value differs substantially from the mp 248–250 °C (toluene) found by us for an analytically pure sample.



Scheme 3

chloride **5** should, therefore, open up a route to hitherto unknown pentacyclic diones.

A solution of semisquaric chloride **5** and 9-vinylphenanthrene **17** in dichloromethane was kept at room temperature. After 12 h yellow crystals had deposited. These were identified as 9,10-dihydrocyclobuta[*a*]triphenylene-11,12-dione **18**. This finding shows that, in contrast to the formation of dihydrocyclobuta[*c*]- and dihydrocyclobuta[*a*]-phenanthrene-1,2-diones, the primary Diels–Alder adduct from **5** and **17** eliminates HCl very easily, heating being unnecessary for this step. Thus, it may be concluded that HCl elimination of the primary Diels–Alder adducts is facilitated by a high degree of annulation. Dehydrogenation of **18** to cyclobuta[*a*]triphenylene-11,12-dione **19** was easily effected, in the usual manner, by treatment with 1.1 equiv. of bromine.



Scheme 4 *Reagents and conditions*: i, CH_2Cl_2, room temp. for 12 h; ii, AcOH, Br_2, reflux, 3 h.

In conclusion, we have described two step syntheses of cyclobuta[*c*]- and cyclobuta[*a*]-phenanthrene-1,2-diones and cyclobuta[*a*]triphenylene-11,12-dione based on the Diels–Alder reaction with semisquaric chloride **5**. This short methodology is potentially adaptable to the preparation of even higher polycycle-fused dihydrobenzocyclobutene-1,2-diones and benzocyclobutene-1,2-diones, starting from easily available (alken-1-yl) aromatics and (alken-1-yl)dihydro aromatics.

Experimental

Melting points were measured in capillary tubes and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer, UV spectra on a Perkin-Elmer Lambda 2 spectrometer. Mass spectra were determined by electron impact on a Varian CH 7A spectrometer at an ionizing voltage of 70 eV. NMR spectra were obtained on a Bruker AM 400 or on a Bruker AMX 500 spectrometer. 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^{-1} 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. Elemental analyses were performed by the Institute of Chemistry, University of Mainz. 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 **5** was obtained by reacting semisquaric acid with oxalic dichloride.[16a] 1-Naphthaldehyde, 2-naphthaldehyde, 9-formylphenanthrene, 1-acetylnaphthalene, 2-acetylnaphthalene, 2-vinylnaphthalene, 1-tetralone and 1-bromoprop-1-ene were obtained from Aldrich.

Preparation of the (alk-1-enyl) aromatics 6b,c, 10a–c, 17

Method 1. A solution of the appropriate aldehyde or ketone (10.00 g) in dry THF (50 cm^3) was added slowly to a suspension of 1.5 equiv. of methyltriphenylphosphonium bromide and 1.5 equiv. of $KOBu^t$ in dry THF (200 cm^3). After magnetic stirring for 30 min at room temperature, water (100 cm^3) was added. The organic layer was separated. The aqueous layer was washed with diethyl ether (3 × 50 cm^3). The combined organic layers were washed with water (2 × 100 cm^3) and dried ($MgSO_4$). The solvent was then removed under reduced pressure. The residue obtained was extracted with light petroleum (5 × 50 cm^3). The light petroleum was then removed under reduced pressure. The residue was distilled *in vacuo* or recrystallized.

Method 2. A solution of 1- or 2-naphthaldehyde (15.00 g, 96 mmol) in dry THF (80 cm^3) was added slowly at 5 °C to a solution of ethylmagnesium bromide (115 mmol) in dry THF (80 cm^3). The reaction mixture was heated to reflux for 45 min. After cooling to 5 °C, water (80 cm^3) was added, then HCl (18%, 40 ml). The organic layer was separated. The aqueous layer was washed with diethyl ether (3 × 50 cm^3). The combined organic layers were washed with water (3 × 50 cm^3) and dried ($MgSO_4$). The solvent was then removed under reduced pressure. The oil obtained was dissolved in a mixture of light petroleum (boiling range 90–110 °C)–toluene (1 : 1) (150 cm^3). To this solution, P_4O_{10} (30 g, 105 mmol) was added and the mixture was then heated to reflux for 5 min under vigorous stirring. The solution was then filtered, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (Al_2O_3, neutral, light petroleum as eluent). The oil obtained was distilled *in vacuo*.

