Rearrangements of Cyclobutenones. Electrocyclic Ring Closure and Thermal Ring Expansions of 3-Allenyl- and 3-Alkynyl-2-dienyl-4,4-dimethoxycyclobutenones

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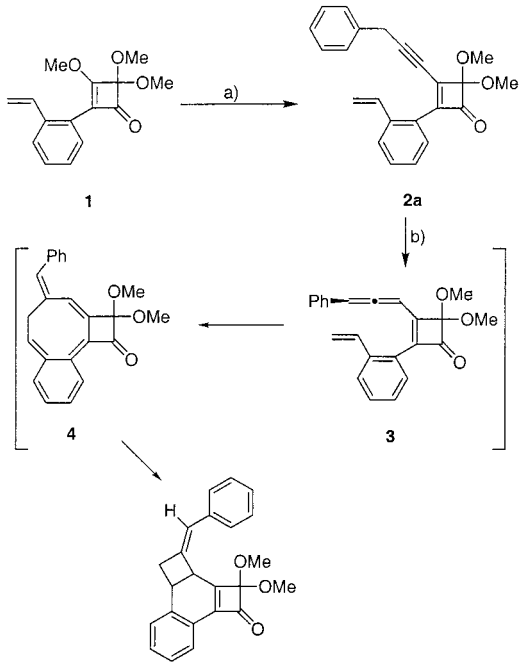
Abstract: Thermal rearrangements of 2-allenyl- and 2-alkynyl-3-(2-ethenylphenyl)-4,4-dimethoxycyclobutenones were studied. At ambient temperature, the allenyl compounds undergo an electrocyclic cascade to give bicyclo[4.2.0]-octadienyl-fused cyclobutenones. These unusual tetracyclic cyclobutenones were shown to be viable synthetic precursors to benzo[*a*]anthracene-7,12-diones, compounds representing the framework of the angucycline group of naturally occurring antibiotics. In contrast, the 2-alkynylcyclobutenones are stable at ambient temperature but undergo a facile rearrangement at 110 °C (toluene) to give the previously unknown naphthalene derivatives, 1,2-dihydro-2,2-dimethoxy-1-(3-alkenylidene)naphtho[2,1-*b*]furans.

Reported here are two unusual rearrangements of 2-(2-ethenylphenyl)-4,4-dimethoxycyclobutenones. The first involves the conversion of 3-allenyl derivatives to highly substituted tetracyclic cyclobutenones.[1] Here, the tetraene moiety comprising the unsaturated cyclobutenone subtituents undergoes facile electrocyclic ring closure to give bicyclo[4.2.0]octadienyl-fused cyclobutenones. The second involves reorganization of 3-alkynyl derivatives to 1,2-dihydro-2,2-dimethoxy-1-(3-alkenylidene)naphtho-[2,1-*b*]furan derivatives.[2]

These studies were encouraged by an unusual transformation observed during the synthesis of 4,4-dimethoxy-3-(3-phenyl-1-propynyl)-2-(2-ethenylphenyl)-2-cyclobuten-1-one (**2a**) from 2-(ethenylphenyl)-3,4,4-trimethoxycyclobutenone (**1**) as outlined in Scheme 1. Specifically, when the starting cyclobutenone was treated with the 1-lithio-3-phenyl-1-propyne in THF at −78 °C followed by triethylamine (TEA) at ambient temperature, 3-[(*Z*)-benzylidene]-2b,3,4,4a-tetrahydro-2,2-dimethoxydicyclobuta[*a*,*c*]naphthalen-1(2*H*)-one (**5**) was realized in 44% isolated yield. The structure of the product is based upon its characteristic spectral properties including a single-crystal X-ray analysis.

The reaction is envisaged to involve base-catalyzed (TEA) isomerization of the alkynyl group in **2a** to the corresponding allenyl derivative **3**. This then undergoes two consecutive electrocyclic reactions, an 8π ring closure to the intermediate cyclooctatetraene **4** followed by a 6π ring closure to provide the product **5**. This mechanism is consistent with the observation that treatment of a THF solution of purified **2a** with TEA resulted in the formation of a green intermediate, presumably **4**, the color of which rapidly faded within a few seconds, and **5**, obtained in 32% yield.

