Regioselective Annulation of Alicyclic−Aromatic Dienes with 3-Halo-3-cyclobutene-1,2-diones. Synthesis of Annulated α-Halobenzocyclobutenones[1]

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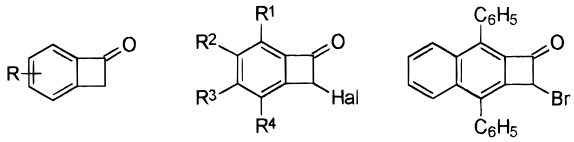
4-(1-Cycloalken-1-yl)-1,2-dialkoxybenzenes **8**, **10**, and **11** and 5-(1-cycloalken-1-yl)-1,3-benzodioxoles **12**−**15** react with the semisquaric halides **5a** and **5b** in a dehydrative annulation process to give the annulated α-halobenzocyclobutenones **9a**,**b** and **16a**,**b**−**21a**,**b** in poor to good yields (20−76%). The reaction failed with alicyclic−aromatic dienes having no or only one alkoxy group in the benzene ring. The dehydrative annulation process could be extended to 4-(3,4-dimethoxyphenyl)-1,2-dihydronaphthalene **(24)**, affording the highly annulated α-chlorobenzocyclobutenone **25** in 50% yield. In the case of 5-(1-cyclobuten-1-yl)-1,3-benzodioxole **(22)**, reaction with the semisquaric halides **5a**,**b** yielded the dicyclobutanaphthodioxole-1,2-dione **(23)** as the sole product in a dehydrochlorinative annulation process. A reaction pathway has been suggested for the dehydrative annulation process. Several of the annulated α-halobenzocyclobutenones prepared were submitted to selected chemical transformations. Thus, the reaction with tributyltin hydride afforded the annulated benzocyclobutenones **26a**−**f** in excellent yields (74−78%), and treatment with silver trifluoroacetate afforded the α-(trifluoroacetoxy)benzocyclobutenones **27a**−**c** in 71−79% yields.

Introduction

Much attention has been focused on benzocyclobutenones **1** in recent years. They have been used as synthons[2] as well as for the construction of complex organic compounds.[3] Surprisingly, α-halogenated benzocyclobutenones **2** have not been extensively examined. Compared with simple benzocyclobutenones, they exhibit additional functionality that should enable a wide range of preparatively useful transformations and afford access to many novel derivatives.

The parent compound, α-bromobenzocyclobutenone **(2b)**, was originally synthesized by Cava *et al.*[4] in 1964. Since then, only α-chlorobenzocyclobutenone **(2a)**,[5,6] the substituted representative **2c**,[7] and the annulated representatives **2d**[8] and **3**[9] have additionally been described. The synthesis of α-bromobenzocyclobutenones **2b**,[4] **2c**,[7] **2d**,[8] and **3**[9] was accomplished by bromination of the respective benzocyclobutenone **1** with NBS, while α-chlorobenzocyclobutenone (**2a**)[5,6] has been obtained by partial hydrolysis of 1,1,2-trichlorobenzocyclobutene[5,6] with silver trifluoroacetate in aqueous acetonitrile.[5] In the present paper we report a novel synthesis of α-halobenzocyclobutenones and further chemical transformations.



1 **2** **3**

2a: R1 - R4 = H, Hal = Cl
2b: R1 - R4 = H, Hal = Br
2c: R1, R4 = OMe, R2, R3 = H, Hal = Br
2d: R1, R4 = H, R2 - R3 = OCH_2O, Hal = Br

Results and Discussion

In preliminary experiments[10] on the annulation of 5-(1-alkenyl)-1,3-benzodioxoles with 3-chloro-3-cyclobutene-1,2-dione (semisquaric chloride) **(5a)** we obtained in the case of 5-isopropenyl-1,3-benzodioxole (pseudosafrole) **(4)** not only the expected dione **6** but also a condensation product, to which we tentatively assigned structure **7** (Scheme 1).

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(1) Oxocarbons and Related Compounds; Part 26. Part 25: Schmidt, A. H.; Lechler, K. O.; Pretz, T.; Franz, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 497.

(2) For examples, see: (a) Liebeskind, L. S.; Iyer, S.; Jewell, C. F. *J. Org. Chem.* **1986**, *51*, 3065. (b) Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067. (c) Liebeskind, L. S.; Lescosky, L. J.; McSwain, C. M., Jr. *J. Org. Chem.* **1989**, *54*, 1435. (d) Hosaya, T.; Kuriyama, Y.; Suzuki, K. *Synlett* 1995, 635.

(3) For examples, see: a) Stevens, R. V.; Bisacchi *J. Org. Chem.* **1982**, *47*, 2396. (b) Azadi-Ardakani, M.; Wallace, T. W. *Tetrahedron* **1988**, *44*, 5939. (c) Azadi-Ardakani, M.; Hayes, R.; Wallace, T. W. *Tetrahedron* **1990**, *46*, 6851. (d) Tomioka, H.; Yamamoto, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1961. (e) Hickman, D. N.; Hodgetts, K. J.; Mackmann, P. S.; Wallace, T. W.; Wardleworth, J. M. *Tetrahedron* **1996**, *52*, 2235.

(4) Cava, M. P.; Mangold, D.; Muth, K. *J. Org. Chem.* **1964**, *29*, 2947.

(5) Abou-Teim, O.; Goodland, M. C.; McOmie, J. F. W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2659.

(6) Filip, P.; Stefan, N.; Chiraleu, F.; Dinulescu, I. G.; Avram, M. *Rev. Roum. Chim.* 1984, *29*, 549.

(7) Azadi-Ardakani, M.; Wallace, T. W. *Tetrahedron* **1988**, *44*, 5939.

(8) Jung, M. E.; Lam, P. Y.; Mansuri, M. M.; Speltz, L. M. *J. Org. Chem.* **1985**, *50*, 1087.

(9) Cava, M. P.; Hwang, B. *Tetrahedron Lett.* **1965**, 2297.

(10) Schmidt, A. H.; Kircher, G.; Künz, C.; Wahl, S.; Hendriok, M. W. *J. Org. Chem.* **1995**, *60*, 3890.