Preparation of 1,2-dihydro-4-(prop-1-enyl)naphthalene 14

Method 3. A solution of 1-tetralone (10.00 g, 68 mmol) in dry THF (50 cm^3) was added slowly at 5 °C to a solution of prop-1-

Table 1 Yields and physical properties of the prepared dienes **6b**,**c**, **10a**–**c**, **14**, **17**

Diene	Method	Bp or Mp/°C	Yield (%)	Purity (%)	$E:Z$ ratio (%)
6b	2	70–73/0.15 mbar	41	88	95:5
6c	1	48–50 (MeOH)	69	>98	—
10a	1	75–76/0.1 mbar	76	>98	—
10b	2	110/2 torr	28	97	94:6
10c	1	108–110/0.12 mbar	79	>98	—
14	3	not determined	70	>98	94:6
17	1	38 (EtOH–hexane)	66	>98	—

enylmagnesium bromide (95 mmol), which was prepared in the usual manner from 1-bromoprop-1-ene (12.41 g, 103 mmol) and magnesium turnings (2.31 g, 95 mmol), in THF (80 cm^3). After heating to reflux for 1 h, water (80 cm^3) was added, and then HCl (18%, 40 cm^3). The organic layer was separated. The aqueous layer was washed with diethyl ether (3 × 50 cm^3). The combined organic layers were washed with water (3 × 50 cm^3) and dried. Then the solvent was removed under reduced pressure. Column chromatography (silica gel, dichloromethane as eluent) of the residue afforded 8.15 g (70%) of **14**. To avoid any polymerization the product was not purified by distillation.

Reaction of semisquaric chloride 5 with (alk-1-enyl)naphthalenes 6a–c and 10a–c. Preparation of 3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-diones 8a–c and 9,10-dihydrocyclobuta[*a*]phenanthrene-1,2-diones 12a–c; general methods

Method A. Semisquaric chloride **5** (1.16 g 10 mmol) and the appropriate (alk-1-enyl)naphthalene **6a**, **10a**,**c** (10 mmol) were dissolved in dichloromethane (20 cm^3). After magnetic stirring for 24 h the solvent was removed under reduced pressure. The obtained red reaction mixture was kept at 70–80 °C under reduced pressure for 45 min. The dark brown, highly viscous oil was then subjected to column chromatography using dichloromethane as eluent. Components are listed in the order of elution.

Method B. Semisquaric chloride **5** (1.16 g 10 mmol) and the appropriate (alk-1-enyl)naphthalene **6b**,**c**, **10b**,**c** (10 mmol) were combined and the solution was stirred magnetically for 6 h. During this time the reaction mixture was heated from 40 °C to 80 °C. At *ca.* 70 °C HCl was released and removed *in vacuo*. The brown, highly viscous oil was subjected to column chromatography using dichloromethane as eluent. Components are listed in the order of elution.

3,4-Dihydrocyclobuta[*c*]phenanthrene-1,2-dione 8a (Method A). Unreacted **6a**: (0.69 g, 44%). **9a**: Pale yellow crystals (0.13 g, 8%), mp 245–247 °C; **8a**: yellow crystals from ethyl acetate–hexane (0.68 g, 52%), mp 171–172 °C (Found: C, 82.14; H, 4.37. $C_{16}H_{10}O_2$ requires C, 82.04; H, 4.30%); ν_{max}(KBr)/cm^{-1} 1780, 1760, 1620, 1595, 1575, 1550 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 264 (4.09), 233 (4.55), 219 (4.55); δ_H(400 MHz; $CDCl_3$) 3.08–3.13 (2 H, m), 3.22–3.27 (2 H, m), 7.38–7.40 (1 H, d, *J* 8.3), 7.49–7.53 (1 H, m), 7.62–7.66 (1 H, m), 7.78–7.80 (1 H, d, *J* 8.2), 8.78–8.80 (1H, d, *J* 8.5); δ_C(100 MHz, $CDCl_3$) 21.21, 28.26, 124.30, 126.54, 126.71, 126.82, 128.20, 128.72, 130.65, 132.88, 134.64, 137.98, 193.07, 194.49, 194.74, 197.63; *m*/*z* 234 (M^+, 38%), 206 (36), 178 (100), 152 (15).