Scheme 1[a]



[a] Key: (a) 1-lithio-3-phenyl-1-propyne/THF, −78 °C; (b) TEA/THF, rt.

These results suggest that 3-allenyl-2-(2-ethenylphenyl)-4,4-cyclobutenones would spontaneously rearrange at ambient temperature to the corresponding bicyclo-[4.2.0]octadiene systems. This was observed to be the case as the results outlined in Scheme 2 indicate. Treatment (−78 °C) of a THF solution of **1** with, respectively, 1-lithio-1-methoxyallene, 1-lithio-1-*tert*-butoxyallene, 1-lithio-3,3-dimethylallene, and 1-lithio-1-methoxy-1,2,3-butatriene followed by an ammonium chloride quench gave the corresponding tetracyclic cyclobutenones, **6** (81%), **7** (71%), **8** (74%), and **9** (35%). For **6**−**8**, after the quench and while warming to ambient temperature, a deep blue coloration developed that faded as the reaction proceeded, (**6**, 30 s), (**7**, 5 min), (**8**, 1 min). No color change was observed during the formation of **9**. Assuming intermediates analogous in structure to **4**, the more persistent color presumably corresponds to the more sterically hindered examples.

In a comparison study, thermolyses (toluene, 110 °C) of the 3-alkynyl derivatives (**2a**−**f**) were investigated (Scheme 3). Unlike the 3-allenyl derivatives, electrocyclic ring closure of the trienyne moiety was not observed, nor was alkyne/allene isomerization. Rather, the cyclobutenone ring is the key reacting group. Specifically, it undergoes electrocyclic ring opening to the vinylketene intermediates **10a**−**f**, which proceed to the naphthols **11a**−**f**. These were not isolated but led to the previously

(1) An analogous transformation involving 2-alkenyl derivatives has recently been reported. See: Tiedemann, R.; Heileman, M. J.; Schaumann, E.; Moore, H. W *J. Org. Chem.* **1999**, *64*, 2170; Heileman, M. J.; Tiedemann, R.;; Moore, H. W. *J. Am. Chem. Soc.* **1998**, *120*, 3801.

(2) For a recent review on the ring expansion of cyclobutenones, see: Moore, H. W.; Yerxa B. R. *Adv. Strain Org. Chem.* **1995**, *4*, 81−162.

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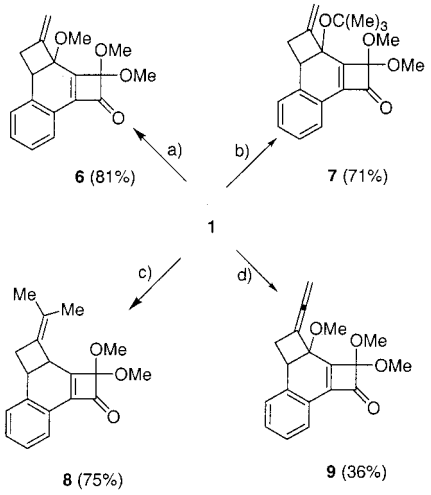
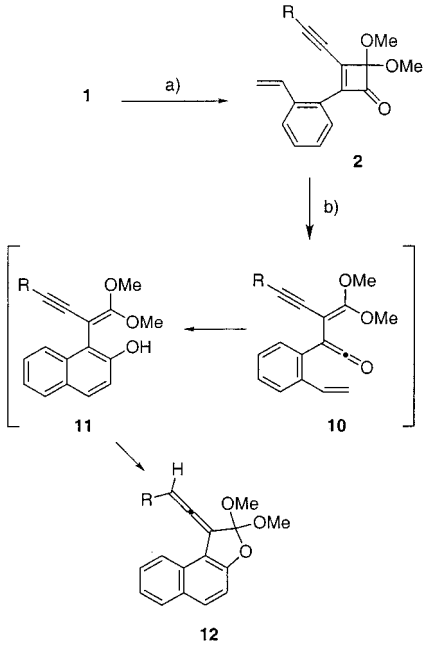
Scheme 2[a]



[a] Key: (a) 1-lithio-1-methoxyallene/THF, −78 °C; (b) 1-lithio-1-*tert*-butoxyallene/THF, −78 °C; (c) 1-lithio-3,3-dimethoxyallene/THF, −78 °C; (d) 1-lithio-1-methoxy-1,2,3-butatriene/THF, −78 °C.