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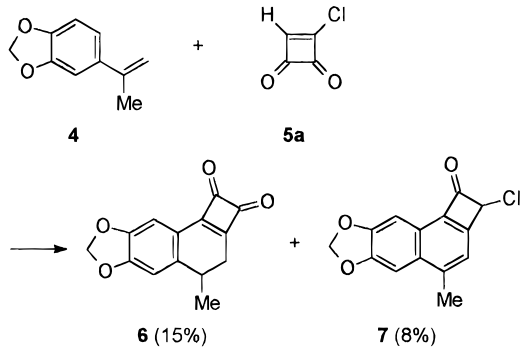
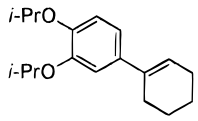
Scheme 1

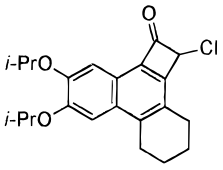


The formation of the α-chlorobenzocyclobutenone **7**, besides the dihydrobenzocyclobutenedione **6**, in the reaction of **4** with **5a** shows that "dehydrative annulation" is in competition with "dehydrochlorinative annulation".

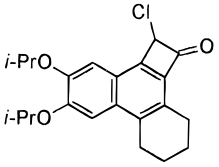
Further investigations have shown that reactions of **5a** and 3-bromo-3-cyclobutene-1,2-dione (semisquaric bromide) **(5b)** with several alicyclic−aromatic dienes yield α-halobenzocyclobutenones as the main or only product. Thus, the treatment of 4-(1-cyclohexen-1-yl)-1,2-diisopropoxybenzene **(8)** with **5a** leads to a condensation product, for which the structures **9a** and **9′a** could be proposed.



8



9a



9′a

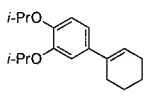
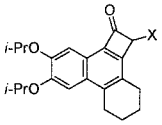
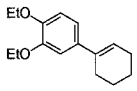
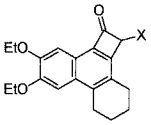
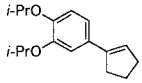
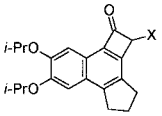
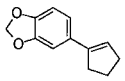
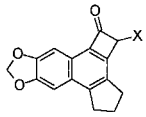
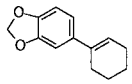
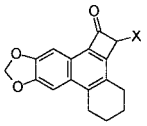
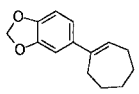
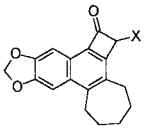
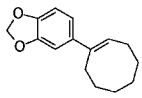
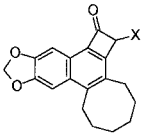
X-ray crystallographic analysis[11] required unambiguously that the structure **9a** be attributed to the condensation product, thus confirming the regiospecificity of this dehydrative annulation.

The general character of this dehydrative annulation has been demonstrated by the reaction of the 4-(1-cycloalken-1-yl)-1,2-dialkoxybenzenes **8**, **10**, and **11** and the 5-(1-cycloalken-1-yl)-1,3-benzodioxoles **12**−**15** with the semisquaric halides **5a** and **5b**. Table 1 gives a view of the results obtained.

Table 1 shows that dehydrative annulation with the generation of α-halobenzocyclobutenones is observed as the main reaction with all of the alicyclic−aromatic dienes **8** and **10**−**15** employed. While the α-chlorobenzocyclobutenones **9a**, **16a**, **17a**, and **19a**−**21a** were obtained in moderate yields ranging from 20 to 48% (Table 1, entries 1, 3, 5, 8, 10, and 12), the respective α-bromobenzocyclobutenones **9b**, and **16b**−**21b** were obtained in markedly better yields: 54−76% (Table 1, entries 2, 4, 6, 7, 9, 11, and 13). It, furthermore, reveals

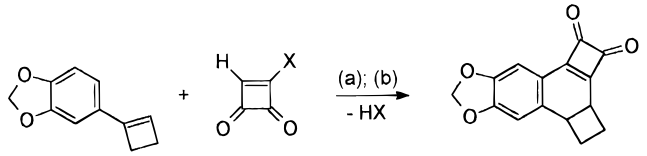
(11) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

Table 1. α-Halobenzocyclobutenones Obtained by the Dehydrative Annulation of Alicyclic-Aromatic Dienes with 3-Halo-3-cyclobutene-1,2-diones

entry	alicyclic-aromatic diene	3-halo-3-cyclobutene-1,2-dione	conditions[a]	product	yield[b] (%)
					
1	**8**	**5a**	A	**9a** X = Cl	20[c]
2	**8**	**5b**	B	**9b** X = Br	58[c]
					
3	**10**	**5a**	A	**16a** X = Cl	31[c]
4	**10**	**5b**	B	**16b** X = Br	50[c]
					
5	**11**	**5a**	A	**17a** X = Cl	48[c]
6	**11**	**5b**	B	**17b** X = Br	54[c]
					
7	**12**	**5b**	B	**18b** X = Br	55[d]
					
8	**13**	**5a**	A	**19a** X = Cl	46[c]
9	**13**	**5b**	B	**19b** X = Br	55[d]
					
10	**14**	**5a**	A	**20a** X = Cl	20[d]
11	**14**	**5b**	B	**20b** X = Br	65[d]
					
12	**15**	**5a**	A	**21a** X = Cl	36[d]
13	**15**	**5b**	B	**21b** X = Br	76[c]

[a]Reaction conditions: (A) neat; 30 °C for 30 min and then heating to 80 °C for 30 min. Product isolated by column chromatography. (B) In THF; reflux for 10 min, then removal of the solvent and heating to 80 °C for 30 min. Product isolated by column chromatography. [b]Yields are of pure isolated products based on (diene used − diene recovered.).[c]No side products were isolated by column chromatography.[d]For side products, see Experimental Section.

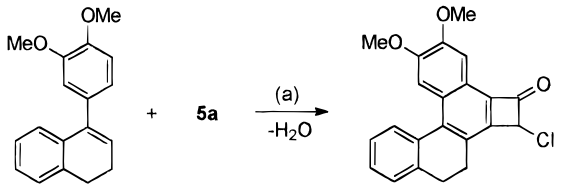
Scheme 2[a]



22 **5a** : X = Cl, **5b** : X = Br **23**

[a] Reaction conditions: (a) With **5a**: in CH_2Cl_2; rt for 12 h. Product isolated by column chromatography. (b) With **5b**: in THF; reflux for 10 min, then removal of solvent and heating to 80 °C for 30 min. Product isolated by column chromatography.