3-Methyl-3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-dione 8b (Method B). Unreacted **6b**: (0.72 g, 43%); **9b**: Pale yellow crystals (0.07 g, 5%), mp 255–257 °C. **8b**: Yellow crystals from ethyl acetate (0.94 g, 66%), mp 157–158 °C (Found: C, 82.20; H, 4.90. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); ν_{max}(KBr)/cm^{-1} 1760–1740, 1580, 1565, 1535 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 266 (4.22), 232 (4.62), 222 (4.62); δ_H(400 MHz; $CDCl_3$) 1.42–1.44 (3 H, d, *J* 7.1), 2.92–2.99 (1 H, dd, *J* 10.0, *J* 16.5), 3.17–3.19 (1 H, dd, *J* 8.0, 16.5), 3.43–3.42 (1 H, m), 7.38–7.40 (1 H, d, *J* 8.3), 7.49–7.52 (1 H, t, *J* 7.5), 7.62–7.66 (1 H, m), 7.78–7.81 (1 H, d, *J* 8.2), 7.93–7.95 (1 H, d, *J* 8.3), 8.79–8.81 (1 H, d, *J* 8.5); δ_C(100 MHz; $CDCl_3$) 16.57, 28.71, 37.10, 124.06, 126.54, 126.64, 126.95, 128.17, 128.67, 130.56, 132.87, 134.61, 137.74, 193.40, 193.52, 194.48, 200.82; *m*/*z* 248 (M^+, 76%), 220 (60), 192 (85), 191 (100), 165 (40).

4-Methyl-3,4-dihydrocyclobuta[*c*]phenanthrene-1,2-dione 8c (Method B). Unreacted **6c**: (0.10 g, 6%); **9c**: Pale yellow crystals (0.21 g, 9%), mp 232–233 °C; **8b**: Yellow crystals from ethyl acetate (0.87 g, 37%), mp 145–147 °C (Found: C, 81.83; H, 4.81. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); ν_{max}(KBr)/cm^{-1} 1770–1745, 1580, 1540 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 266 (4.27), 230 (4.64), 221 (4.64); δ_H(400 MHz; $CDCl_3$) 1.26–1.28 (3 H, d, *J* 7.2), 3.05–3.10 (1 H, dd, *J* 3.5, 19.0), 3.17–3.19 (1 H, dd, *J* 7.9, 19.0), 3.43–3.48 (1 H, m), 7.44–7.46 (1 H, d, *J* 8.4), 7.51–7.55 (1 H, m), 7.65–7.69 (1 H, m), 7.81–7.83 (1 H, d, *J* 8.2), 7.99–8.01 (1 H, d, *J* 8.4), 8.86–8.88 (1 H, dd, *J* 0.7, 8.5); δ_C(100 MHz; $CDCl_3$) 22.84, 28.89, 34.17, 123.20, 126.21, 126.81, 128.19, 128.79, 130.79, 132.82, 135.13, 143.83, 193.20, 193.91, 195.36, 196.92; *m*/*z* 248 (M^+, 77%), 220 (71), 192 (72), 191 (100), 165 (42).