Scheme 3[a]



	R	% Yield **2**	% Yield **12**
a	$PhCH_2$	40	45
b	Me	48	25
c	TMS	64	83
d	Ph	52	81
e	n-Bu	68	38
f	$PhCH_2CH_2$	62	61

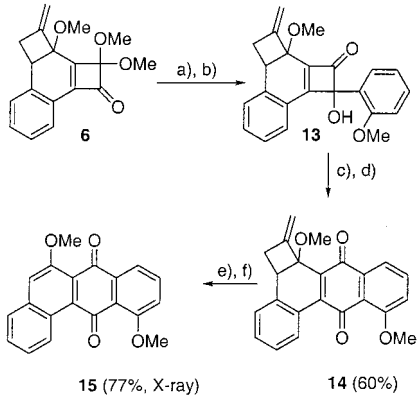
[a] Key: (a) R-C≡C-Li, THF, −78 °C; (b) toluene, 110 °C.

unknown naphthalene derivative **12a**−**f** (25−81%) upon addition of the naphtholic hydroxy group to the proximal enyne substituent.

The structures of **12a**−**f** are in agreement with their observed spectral properties. Of particular note are the absence of carbonyl group absorptions in their IR spectra and the presence of an allenyl group stretch in the range of 1932−1955 cm^{-1}.

The 3-alkylidene-2b,3,4,4a-tetrahydro-2,2-dimethoxydicyclobuta[*a*,*c*]naphthalen-1(2*H*)-one, **5**−**9**, are useful

Scheme 4[a]



[a] Key: (a) 2-lithioanisole/THF, −78 °C; (b) HCl, rt; (c) benzene, reflux; (d) Ag_2O, K_2CO_3; (e) bromine/$CHCl_3$, −10 °C; (f) visible light/$CHCl_3$, rt.

starting materials for the synthesis of benza[*a*]anthracene-7,12-diones, compounds representing the framework of the angucycline group of natural products.[3] An example is outlined in Scheme 4. Here, the tetracylic cyclobutenone **6** was converted to **13** upon treatment with 2-lithioanisole in THF at −78 °C followed by hydrolysis of the acetal linkage (HCl, ambient temperature). The crude product was dissolved in benzene and subjected directly to thermolysis at refluxing temperature followed by an oxidative workup (Ag_2O) to provide the quinone **14** in 60% overall yield.[2]

Quinone **14** was stable to further thermolysis or photolysis. This is of note since previously reported examples lacking the 3-alkylidene moiety readily cleave to the corresponding benza[*a*]anthracene-7,12-dione when subjected to irradiation with fluorescent laboratory light.[1,4] Such a transformation could also be accomplished with **14** by first addition of bromine to the ethylidene group followed by photolysis with visible light.[4] This provided 6,11-dimethoxybenzo[*a*]anthracene-7,12-dione (**15**) in 77% overall yield from **14**. The structure of **15** is in strict agreement with its observed spectral properties.

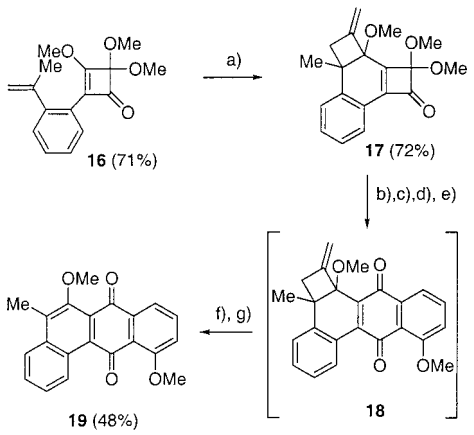
In an analogous fashion, 6,11-dimethoxy-5-methylbenza[*a*]anthracene-7,12-dione (**19**) was prepared from dimethyl squarate as outlined in Scheme 5. Initially, the cyclobutenone **16** was obtained in 71% yield upon treatment of dimethyl squarate with 1-lithio-2-(1-methylethenyl)benzene followed by a methanol quench.[5] This was then converted to **17** (72%) upon treatment 1-lithio-1-methoxyallene in THF at −78 °C. This was then converted to **19** in 48% overall yield by the method outlined above.