Scheme 3[a]



24 **25**

[a] Reaction conditions: (a) in THF; reflux for 10 min, then removal of solvent and heating to 80 °C for 30 min. Product isolated by column chromatography.

that the reactions with semisquaric bromide **(5b)** take place under much smoother conditions than the reactions with semisquaric chloride **(5a)**.

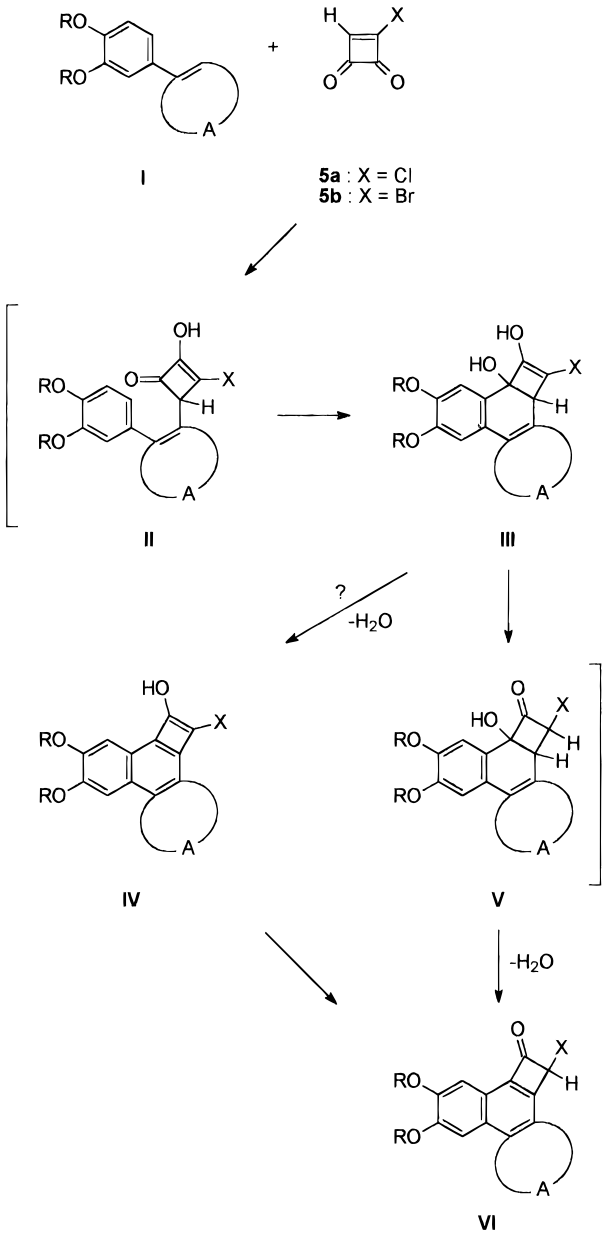
In contrast to the 5-(1-cycloalken-1-yl)-1,3-benzodioxoles **12**−**15**, 5-(1-cyclobuten-1-yl)-1,3-benzodioxole **(22)** reacted with the semisquaric halides **5a**,**b** in a dehydrochlorinative annulation to afford the pentacyclic dicyclobuta[5,6:7,8]naphthodioxole-1,2-dione **(23)** as the sole product in 20% and 45% yield, respectively. (Scheme 2).

It is of importance to note that the dehydrative annulation is restricted to alicyclic−aromatic dienes bearing two alkoxy groups in positions 1 and 2 of the benzene ring. Thus, 1-phenylcyclohexene, 1-(4-anisyl)-cyclohexene, and 1-(4-tolyl)cyclohexene failed to react with **5a** and **5b** to give α-halobenzocyclobutenones. Interestingly, with the aforementioned dienes, dehydrochlorinative annulation was also not observed.

Scheme 3, on the other hand, shows how the dehydrative annulation process can be profitably employed to rapidly assemble structurally complex target molecules. Reaction of semisquaric chloride **(5a)** with 4-(3,4-dimethoxyphenyl)-1,2-dihydronaphthalene **(24)**, under conditions B, afforded the pentacyclic condensation product **25** in 50% yield.

To explain the formation of the α-halobenzocyclobutenones **VI** (see Scheme 4) we hypothesize the initial formation of adduct **II**. Similar 1,4-addition reactions of simple arenes to semisquaric chloride **(5a)**, in the presence of $AlCl_3$, have recently been reported.[12] Owing to the substitution pattern and the high electron density of the dialkoxylated benzene ring of **II**, as well as a favorable geometry, electrophilic attack of the four-membered ring onto the benzene moiety is assumed to give the tetracyclic compound **III**. Elimination of H_2O from **III** seems to be an energetically unfavorable process

Scheme 4



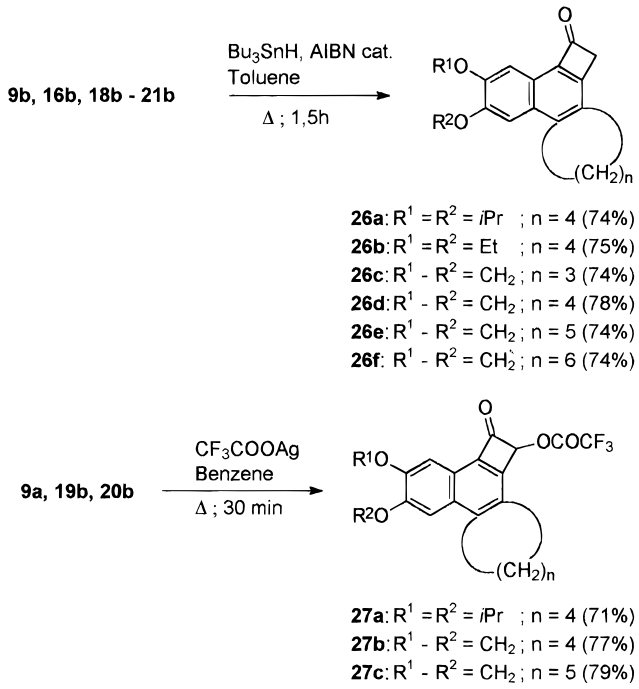
since a benzocyclobutadiene **IV** would be formed. Instead, ketonization of **III** is assumed with the formation of **V**. **V** can easily release H_2O, providing the α-halobenzocyclobutenones **VI**. This elimination process is supported by the aromatization of the newly formed six-membered ring.