9,10-Dihydrocyclobuta[*a*]phenanthrene-1,2-dione 12a (Method A). Unreacted **10a**: (0.55 g, 18%); **12a**: Yellow crystals from toluene (0.68 g, 52%), mp 221–222 °C (Found: C, 81.91; H, 4.23. $C_{16}H_{10}O_2$ requires C, 82.04; H, 4.30%); ν_{max}(KBr)/cm^{-1} 1775, 1760, 1600, 1560 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 285 (4.61), 275 (4.50), 219 (4.52); δ_H(500 MHz; $C_2D_2Cl_4$) 3.20–3.23 (2 H, t, *J* 8.7), 3.53–3.56 (2 H, t, *J* 8.7), 7.55–7.59 (2 H, m), 7.75–7.85 (3 H, m), 8.04–8.05 (1 H, d, *J* 7.1); δ_C(125 MHz, $C_2D_2Cl_4$) 22.16, 23.38, 122.83, 123.25, 125.06, 127.86, 128.61, 129.08, 129.65, 131.49, 135.94, 136.51, 194.36, 194.65, 195.43, 197.70; *m*/*z* 234 (M^+, 46%), 206 (42), 178 (100), 152 (12).

10-Methyl-9,10-dihydrocyclobuta[*a*]phenanthrene-1,2-dione 12b (Method B). Unreacted **10b**: (0.74 g, 44%); **12b**: Orange crystals from ethyl acetate (0.44 g, 32%), mp 175–176 °C (Found: C, 82.45; H, 4.87. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); ν_{max}(KBr)/cm^{-1} 1790–1760, 1595, 1550 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 286 (4.65), 275 (4.54), 219 (4.56); δ_H(400 MHz; $CDCl_3$) 1.43–1.44 (3 H, d, *J* 7.2), 3.10–3.17 (1 H, dd, *J* 9.5, 17.1), 3.42–3.51 (1 H, m), 3.65–3.72 (1 H, dd, *J* 8.5, 17.1), 7.50–7.58 (2 H, m), 7.71–7.84 (3 H, m), 8.06–8.10 (1 H, m); δ_C(100 MHz; $CDCl_3$) 16.90, 28.66, 31.38, 121.89, 122.09, 124.27, 126.78, 127.51, 127.95, 128.63, 130.80, 134.94, 135.61, 192.16, 193.97, 194.39, 200.04; *m*/*z* 248 (M^+, 53%), 220 (40), 192 (84), 191 (100), 165 (39).

9-Methyl-9,10-dihydrocyclobuta[*a*]phenanthrene-1,2-dione 12c (Method A). Unreacted **10c**: (1.03 g, 61%); **13c**: Pale yellow crystals (0.08 g, 8%), mp 261–262 °C; **12c**: Orange crystals from ethyl acetate (0.09 g, 9%), mp 175–176 °C (Found: C, 82.11; H, 4.79. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); ν_{max}(KBr)/cm^{-1} 1790–1760, 1600, 1550 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 285 (4.64), 275 (4.53), 219 (4.53); δ_H(400 MHz; $CDCl_3$) 1.24–1.25 (3 H, d, *J* 7.3), 3.22–3.24 (2 H, m), 4.16–4.20

(1 H, m), 7.59–7.63 (2 H, m), 7.82–7.91 (3 H, m), 8.12–8.15 (1 H, m); δ_C(100 MHz; $CDCl_3$) 22.56, 29.09, 29.68, 121.64, 123.17, 124.51, 127.58, 128.32, 128.49, 129.54, 130.49, 136.67, 141.46, 193.25, 194.29, 195.95, 196.53; *m/z* 248 (M^+, 76%), 220 (74), 205 (88), 192 (51), 43 (100). (**Method B**): Unreacted **10c**: (0.58 g, 35%); **13c**: (0.36 g, 22%); **12c**: (0.25 g, 15%).

Preparation of cyclobuta[*c*]phenanthrene-1,2-diones 9a–c and cyclobuta[*a*]phenanthrene-1,2-diones 13a–c; general method

To a boiling solution of a dihydrocyclobutaphenanthrene-1,2-dione (0.3 g) in tetrachloromethane (25 cm^3) was added a solution of bromine (1.1 equiv.) in the same solvent (10 cm^3) in one portion. It was heated to reflux until no further HBr was evolved (*ca.* 3 h). Within this period of time the product precipitated. After cooling to −15 °C the product was collected by filtration and recrystallized.