(3) For a recent review on these compounds, see: Rohr, J.; Thiericke, R. *Natural Prod. Rep.* **1992**, 103. Also see: (a) Krohn, K.; Ballwanz, F.; Baltus, W. *Liebigs Ann. Chem.* **1993**, 911. (b) Larsen, D. S.; O'Shea, M. D. *Tetrahedron Lett.* **1993**, *34*, 1373. (c) Krohn, K.; Khanbabaee, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 99. (d) Larsen, D. S.; O'Shea, M. D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1019 e) Kim, K.; Sulikowski, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2397. (f) Matsuo, G.; Miki, Y.; Nakata, M.; Matsumura, S.; Toshima, K. *Chem. Commun.* **1996**, 225. (g) Carreno, M. C.; Urbano, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1621. (h) Larsen, D. S.; O'Shea, M. D.; Brooker, S. *Chem. Commun.* **1996**, 203.

(4) Photolysis was carried out by exposing a benzene solution of the quinone to two 40 W fluorescent lights for a few hours.

(5) This method is particularly efficient for the synthesis of substituted cyclobutendione monoketals from squaric acid. See, for example: Gayo, L.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 6896;. Santora, V. J.; Moore, H. W. *J. Am. Chem. Soc.* **1995**, *117*, 8486.

Scheme 5[a]



[a] Key: (a) 1-lithio-1-methoxyallene/THF, −78 °C; (b) 2-lithioanisole/THF, −78 °C; (c) HCl, rt; (d) benzene, reflux; (e) Ag_2O/K_2CO_3; (f) bromine/Cl_3CH, −10 °C; (g) visible light/$CHCl_3$, rt.

The significant points to arise from this study include the following: (1) thermal rearrangements of 2-allenyl-3-(2-ethenylphenyl)-4,4-dimethoxycyclobutenones were observed to take place at ambient temperature to give 3-alkylidene-2b,3,4,4a-tetrahydro-2,2-dimethoxydicyclobuta[*a*,*c*]naphthalen-1(2*H*)-one, **5**−**9**. Such compounds were found to be useful synthetic precursors to benza[*a*]anthracene-7,12-diones, e.g., **15** and **19**; (2) in comparison, 2-alkynyl-3-(ethenylphenyl)-4,4-dimethoxycyclobutenones were observed to be stable at ambient temperature but rearranged to the unusual 1-(1-alkylidene)-1,2-dihydro-2,2-dimethoxynaphtho[2,1-*b*]furan, **12a**−**f**, at 110 °C (refluxing toluene).

Experimental Section

General Methods. All air- or water-sensitive reactions were carried out in flame-dried glassware under nitrogen. Tetrahydrofuran (THF) was dried by passing it through two 4 × 36 in. columns of anhydrous neutral A-2 alumina. Flash column chromatography was performed using silica gel (230−400 mesh) according to the procedure of Still, Kahn, and Mitra.[6] Analytical TLC was performed on E. Merck silica gel 60 F_{254} coated on glass. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively, on $CDCl_3$ solutions. All NMR spectra were referenced to $CHCl_3$ resonance (7.26 and 77.0 ppm) and are reported in units of δ with coupling constants in hertz (Hz).