The great synthetic potential of the α-halobenzocyclobutenones prepared has been demonstrated by the following chemical transformations. Treatment of the α-bromocyclobutenones **9b**, **16b**, **18b**−**21b** with tributyltin hydride afforded the annulated benzocyclobutenones **26a**−**f** in excellent yields (74−78%). **9a**, **19b**, and **20b** also reacted easily with silver trifluoroacetate to give the α-(trifluoroacetoxy)benzocyclobutenones **27a**−**c** (Scheme 5).

In summary, rapid access to annulated α-halobenzocyclobutenones can be easily achieved by an unprecedented dehydrative annulation of various alicyclic−aromatic dienes with semisquaric halides. Extension of this process to other dienes is in progress. Further

(12) Schmidt, A. H.; Kircher, G.; Maus, S.; Bach, H. *J. Org. Chem.* **1996**, *61*, 2085.

Scheme 5



studies are also being directed toward the investigation of the synthetic potential of the annulated α-halobenzocyclobutenones.

Experimental Section

For general experimental techniques, see our previous paper.[12]

Starting Materials. Semisquaric halides **5a** and **5b** were obtained by reacting semisquaric acid[13] with the appropriate oxalic dihalide.[14] 1-Phenylcyclohexene,[15] 1-(4-anisyl)cyclohexene,[16] 1-(4-tolyl)cyclohexene,[17] 5-(1-cyclopenten-1-yl)-1,3-benzodioxole **(12)**,[18] 5-(1-cyclohexen-1-yl)-1,3-benzodioxole **(13)**,[19] and 4-(3,4-dimethoxyphenyl)-1,2-dihydronaphthalene **(24)**[20] were prepared following literature procedures. Alicyclic−aromatic dienes not mentioned in the literature were obtained analogously or in modified procedures by the reaction of the appropriate alicyclic ketone with the corresponding substituted arylmagnesium bromide followed by treatment with hydrochloric acid.[21]

Reaction of Alicyclic−Aromatic Dienes 8, 10−15, 24 with Semisquaric Halides 5a and 5b. Synthesis of α-Halobenzocyclobutenones. General Procedures. Method A. Semisquaric chloride **(5a)** (1.16 g 10 mmol) and the appropriate alicyclic−aromatic diene (10 mmol) were combined, and the mixture was magnetically stirred at 30 °C for 30 min. The reaction mixture was then heated to 80 °C for 30 min. The brown reaction mixture obtained was subjected to column chromatography (silica gel 60, 500 g) using CH_2Cl_2 as eluent. Components are listed in the order of elution.

Method B. A solution of semisquaric chloride **(5a)** (1.16 g, 10 mmol) or semisquaric bromide **(5b)** (1.61 g 10 mmol) and the appropriate alicyclic−aromatic diene (10 mmol) in THF (10 mL) was magnetically stirred and heated to reflux for 10 min. The solvent was removed under reduced pressure, and the reaction mixture was then heated to 80 °C for 30 min. The brown reaction mixture was subjected to column chromatography (silica gel 60, 500 g) using CH_2Cl_2 as eluent. Components are listed in the order of elution.

2-Chloro-3,4,5,6-tetrahydro-8,9-diisopropoxycyclobuta[*l*]phenanthren-1(2*H*)-one (9a). Method A. Unreacted **8**: 0.25 g (9%). **9a**: white crystals; mp 161−162 °C (MeOH); yield 0.67 g (20%); IR 1750 (vs), 1620 (w), 1590 (w), 1550 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38−1.41 (m, 12H), 1.84−1.90 (m, 2H), 1.91−2.01 (m, 2H), 2.83−2.89 (m, 1H), 3.00−3.08 (m, 3H), 4.59−4.64 (m, 1H), 4.70−4.74 (m, 1H), 5.89 (s, 1H), 7.40 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.75, 21.91, 22.03, 22.69, 25.38, 27.38, 67.86, 71.50, 72.76, 108.17, 110.80, 120.71, 128.07, 130.34, 139.17, 142.94, 150.03, 151.41, 152.77, 180.46; MS *m/z* (relative intensity) 374 (M^+, 35), 372 (M^+, 100), 330 (22), 288 (37), 225 (44). Anal. Calcd for $C_{22}H_{25}ClO_3$: C, 70.86; H, 6.76; Cl, 9.51. Found: C, 70.80; H, 6.69; Cl, 9.34. Crystal data for **9a**: triclinic, *P*-1, unit cell parameters a = 9.272(3) Å, b = 10.839(3) Å, c = 11.051(4) Å, α = 73.76(2)°, β = 66.61(3)°, γ = 84.53(2)°, V = 980.7(5) Å^3, Z = 2, d_c = 1.242, 5048 data collected with 4° < θ < 60°, 4243 unique reflections, 2221 reflections with I < 3σ(*I*) criterion used in refinement. Data were collected on a Siemens P4 at −30 °C. The structure was solved by direct methods, all nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were isotropically with fixed temperature factors U = 0.08. A total of 236 parameters were refined with a weigthing scheme [w^{-1} = $\sigma^2(F) + 0.000344(F^2)$]. Refinement converged with R = 0.0689 and R_w = 0.0717. The program used for structure solution and refinement was Siemens SHELXTL PLUS.

2-Bromo-3,4,5,6-tetrahydro-8,9-diisopropoxycyclobuta[*l*]phenanthren-1(2*H*)-one (9b). Method B. Unreacted **8**: 0.70 g (25%). **9b**: white crystals; mp 153−154 °C (EtOH); yield 1.79 g (58%); IR 1760 (vs), 1620 (w), 1590 (w), 1550 (m) (C=O, C=C) cm_{-1}; ^1H NMR ($CDCl_3$) δ 1.37−1.41 (m, 12H), 1.87−1.90 (m, 2H), 1.94−1.98 (m, 2H), 2.71−2.84 (m, 1H), 2.98−3.05 (m, 3H), 4.58−4.62 (m, 1H), 4.69−4.72 (m, 1H), 5.98 (s, 1H), 7.38 (s, 1H), 7.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.71, 21.88, 21.93, 22.02, 22.65, 25.30, 27.38, 56.91, 71.51, 72.73, 108.11, 110.91, 120.66, 128.13, 130.38, 138.66, 143.08, 150.06, 151.41, 152.37, 179.95; MS *m/z* (relative intensity) 418 (M^+, 86), 416 (M^+, 85), 337 (33), 295 (68), 253 (100), 225 (74). Anal. Calcd for $C_{22}H_{25}BrO_3$: C, 63.32; H, 6.04; Br, 19.15. Found: C, 63.37; H, 6.16; Br, 19.20.