Cyclobuta[*c*]phenanthrene-1,2-dione 9a. Pale yellow crystals from toluene (0.27 g, 91%), mp 248–250 °C (Found: C, 82.51; H, 3.43. $C_{16}H_8O_2$ requires C, 82.75; H, 3.47%); ν_{max}(KBr)/cm^{-1} 1765–1740, 1590, 1570 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 306 (4.56), 224 (4.80); δ_H[500 MHz; $(CD_3)_2SO$] 7.85–7.87 (1 H, m), 7.90–7.93 (1 H, m), 8.15–8.18 (2 H, m), 8.21–8.24 (1 H, m), 8.27–8.30 (1 H, m), 8.49–8.52 (1 H, m), 9.40–9.42 (1 H, m); δ_C[125 MHz; $(CD_3)_2SO$] 117.94, 125.57, 126.12, 126.79, 127.86, 128.01, 128.51, 128.71, 132.31, 132.34, 135.13, 138.07, 172.49, 173.03, 192.52, 192.71; *m/z* 232 (M^+, 35%), 204 (57), 176 (100), 119 (11), 88 (19).

3-Methylcyclobuta[*c*]phenanthrene-1,2-dione 9b. Pale yellow crystals from toluene (0.29 g, 97%), mp 255–257 °C (Found: C, 82.63; H, 3.97. $C_{17}H_{10}O_2$ requires C, 82.91; H, 4.09%); ν_{max}(KBr)/cm^{-1} 1750, 1595 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 309 (4.67), 226 (4.91); δ_H(500 MHz; $C_2D_2Cl_4$) 2.69 (3 H, s), 7.70–7.85 (4 H, m), 7.91–7.93 (1 H, d, *J* 7.9), 8.00–8.02 (1 H, d, *J* 8.7), 9.29–9.31 (1 H, d, *J* 8.3); δ_C(125 MHz; $C_2D_2Cl_4$) 18.25, 125.53, 126.37, 128.24, 128.89, 129.27, 129.54, 130.09, 131.68, 133.06, 133.89, 136.75, 138.33, 174.06, 174.08, 194.28, 194.67; *m/z* 246 (M^+, 46%), 218 (84), 190 (99), 189 (100), 95 (53).

4-Methylcyclobuta[*c*]phenanthrene-1,2-dione 9c. Pale yellow crystals from toluene (0.24 g, 81%), mp 233–234 °C (Found: C, 82.99; H, 4.16. $C_{17}H_{10}O_2$ requires C, 82.91; H, 4.09%); ν_{max}(KBr)/cm^{-1} 1750, 1595 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 306 (4.54), 227 (4.74); *m/z* 246 (M^+, 46%), 218 (84), 190 (99), 189 (100), 95 (53).

Cyclobuta[*a*]phenanthrene-1,2-dione 13a. Pale yellow crystals from xylene (0.20 g, 67%), mp 286–287 °C (Found: C, 82.38; H, 3.30. $C_{16}H_8O_2$ requires C, 82.75; H, 3.47%); ν_{max}(KBr)/cm^{-1} 1770–1750, 1580 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 297 (4.56), 262 (4.56), 207 (4.40); *m/z* 232 (M^+, 30%), 204 (50), 176 (100), 88 (25).

10-Methylcyclobuta[*a*]phenanthrene-1,2-dione 13b. Pale yellow crystals from toluene (0.22 g, 74%), mp 282–283 °C (Found: C, 82.50; H, 3.96. $C_{17}H_{10}O_2$ requires C, 82.91; H, 4.09%); ν_{max}(KBr)/cm^{-1} 1760–1745, 1605, 1590 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 300 (4.55), 266 (4.59), 207 (4.37); δ_H(500 MHz; $C_2D_2Cl_4$) 2.76 (3 H, s), 7.73–7.74 (2 H, m), 7.96–7.98 (2 H, m), 8.20–8.21 (1 H, m), 8.64–8.66 (2 H, m); δ_C(125 MHz; $C_2D_2Cl_4$) 18.82, 123.00, 123.78, 124.46, 128.76, 129.50, 129.75, 129.96, 131.42, 131.67, 131.77, 134.70, 134.74, 174.40 (2 C), 195.01, 195.16; *m/z* 246 (M^+, 39%), 218 (74), 190 (100), 95 (33).