3-[(*Z*)-Benzylidene]-2b,3,4,4a-tetrahydro-2,2-dimethoxydicyclobuta[*a*,*c*]naphthalen-1(2*H*)-one (5). To a solution of 3-phenyl-1-propyne (0.25 g, 2.15 mmol) in THF (25 mL) at −78 °C was added ^{n}BuLi (1.34 mL, 1.6 M in hexanes, 2.15 mmol). The resulting reaction mixture was stirred for 30 min (−78 °C) and then transferred via cannula to a solution of 2-(2-vinylphenyl)-3,4,4-trimethoxy-2-cyclobutene-1-one (**1**)[2] (0.26 g, 1.00 mmol) in THF (25 mL). The resulting solution was stirred for 1 h at −78 °C, quenched with saturated ammonium chloride (20 mL), and extracted with diethyl ether. The combined organic portion was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was dissolved in THF (25 mL), and dry TEA was added (0.30 mL, 2.15 mmol). This solution was stirred for 1 h at room temperature and concentrated in vacuo. Chromatography (hexanes/EtOAc = 15:1) gave **5** (0.15 g, 44% overall yield from **1**) as a white solid: mp 122−123 °C (from hexanes/EtOAc); IR (KBr) 2942, 1758, 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) 3.17−3.21 (m, 2H), 3.33 (s, 3H), 3.58 (s, 3H), 3.97 (q, J = 8.4 Hz, 1H), 4.59 (dd, J = 2.0, 8.1 Hz, 1H), 6.35 (d, J = 2.0 Hz, 1H), 7.15 (d, J = 7.4 Hz, 1H), 7.22−7.24 (m, 2H), 7.26 (dt, J = 1.4, 7.5 Hz, 1H), 7.31 (dt, J = 1.4, 7.5 Hz, 1H), 7.34−7.37 (m, 1H), 7.37−7.42 (m, 2H), 7.63 (dd, J = 1.3, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 191.6, 177.1, 152.4, 139.3, 137.8, 135.8, 130.7, 128.4, 127.9, 127.5, 127.4, 127.0, 126.2, 123.9, 123.4, 119.0, 53.8, 53.0, 46.0, 43.9, 37.3; exact mass calcd for $C_{23}H_{20}O_3$ 344.1412, found 344.1423.

2b,3,4,4a-Tetrahydro-2,2,2b-trimethoxy-3-methylenedicyclobuta[*a*,*c*]naphthalen-1(2*H*)-one (6). To a solution of methoxyallene (0.50 g, 7.14 mmol) in THF (25 mL) at −40 °C was added ^{n}BuLi (4.46 mL, 1.6 M in hexanes, 7.14 mmol).[7] The resulting reaction mixture was stirred for 30 min (−40 °C), cooled to −78 °C, and then transferred via *cannula* to a solution of **1** (0.41 g, 1.60 mmol) in THF (25 mL). The resulting solution was stirred for 30 min at −78 °C, quenched with saturated ammonium chloride (20 mL), and extracted with diethyl ether. The combined organic portion was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Chromatography (hexanes/EtOAc = 12:1) gave **6** (0.38 g, 81%) as a white solid: mp 92.5−94.0 °C; IR (KBr) 2943, 1765, 1449 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) 2.28 (ddt, J = 2.8, 9.1, 15.5 Hz, 1H), 3.00 (dddd, J = 1.8, 1.9, 10.1, 15.5 Hz, 1H), 3.23 (s, 3H), 3.53 (s, 3H), 3.60 (s, 3H), 3.81 (dd, J = 9.1, 10.1 Hz, 1H), 5.13 (s, 1H), 5.36 (s, 1H), 7.26 (d, J = 7.5 Hz, 1H), 7.30 (dt, J = 1.3, 7.5 Hz, 1H), 7.35 (dt, J = 1.3, 7.5 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 189.4, 171.5, 154.5, 147.9, 138.3, 130.8, 127.3, 126.4, 122.8, 118.4, 108.2, 79.7, 53.2, 52.8, 51.9, 43.0, 35.0; exact mass calcd for $C_{18}H_{18}O_4$ 298.1204, found 298.1197.