2-Chloro-8,9-diethoxy-3,4,5,6-tetrahydrocyclobuta[*l*]-phenanthren-1(2*H*)-one (16a). Method A. Unreacted **10**: 0.52 g (21%). **16a**: white crystals; mp 225−227 °C (EtOH); yield 0.85 g (31%); IR 1765 (vs), 1630 (w), 1565 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50−1.54 (m, 6H), 1.82−1.90 (m, 2H), 1.94−2.00 (m, 2H), 2.80−2.86 (m, 1H), 2.96−3.04 (m, 3H), 4.14−4.21 (m, 4H), 5.87 (s, 1H), 7.21 (s, 1H), 7.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.49, 14.56, 21.70, 22.66, 25.37, 27.39, 64.57, 67.84, 105.31, 105.33, 120.06, 128.13, 130.27, 139.10, 142.75, 150.14, 150.93, 152.23, 180.49; MS *m/z* (relative intensity) 346 (M^+, 33), 344 (M^+, 100), 281 (61), 259 (20). Anal. Calcd for $C_{20}H_{21}ClO_3$: C, 69.66; H, 6.14; Cl, 10.28. Found: C, 69.66; H, 5.92; Cl, 9.90.

2-Bromo-8,9-diethoxy-3,4,5,6-tetrahydrocyclobuta-[*l*]phenanthren-1(2*H*)-one (16b). Method B. Unreacted **10**: 0.74 g (30%). **16b**: white crystals; mp 206−208 °C (THF/hexane); yield 1.37 g (50%); IR 1750 (vs), 1620 (w), 1560 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49−1.54 (m, 6H), 1.82−1.91 (m, 2H), 1.95−1.99 (m, 2H), 2.80−2.86 (m, 1H), 2.97−3.05 (m, 3H), 4.15−4.22 (m, 4H), 5.99 (s, 1H), 7.24 (s, 1H), 7.32 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.48, 14.55, 21.67, 22.64, 25.31, 27.42, 56.88, 64.56, 105.21, 105.30, 120.05, 128.22,

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130.31, 138.38, 142.90, 150.15, 150.93, 151.87, 179.99; MS *m/z* (relative intensity) 390 (M^+, 42), 388 (M^+, 42), 309 (100), 281 (35). Anal. Calcd for $C_{20}H_{21}BrO_3$: C, 61.71; H, 5.44; Br, 20.52. Found: C, 61.66; H, 5.39; Cl, 20.38.

2-Chloro-2,3,4,5-tetrahydro-7,8-diisopropoxy-1*H*-cyclobuta[*a*]cyclopenta[*c*]naphthalen-1-one (17a). Method A. Unreacted **11**: 0.12 g (5%). **17a**: white crystals; mp 156−157 °C (EtOH); yield 1.65 g (48%); IR 1770−1750 (vs), 1630 (w), 1560 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39−1.41 (m, 12H), 2.27−2.34 (m, 2H), 3.03−3.22 (m, 4H), 4.58−4.65 (m, 1H), 4.68−4.74 (m, 1H), 5.89 (s, 1H), 7.19 (s, 1H), 7.44 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.90, 21.92, 22.00, 24.51, 30.24, 32.33, 67.87, 71.64, 72.52, 108.28, 111.30, 121.21, 128.17, 132.98, 140.54, 149.73, 150.30, 151.81, 151.88, 180.92; MS *m/z* (relative intensity) 360 (M^+, 35), 358 (M^+, 100), 316 (28), 274 (76), 211 (89). Anal. Calcd for $C_{21}H_{23}ClO_3$: C, 70.28; H, 6.46; Cl, 9.88. Found: C, 70.17; H, 6.54; Cl, 9.91.

2-Bromo-2,3,4,5-tetrahydro-7,8-diisopropoxy-1*H*-cyclobuta[*a*]cyclopenta[*c*]naphthalen-1-one (17b). Method B. Unreacted **11**: 0.23 g (9%). **17b**: white crystals; mp 157−158 °C (EtOH); yield 1.98 g (54%); IR 1770−1760 (vs), 1620 (w), 1555 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38−1.41 (m, 12H), 2.26−2.34 (m, 2H), 3.03−3.20 (m, 4H), 4.59−4.65 (m, 1H), 4.67−4.73 (m, 1H), 6.00 (s, 1H), 7.18 (s, 1H), 7.43 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.91, 21.95, 22.01, 24.50, 30.15, 32.37, 56.85, 71.66, 72.52, 108.20, 111.29, 121.23, 128.21, 133.09, 139.77, 149.51, 150.31, 151.82, 152.02, 180.42; MS *m/z* (relative intensity) 360 (26), 358 (80), 356 (83), 277 (65), 115 (100). Anal. Calcd for $C_{21}H_{23}BrO_3$: C, 62.54; H, 5.75; Br, 19.81. Found: C, 62.58; H, 5.80; Br, 19.21.

2-Bromo-2,3,4,5-tetrahydro-1*H*-cyclobuta[5,6]cyclopenta[7,8]naphtho[2,3-*d*][1,3]dioxol-1-one (18b). Method B. Unreacted **12**: 0.72 g (38%). 3,4,5,5a-Tetrahydro-1*H*-cyclobuta[5,6]cyclopenta[7,8]naphtho[2,3-*d*][1,3]dioxole-1,2(2b*H*)-dione: yellow crystals; mp 205−207 °C (ethyl acetate); yield 0.18 g (11%); IR 1770, 1750 (vs), 1610 (w), 1565 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37−1.47 (m, 1H), 1.56−1.68 (m, 2H), 1.94−2.03 (m, 1H), 2.17−2.24 (m, 1H), 2.38−2.46 (m, 1H), 3.31−3.38 (m, 1H), 3.53−3.59 (m, 1H), 6.03 (s, 2H), 6.83 (s, 1H), 7.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.92, 30.82, 37.06, 37.63, 44.49, 102.03, 106.80, 109.56, 116.88, 139.34, 146.86, 152.70, 189.74, 194.72, 195.50, 197.06; MS *m/z* (relative intensity) 268 (M^+, 78), 240 (81), 212 (100), 184 (49), 153 (31). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.21; H, 4.64. **18b**: white crystals; mp 247−248 °C (toluene); yield 1.13 g (55%); IR 1765 (vs), 1620 (w), 1595 (w), 1540 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30−2.35 (m, 2H), 3.06−3.21 (m, 4H), 6.01 (s, 1H), 6.09 (s, 2H), 7.15 (s, 1H), 7.44 (s, 1H); MS *m/z* (relative intensity) 332 (M^+, 27), 330 (M^+, 28), 251 (34), 223 (100), 165 (35). Anal. Calcd for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35; Br, 24.13. Found: C, 58.22; H, 3.37; Cl, 24.25.