9-Methylcyclobuta[*a*]phenanthrene-1,2-dione 13c. Pale yellow crystals from toluene (0.24 g, 81%), mp 261–262 °C (Found: C, 82.72; H, 4.01. $C_{17}H_{10}O_2$ requires C, 82.91; H, 4.09%); ν_{max}(KBr)/cm^{-1} 1780–1750, 1585, 1550 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 304 (4.60), 295 (4.60), 262 (4.56), 207 (4.43); δ_H(500 MHz; $C_2D_2Cl_4$) 3.25 (3 H, s), 7.74–7.77 (2 H, m), 7.94 (1 H, s), 8.02–8.07 (2 H, m), 8.32–8.34 (1 H, d, *J* 8.6), 8.88–8.90 (1 H, m); δ_C(125 MHz; $C_2D_2Cl_4$) 29.33, 122.35, 123.63, 127.09, 128.04, 128.66, 129.05, 130.36, 131.01, 132.75, 134.39, 135.98, 147.63, 172.84, 172.88, 194.53, 194.61; *m/z* 4246 (M^+, 31%), 218 (79), 190 (100), 163 (21), 95 (27).

cis/*trans*-10-Methyl-2b,3,4,10-tetrahydrocyclobuta[*a*]phenanthrene-1,2-dione 15

A solution of 1,2-dihydro-4-(prop-1-enyl)naphthalene **14** (3.40 g, 20 mmol) in dichloromethane (30 cm^3) was combined with semisquaric chloride **5** (2.32 g, 20 mmol) dissolved in dichloromethane (10 cm^3). The resulting mixture heated up and took on an intense dark red colour. It was stirred magnetically at room temperature for 30 min. The solvent was then removed under reduced pressure and the red oil left behind was kept at 70–80 °C *in vacuo* for 30 min. The resulting brown, highly viscous oil was crystallized twice from ethanol to give **15**. Orange crystals from ethanol (3.46 g, 69%), mp 128 °C (Found: C, 81.64; H, 5.51. $C_{17}H_{14}O_2$ requires C, 81.58; H, 5.64%); ν_{max}(KBr)/cm^{-1} 1790–1760, 1595, 1550 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 214 (4.45); signals in the ^1H and ^{13}C NMR spectra appeared in pairs, indicating a mixture of isomers; *m/z* 250 (M^+, 52%), 222 (20), 207 (25), 194 (30), 179 (100), 165 (42).

10-Methylcyclobuta[*a*]phenanthrene-1,2-dione 13b from 15

The dehydrogenation was carried out in analogy to the preparation of cyclobutaphenanthrenediones from dihydrocyclobutaphenanthrenediones (see general procedure), with the exception that 2.2 equiv. of bromine were used. **13b** was obtained in 85% yield.

10-Methyl-3,4-dihydrocyclobuta[*a*]phenanthrene-1,2-dione 16

By dehydrogenation with DDQ. A solution of the tetrahydrocyclobuta[*a*]phenanthrene-1,2-dione **15** (0.6 g, 2.4 mmol) and DDQ (0.6 g, 2.6 mmol) in dioxane (50 cm^3) was heated to reflux for 3 h under magnetic stirring. The solution was then cooled to room temperature and filtered from precipitated hydroquinone. The solvent was removed under reduced pressure to leave **16**. Orange crystals from ethyl acetate (0.38 g, 64%), mp 185–186 °C (Found: C, 82.19; H, 4.88. $C_{17}H_{12}O_2$ requires C, 82.24; H, 4.87%); ν_{max}(KBr)/cm^{-1} 1770–1750, 1610, 1600, 1550 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 284 (4.49), 238 (4.25), 207 (4.26); δ_H(400 MHz; $CDCl_3$) 1.27 (3 H, s), 2.89–2.94 (2 H, t, *J* 6.9), 3.13–3.16 (2 H, t), 7.28–7.30 (1 H, m), 7.33–7.36 (2 H, m), 7.79–7.81 (1 H, m), 7.83 (1 H, s); δ_C(100 MHz; $CDCl_3$) 18.01, 24.06, 27.63, 125.28, 127.53, 128.81, 130.07, 130.35, 131.81, 131.99, 133.66, 138.25, 141.69, 170.86, 171.10, 194.66, 195.68; *m/z* 248 (M^+, 22%), 220 (100), 192 (80), 191 (42), 165 (18).