3-(1-Hexynyl)-4,4-dimethoxy-2-(2-vinylphenyl)-2-cyclobuten-1-one (2e). To a solution of 1-hexyne (0.13 mL, 1.15 mmol) in THF (15 mL) at −78 °C was added ^{n}BuLi (0.72 mL, 1.6 M in hexanes, 1.15 mmol). The resulting reaction mixture was stirred for 30 min (−78 °C) and then transferred via cannula to a solution of **1** (0.25 g, 0.96 mmol) in THF (25 mL). The resulting solution was stirred for 1 h at −78 °C, quenched with saturated sodium bicarbonate (20 mL), and extracted with diethyl ether. The combined organic portion was washed with brine, dried over anhyd. magnesium sulfate, and concentrated in vacuo. Chromatography (hexanes/EtOAc = 15:1) gave **2e** (0.203 g, 68%) as a yellow oil: IR (film) 2959, 2212, 1765, 1341 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) 0.93 (t, J = 7.5, 3H), 1.44 (sextet, J = 7.5 Hz, 2H), 1.58−1.64 (m, 2H), 2.59 (t, J = 7.0 Hz, 2H), 3.63 (s, 6H), 5.34 (d, J = 11.1 Hz, 1H), 5.72 (d, J = 17.1 Hz, 1H), 7.06 (dd, J = 11.1, 17.1 Hz, 1H), 7.29−7.32 (m, 1H), 7.39 (dd, J = 7.2, 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 1.0, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz)192.6, 157.3, 155.3, 136.9, 135.2, 130.2, 129.1, 127.5, 126.5, 125.9, 121.2, 116.0, 115.3, 72.8, 53.1, 29.9, 22.0, 20.5, 13.4; exact mass calcd for $C_{20}H_{22}O_3$ 310.1569, found 310.1560.

1-(1-Hexenylidene)-1,2-dihydro-2,2-dimethoxynaphtho-[2,1-*b*]furan (12e). A solution of **2e** (0.10 g, 0.32 mmol) in toluene (10 mL) was refluxed for 8 h. Concentration in vacuo and chromatography in Florisil (hexanes/EtOAc 75:1) gave **3a** (0.038 g, 38%) as a pale yellow oil: IR (film) 2950, 1955, 1627, 1459 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) 0.93 (t, J = 9.3 Hz, 3H), 1.46 (sextet, J = 7.4 Hz, 2H), 1.60 (tq, J = 7.4, 9.3 Hz, 2H), 2.32 (dq, J = 6.8, 7.4 Hz, 2H), 3.47 (s, 3H), 3.50 (s, 3H), 6.08 (t, J = 6.8 Hz, 1H), 7.14 (d, J = 8.8 Hz, 1H), 7.35 (dt, J = 1.0, 7.5 Hz, 1H), 7.48 (dt, J = 1.0, 8.2 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 200.9, 154.6, 130.6, 129.7, 129.1, 129.0, 127.2, 123.7, 122.2, 113.5, 111.6, 101.5, 99.9, 51.6, 51.5, 31.0, 29.2, 22.3, 13.9; exact mass calcd for $C_{20}H_{22}O_3$ 310.1569, found 310.1580.

1,2,2a,12b-Tetrahydro-8,12b-dimethoxy-1-methylenebenzo[*a*]cyclobuta[*c*]anthracene-7,12-dione (14). To a solution of 2-bromoanisole (0.50 g, 2.64 mmol) in THF (20 mL) at −78 °C was added ^{n}BuLi (1.65 mL, 1.6 M in hexanes, 2.64 mmol). The resulting reaction mixture was stirred for 1 h (−78 °C) and then transferred via cannula to a solution of **6** (0.20 g, 0.67 mmol) in THF (20 mL). The resulting solution was stirred for 1 h at −78 °C, and HCl (2 mL, 12 N) was added. This mixture was stirred for 1 h to room temperature, neutralized with saturated aqueous sodium bicarbonate (20 mL), and extracted with diethyl

(6) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(7) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim.* **1968**, *87*, 916. Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim.* **1968**, *87*, 1179. For a review, see: Zimmer, R. *Synthesis* **1993**, 165.