2-Chloro-3,4,5,6-tetrahydrocyclobuta[9,10]phenanthro[2,3-*d*][1,3]dioxol-1-(2*H*)-one (19a). Method A. Unreacted **13**: 0.31 g (15%). **19a**: white crystals; mp 225−227 °C (toluene); yield 1.17 g (46%); IR 1760 (vs), 1620 (w), 1590 (w) (C=O, C=C) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.86−1.95 (m, 2H), 1.96−2.02 (m, 2H), 2.85−2.89 (m, 1H), 2.98−3.08 (m, 3H), 5.93 (s, 1H), 6.12 (s, 2H), 7.36 (s, 1H), 7.39 (s, 1H); ^{13}C NMR (CD_2Cl_2) δ 22.13, 23.17, 25.90, 28.13, 68.57, 102.16, 102.36, 102.59, 121.59, 129.41, 132.60, 139.11, 143.98, 149.21, 149.29, 152.00, 179.99; MS *m/z* (relative intensity) 302 (M^+, 34), 300 (M^+, 100), 237 (78), 178 (16), 69 (24). Anal. Calcd for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36; Cl, 11.79. Found: C, 67.93; H, 4.25; Cl, 11.94.

2-Bromo-3,4,5,6-tetrahydrocyclobuta[9,10]phenanthro[2,3-*d*][1,3]dioxol-1-(2*H*)-one (19b). Method B. Unreacted **13**: 0.90 g (45%). Mixture of two side products (0.41 g). **19b**: white crystals; mp 244−245 °C (toluene); yield 1.06 g (55%); IR 1765 (vs), 1625 (w), 1595 (w) (C=O, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.78−1.86 (m, 2H), 1.89−1.90 (m, 2H), 2.84−2.87 (m, 2H), 3.02−3.05 (m, 2H), 6.22 (s, 2H), 6.41 (s, 1H), 7.27 (s, 1H), 7.55 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 21.03, 22.07, 24.77, 27.01, 57.86, 100.74, 102.08, 102.22, 120.29, 128.35, 131.56, 137.89, 143.81, 149.31, 151.71, 179.40; MS *m/z* (relative intensity) 347 (M^+, 72), 345 (M^+, 74), 265 (100), 237 (96), 179 (19). Anal. Calcd for $C_{17}H_{13}BrO_3$: C, 59.15; H, 3.80; Br, 23.15. Found: C, 59.17; H, 3.79; Cl, 22.94.

2-Chloro-2,3,4,5,6,7-hexahydro-1*H*-cyclobuta[5,6]cyclohepta[7,8]naphtho[2,3-*d*][1,3]dioxol-1-one (20a). Method A. Unreacted **14**: 0.17 g (8%). 3,4,5,6,7,7a-Hexahydro-1*H*-cyclobuta[5,6]cyclohepta[7,8]naphtho[2,3-*d*][1,3]dioxole-1,2(2b,*H*)-dione: yellow crystals; mp 167−168 °C (EtOH); yield 0.27 g (10%); IR 1780−1750 (vs, br), 1610 (m), 1560 (s) (C=O, C=C) cm^{-1}; MS *m/z* (relative intensity) 296 (M^+, 97), 268 (53), 212 (100), 199 (94), 185 (55). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.93; H, 5.43. 4,5,6,7-Tetrahydro-1*H*-cyclobuta[5,6]cyclohepta[7,8]naphtho[2,3-*d*]-[1,3]dioxole-1,2(3*H*)-dione: yellow crystals; mp 247−250 °C; yield 0.08 g (3%); IR 1780−1740 (vs, br), 1605 (m), 1550 (m) (C=O, C=C) cm^{-1}; MS *m/z* (relative intensity) 294 (M^+, 38), 266 (100), 238 (37). Anal. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.12; H, 4.63. **20a**: white crystals; mp 226−227 °C (toluene); yield 0.57 g (20%); IR 1750 (vs), 1620 (w), 1590 (w) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67−1.74 (m, 4H), 1.90−1.95 (m, 2H), 3.03−3.07 (m, 2H), 3.16−3.20 (m, 2H), 5.93 (s, 1H), 6.09 (s, 2H), 7.42 (s, 1H), 7.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.03, 26.54, 29.89, 30.08, 31.83, 67.81, 101.69, 102.08, 102.11, 122.18, 131.29, 134.17, 139.17, 149.29, 149.48, 150.86, 151.49, 180.04; MS *m/z* (relative intensity) 316 (M^+, 34), 314 (M^+, 100), 279 (46), 258 (23), 251 (40), 165 (11). Anal. Calcd for $C_{18}H_{15}ClO_3$: C, 68.68; H, 4.80; Cl, 11.26. Found: C, 68.58; H, 4.70; Cl, 11.15.

2-Bromo-2,3,4,5,6,7-hexahydro-1*H*-cyclobuta[5,6]cyclohepta[7,8]naphtho[2,3-*d*][1,3]dioxol-1-one (20b). Method B. Unreacted **14**: 0.98 g (45%), mixture of two side products (0.27 g). **20b**: white crystals; mp 248−249 °C (toluene); yield 1.27 g (65%); IR 1760, 1750 (vs), 1620 (w), 1590 (w), 1530 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65−1.75 (m, 4H), 1.90−1.96 (m, 2H), 2.97−3.09 (m, 2H), 3.12−3.23 (m, 2H), 6.03 (s, 1H), 6.09 (s, 2H), 7.41 (s, 1H), 7.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.10, 26.49, 30.02, 30.10, 31.89, 56.80, 101.81, 102.17, 122.31, 131.51, 134.34, 138.57, 149.43, 149.61, 151.05, 151.26, 179.59; MS *m/z* (relative intensity) 360 (M^+, 21), 358 (M^+, 21), 279 (100), 251 (48), 165 (21). Anal. Calcd for $C_{18}H_{15}BrO_3$: C, 60.19; H, 4.21; Br, 22.24. Found: C, 60.29; H, 4.29; Br, 22.52.