By dehydrogenation of 15 with bromine. To a solution of the tetrahydrocyclobuta[*a*]phenanthrene-1,2-dione **15** (0.5 g, 2 mmol) in tetrachloromethane (30 cm^3) was added bromine (0.35 g, 2.2 mmol) in tetrachloromethane (10 cm^3) within 10 min at room temperature. The reaction solution was stirred magnetically at room temperature until the brown colour faded and HBr started to evolve. It was then heated to reflux for 3 h and the solvent removed under reduced pressure. The solid obtained was recrystallized from ethyl acetate to give **16** as orange crystals (0.26 g, 52%).

10-Methylcyclobuta[*a*]phenanthrene-1,2-dione 13b from 16

The reaction was carried out as described for the preparation of cyclobutaphenanthrenediones from dihydrocyclobutaphenanthrenediones to give **13b** as pale yellow crystals (0.23 g, 77%).

9,10-Dihydrocyclobuta[*a*]triphenylene-11,12-dione 18

A solution of 9-vinylphenanthrene **17** (1.53 g, 7.5 mmol) and semisquaric chloride **5** (0.87 g, 7.5 mmol) in dichloromethane (25 cm^3) was stirred magnetically for 12 h at room temperature. During this time yellow crystals precipitated from the solution. After cooling to −15 °C the crystals were collected by filtration to give **18**. Orange crystals from THF (0.51 g, 24%), mp 220–221 °C (Found: C, 84.46; H, 4.31. $C_{20}H_{12}O_2$ requires C, 84.49; H, 4.25%); ν_{max}(KBr)/cm^{-1} 1780, 1750, 1590, 1560 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 256 (4.68), 213 (4.60); δ_H(500 MHz; $C_2D_2Cl_4$) 3.17–3.21 (2 H, t, *J* 8.9), 3.53–3.56 (2H, t, *J* 8.9), 7.64–7.74 (4 H, m), 8.11–8.13 (1 H, d, *J* 8.3), 8.60–8.62 (1 H, d, *J* 8.2), 8.66–8.68 (1 H, d, *J* 8.3), 8.75–8.77 (1 H, d, *J* 8.0); δ_C(125 MHz; $C_2D_2Cl_4$) 21.40, 24.48, 123.02, 123.88, 124.30, 126.14, 127.43, 127.98, 128.05, 128.19, 128.59, 129.77, 129.90, 129.99, 133.09, 137.00, 193.26, 194.80, 195.91, 197.82; *m/z* 284 (M$^+$, 60%), 256 (41), 228 (100), 226 (87), 224 (23).

Cyclobuta[*a*]triphenylene-11,12-dione 19

The dehydrogenation of **18** was performed in analogy to the preparation of cyclobutaphenanthrenediones (see general procedure), with the exception that acetic acid was used as the solvent to give **19**. Yellow crystals from xylene (0.28 g, 94%), mp 278–279 °C (Found: C, 85.10; H, 3.68. $C_{20}H_{12}O_2$ requires C, 85.09; H, 3.57%); ν_{max}(KBr)/cm^{-1} 1790–1750, 1610, 1590 (C=O, C=C); λ_{max}(MeOH)/nm (log ε/dm^3 mol^{-1} cm^{-1}) 304 (4.49), 272 (4.46), 240 (4.49); *m/z* 282 (M$^+$, 34%), 254 (55), 226 (100), 145 (25), 119 (37).

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