ether. The combined organic portion was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product was immediately heated in refluxing benzene (20 mL) for 1 h, the reaction mixture was cooled to room temperature and potassium carbonate (0.27 g, 1.98 mmol), and silver(I) oxide (4.58 g, 1.98 mmol) were added. The reaction mixture was stirred for 1 h to room temperature, filtrated, and concentrated in vacuo. Chromatography (hexanes/EtOAc = 10:1) gave product **14** (0.145 g, 60% overall yield from **6**) as an orange solid: mp 164−166 °C; IR (KBr) 2924, 1664, 1586, 1560 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) 2.34 (ddt, J = 2.5, 9.6, 14.8 Hz, 1H), 2.89 (ddd, J = 2.2, 10.0, 14.8 Hz, 1H), 3.12 (s, 3H), 3.74 (dd, J = 9.6, 10.0 Hz, 1H), 4.03 (s, 3H), 5.15 (s, 1H), 5.69 (dd, J = 2.2, 2.5 Hz, 1H), 7.24−7.27 (m, 2H), 7.35 (dd, J = 1.4, 7.0 Hz, 1H), 7.40 (dt, J = 1.2, 7.4 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 185.2, 182.8, 158.6, 147.6, 145.2, 138.7, 134.9, 134.5, 131.4, 131.2, 131.2, 127.7, 127.1, 126.6, 122.2, 118.7, 116.9, 110.2, 79.1, 56.5, 51.4, 41.1, 33.9; exact mass calcd for $C_{23}H_{18}O_4$ 358.1204, found 358.1221.

6,11-Dimethoxybenza[*a*]anthracene-7,12-dione (15). To a solution of **14** (0.10 g, 0.27 mmol) in $CHCl_3$ (25 mL) at −10 °C was added bromine (0.014 mL, 0.27 mmol) in $CHCl_3$ (1 mL). The resulting reaction mixture was stirred for 1 h (−10 °C), stirred overnight to room temperature in an aluminum foil lined cardboared box containing two (2 ft, 40 W) fluorescent light bulbs, and concentrated in vacuo. Chromatography (hexanes/EtOAc = 8:1) gave **15** (0.068 g, 77%) as an orange-yellow solid: mp 219−220 °C (from EtOAc/hexanes); IR (KBr) 2927, 1669, 1587, 1283 cm^{-1};^1H NMR ($CDCl_3$, 500 MHz) 4.04 (s, 3H), 4.09 (s, 3H), 7.25 (d, J = 8.4 Hz, 1H), 7.48 (s, 1H), 7.53 (dt, J = 1.6, 7.6 Hz, 2H), 7.57 (dt, J = 1.2, 8.1 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 9.04 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 186.4, 184.1, 158.3, 154.9, 137.5, 136.7, 135.9, 134.2, 129.2, 128.4, 127.0, 126.7, 124.9, 124.3, 123.5, 118.7, 116.6, 112.9, 56.5, 56.4; exact mass calcd for $C_{20}H_{14}O_4$ 318.0892, found 318.0887.

4-(2-Isopropenylphenyl)-2,2,3-trimethoxycyclobutenone (16). In analogy to the synthesis of **1**, compound **16** (0.75 g, 71%, chromatography, hexanes/EtOAc 10:1) was obtained as a yellow oil from 1-bromo-2-isopropenylbenzene[8] (1.00 g, 5.07 mmol) and dimethyl squarate (0.55 g, 3.90 mmol): IR (film) 2946, 1763, 1635 cm^{-1};^1H NMR ($CDCl_3$, 500 MHz) 2.12 (d, J = 0.8 Hz, 3H), 3.57 (s, 6H), 4.10 (s, 3H), 4.84 (dd, J = 0.8, 1.7 Hz, 1H), 5.39 (dd, J = 1.5, 1.7 Hz, 1H), 7.24 (dd, J = 1.9, 5.5 Hz, 1H), 7.27 (dd, J = 5.5, 7.4 Hz, 1H), 7.30 (dt, J = 1.4, 7.4 Hz, 1H), 7.45 (dd, J = 1.4, 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz)-188.9, 181.0, 145.1, 143.5, 131.2, 129.4, 128.5, 128.0, 126.8, 125.0, 115.5, 113.7, 60.0, 53.7, 23.9; exact mass calcd for $C_{16}H_{18}O_4$ 274.1204, found 274.1209.