2-Chloro-3,4,5,6,7,8-hexahydrocyclobuta[5,6]cycloocta[7,8]naphtho[2,3-*d*][1,3]dioxol-1(2*H*)-one (21a). Method A. Unreacted **15**: 0.86 g (37%). 3,4,5,6,7,8-Hexahydrocyclobuta[5,6]cycloocta[7,8]naphtho[2,3-*d*][1,3]dioxole-1,2-dione: yellow crystals; mp 271−272 °C; yield 0.16 g (8%); IR 1755 (vs), 1610 (m) (C=O, C=C) cm^{-1}; MS *m/z* (relative intensity) 308 (M^+, 89), 280 (100), 252 (62), 237 (29), 224 (49). Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.85; H, 5.11. **21a**: white crystals; mp 243−244 °C (ethyl acetate); yield 0.75 g (36%); IR 1750 (vs), 1620 (w), 1590 (w) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21−1.29 (m, 2H), 1.50−1.61 (m, 2H), 1.79−1.86 (m, 4H), 2.99−3.03 (m, 2H), 3.20−3.23 (m, 2H), 5.92 (s, 1H), 6.09 (s, 2H), 7.41 (s, 1H), 7.42 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.38, 27.08, 27.12, 29.02, 29.94, 31.61, 67.76, 101.67, 102.17, 102.51, 122.04, 131.33, 132.98, 139.84, 147.38, 149.19, 149.39, 152.13, 180.18; MS *m/z* (relative intensity) 330 (M^+, 34), 328 (M^+, 100), 293 (54), 265 (40), 209 (18). Anal. Calcd for $C_{19}H_{17}ClO_3$: C, 69.41; H, 5.21; Cl, 10.78. Found: C, 69.43; H, 5.15; Cl, 10.91.

2-Bromo-3,4,5,6,7,8-hexahydrocyclobuta[5,6]cycloocta[7,8]naphtho[2,3-*d*][1,3]dioxol-1(2*H*)-one (21b). Method B. Unreacted **15**: 0.71 g (31%). **21b**: white crystals; mp 257−259 °C (toluene); yield 1.96 g (76%); IR 1770, 1760 (vs), 1625 (w), 1590 (w), 1530 (m) (C=O, C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24−1.30 (m, 2H), 1.53−1.59 (m, 2H), 1.77−1.91 (m, 4H), 3.00−3.03 (m, 2H), 3.19−3.22 (m, 2H), 6.02 (s, 1H), 6.09 (s, 2H), 7.40 (s, 1H), 7.41 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.53, 27.26, 27.30, 29.09, 30.05, 31.60, 56.79, 101.83, 102.24, 102.67, 122.19, 131.57, 133.20, 139.27, 147.68, 149.36, 149.55, 151.95, 179.82; MS *m/z* (relative intensity) 374 (M^+, 25), 372 (M^+, 25), 293 (100), 265 (52), 165 (17). Anal. Calcd for $C_{19}H_{17}ClO_3$: C, 61.14; H, 4.59; Br, 21.41. Found: C, 61.33; H, 4.52; Br, 20.99.

Reaction of 5-(1-Cyclobuten-1-yl)-1,3-benzodioxole (22) with Semisquaric Chloride (5a) and Semisquaric Bromide (5b). Synthesis of 2b,3,4,4a-Tetrahydrodicyclobuta[5,6:7,8]naphtho[2,3-*d*][1,3]dioxole-1,2-dione (23). A solution of 5-(1-cyclobuten-1-yl)-1,3-benzodioxole **(22)** (1.74 g, 10 mmol) and semisquaric chloride **(5a)** (1.16 g, 10 mmol) in CH_2Cl_2 (10 mL) was stirred for 12 h. The resulting black solution was subjected to column chromatography (silica gel 60, 500 g) using CH_2Cl_2 as eluent. Unreacted **22**: 0.24 g (14%). **23**: Orange crystals; mp 174−176 °C (EtOH); yield 0.43 g (20%); IR 1775, 1750 (vs), 1610 (w), 1570 (m) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25−2.36 (m, 2H), 2.48−2.52 (m, 1H), 2.78−2.86 (m, 1H), 3.84−3.97 (m, 2H), 6.01 (s, 2H), 7.63 (s, 1H), 7.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.16, 33.16, 33.62, 39.63, 102.11, 107.28, 108.41, 117.47, 137.50, 147.12, 153.05, 191.88, 194.89, 195.38, 196.80; MS *m*/*z* (relative intensity) 254 (M^+, 68), 226 (56), 198 (96), 170 (46), 140 (100). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 70.67; H, 3.97.

The reaction of **22** (1.74 g, 10 mmol) with semisquaric bromide **(5b)** (1.61 g, 10 mmol) was carried out according to method B yielding **23**: 1.17 g (46%). No unreacted **22** was obtained.

6-Chloro-7,8-dihydro-2,3-dimethoxybenzo[*c*]cyclobuta[*a*]phenanthren-5(6*H*)-one (25). Method B. Unreacted **24**: 0.54 g (20%). **25**: yellow powder; mp 229−230 °C (toluene/hexane); yield 1.46 g (50%); IR 1755 (vs), 1620 (w), 1560 (w) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82−2.88 (m, 3H), 2.95−3.01 (m, 1H), 3.93 (s, 3H), 4.01 (s, 3H), 5.97 (s, 1H), 7.35−7.42 (m, 4H), 7.86−7.89 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.64, 28.76, 55.85, 56.22, 67.58, 104.19, 107.31, 122.23, 126.30, 128.02, 128.44, 128.74, 128.78, 129.55, 133.44, 139.91, 140.38, 141.37, 150.24, 150.62, 151.46, 180.43; MS *m*/*z* (relative intensity) 366 (M^+, 37), 364 (M^+, 98), 301 (100), 256 (18), 226 (20), 212 (27). Anal. Calcd for $C_{22}H_{17}ClO_3$: C, 72.43; H, 4.70; Cl, 9.72. Found: C, 72.60; H, 4.88; Cl, 9.64.