2b,3,4,4a-Tetrahydro-2,2,2b-trimethoxy-4a-methyl-3-methylenedicyclobut[*a*,*c*]naphthalen-1(2*H*)-one (17). In analogy to the synthesis of **6**, compound **17** (0.41 g, 72%, chromatography, hexanes/EtOAc 15:1) was obtained as a white solid from **16** (0.50 g, 1.82 mmol) and methoxyallene (0.57 g, 8.19 mmol): mp 98−99 °C; IR (KBr) 2944, 1767, 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) 1.73 (s, 3H), 2.35 (s, 2H), 3.16 (s, 3H), 3.52 (s, 3H), 3.61 (s, 3H), 5.13 (s, 1H), 5.39 (s, 1H), 7.31 (dd, J = 1.2, 7.4 Hz, 1H), 7.39−7.44 (m, 2H), 7.72 (d, J = 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 189.5, 172.2, 154.2, 148.9, 142.5, 130.9, 126.9, 126.6, 124.8, 122.8, 108.4, 80.4, 53.2, 53.1, 52.8, 45.5, 42.9, 17.8; exact mass calcd for $C_{19}H_{20}O_4$ 312.1361, found 312.1349.

6,11-Dimethoxy-5-methylbenza[*a*]anthracene-7,12-dione (19). To a solution of 2-bromoanisole (0.48 g, 2.56 mmol) in THF (20 mL) at −78 °C was added ^{n}BuLi (1.60 mL, 1.6 M in hexanes, 2.56 mmol). The resulting reaction mixture was stirred for 1 h (−78 °C) and then transferred via cannula to a solution of **17** (0.20 g, 0.64 mmol), in THF (20 mL). The resulting solution was stirred for 1 h at −78 °C, and HCl (2 mL, 12 N) was added. This mixture was stirred for 1 h to room temperature, neutralized with saturated sodium bicarbonate (20 mL), and extracted with diethyl ether. The combined organic portion was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The crude product (protected from light by aluminum foil) was immediately heated in refluxing benzene (20 mL) for 1 h then, the reaction mixture was cooled to room temperature, and potassium carbonate (0.26 g, 1.92 mmol), and silver(I) oxide (4.44 g, 1.92 mmol) were added. The reaction mixture was stirred for 1 h to room temperature, filtered, and concentrated in vacuo to give a light-sensitive orange oil that was dissolved in $CHCl_3$ (20 mL) and cooled to −10 °C, and bromine (0.032 mL, 0.64 mmol) in $CHCl_3$ (6 mL) was added. The resulting reaction mixture was stirred for 1 h (−10 °C), stirred overnight to room temperature in an aluminum foil lined cardboared box containing two (2 ft, 40 W) fluorescent light bulbs, and concentrated in vacuo. Chromatography (hexanes/EtOAc = 9:1) gave product **19** (0.10 g, 48% overall yield from **17**) as an orange solid: mp 210 °C dec (from diethyl ether/hexanes); IR (KBr) 2935, 1670, 1576, 1275 cm^{-1};^1H NMR ($CDCl_3$, 500 MHz) 2.72 (s, 3H), 3.95 (s, 3H), 4.04 (s, 3H), 7.27−7.30 (m, 1H), 7.59−7.71 (m, 3H), 7.76 (d, J = 7.4 Hz, 1H), 8.04 (dd, J = 1.3, 7.4 Hz, 1H), 9.15 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 186.6, 184.2, 158.3, 152.5, 136.8, 136.5, 134.4, 134.1, 134.0, 128.9, 128.9, 127.6, 126.9, 126.9, 124.1, 123.7, 118.6, 116.8, 62.2, 56.5, 11.8; exact mass calcd for $C_{21}H_{16}O_4$ 332.1048, found 332.1049.

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Supporting Information Available: X-ray crystallographic data for compounds **5** as well as spectral data for compounds **7**, **8**, **9**, **2a**−**d**,**f**, and **12a**−**d**,**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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