Preparation of Benzocyclobutenones 26a−f. General Procedure. To a boiling solution of an α-bromocyclobutenone **9b**, **16b**, or **18b**−**21b** (0.50 g) in toluene (30 mL) were added tributyltin hydride (1.2 equiv) and AIBN (catalytic amount). After 1.5 h of reflux, the solvent was removed. The solid obtained was purified by recrystallization.

3,4,5,6-Tetrahydro-8,9-diisopropoxycyclobuta[*l*]phenanthren-1(2*H*)-one (26a): pale yellow crystals; mp 161−162 °C (EtOH); yield 0.30 g (74%); IR 1740 (vs), 1620 (w), 1550 (m) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36−1.40 (m, 12H), 1.82−1.88 (m, 2H), 1.92−1.98 (m, 2H), 2.78−2.81 (t, 2H, J = 6.0 Hz), 3.03−3.06 (t, 2H, J = 6.1 Hz), 3.84 (s, 2H), 4.52−4.59 (m, 1H), 4.67−4.73 (m, 1H), 7.35 (s, 1H), 7.39 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.98, 22.12, 22.91, 26.40, 27.22, 49.98, 71.28, 72.89, 107.50, 111.60, 121.07, 128.53, 128.77, 138.83, 140.59, 148.71, 151.08, 151.98, 186.09; MS *m*/*z* (relative intensity) 338 (M^+, 14), 226 (16), 152 (11), 43 (100). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 77.96; H, 7.75.

8,9-Diethoxy-3,4,5,6-tetrahydrocyclobuta[*l*]phenanthren-1(2*H*)-one (26b): pale yellow crystals; mp 223−225 °C (toluene); yield 0.30 g (75%); IR 1745 (vs), 1630 (w), 1570 (m) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49−1.53 (m, 6H), 1.82−1.88 (m, 2H), 1.92−1.98 (m, 2H), 2.77−2.80 (t, 2H, J = 6.1 Hz), 3.01−3.04 (t, 2H, J = 6.2 Hz), 3.83 (s, 2H), 4.14−4.22 (m, 4H), 7.21 (s, 1H), 7.28 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.54, 14.64, 22.07, 22.91, 26.40, 27.25, 49.97, 64.41, 64.57, 104.64, 105.52, 120.33, 128.54, 128.63, 138.84, 140.35, 148.90, 150.56, 151.35, 186.14; MS *m*/*z* (relative intensity) 310 (M^+, 100), 282 (23), 252 (16), 224 (39), 152 (11). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.46; H, 7.37.

2,3,4,5-Tetrahydro-1*H*-cyclobuta[5,6]cyclopenta[7,8]naphtho[2,3-*d*][1,3]dioxol-1-one (26c): pale yellow crystals; mp 217−219 °C (toluene); yield 0.28 g (74%); IR 1750−1735 (vs), 1605 (w), 1590 (m) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23−2.30 (m, 2H), 3.02−3.06 (t, 2H, J = 7.5 Hz), 3.14−3.18 (t, 2H, J = 7.3 Hz), 3.92 (s, 2H), 6.04 (s, 2H), 7.08 (s, 1H), 7.37 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 24.51, 30.96, 32.41, 50.78, 101.40, 101.52, 102.35, 121.79, 127.83, 134.54, 141.50, 147.59, 147.91, 149.13, 149.61, 186.91; MS *m*/*z* (relative intensity) 252 (M^+, 100), 224 (96), 165 (56), 139 (13). Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.79. Found: C, 76.24; H, 4.73.

3,4,5,6-Tetrahydrocyclobuta[9,10]phenanthro[2,3-*d*][1,3]dioxol-1(2*H*)-one (26d): pale yellow crystals; mp 215−217 °C (toluene); yield 0.30 g (78%); IR 1750−1735 (vs), 1625 (w), 1595 (m) (C═O, C═C) cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.83−1.88 (m, 2H), 1.93−1.97 (m, 2H), 2.78−2.81 (t, 2H, J = 6.1 Hz), 2.98−3.01 (t, 2H, J = 6.3 Hz), 3.85 (s, 2H), 6.04 (s, 2H), 7.26 (s, 1H), 7.30 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 21.99, 22.90, 26.42, 27.44, 50.13, 101.22, 101.38, 101.40, 121.23, 129.11, 130.22, 139.52, 140.82, 148.02, 148.58, 151.21, 185.88; MS *m*/*z* (relative intensity) 266 (M^+, 100), 238 (57), 210 (32), 178 (12), 152 (27). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.34; H, 5.23.

2,3,4,5,6,7-Hexahydro-1*H*-cyclobuta[5,6]cyclohepta[7,8]naphtho[2,3-*d*][1,3]dioxol-1-one (26e): white crystals; mp 203−205 °C (toluene); yield 0.29 g (74%); IR 1745 (vs), 1630 (w), 1590 (w) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62−1.69 (m, 4H), 1.87−1.93 (m, 2H), 2.90−2.93 (t, 2H, J = 5.6 Hz), 3.12−3.14 (t, 2H, J = 5.4 Hz), 3.92 (s, 2H), 6.03 (s, 2H), 7.33 (s, 1H), 7.41 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.41, 26.93, 29.87, 31.05, 32.05, 50.52, 101.29, 101.42, 101.79, 122.13, 129.67, 134.64, 139.18, 148.27, 148.42, 148.81, 150.13, 185.69; MS *m*/*z* (relative intensity) 280 (M^+, 100), 252 (54), 242 (38), 224 (34), 165 (39), 132 (26). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.13; H, 5.75. Found: C, 77.22; H, 5.74.

3,4,5,6,7,8-Hexahydrocyclobuta[5,6]cycloocta[7,8]naphtho[2,3-*d*][1,3]dioxol-1(2H)-one (26f): white crystals; mp 187−188 °C (ethyl acetate); yield 0.30 g (74%); IR 1760, 1740 (vs), 1630 (w), 1595 (s) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21−1.24 (m, 2H), 1.45−1.51 (m, 2H), 1.68−1.71 (m, 2H), 1.74−1.79 (m, 2H), 2.85−2.88 (t, 2H, J = 6.1 Hz), 3.13−3.16 (t, 2H, J = 6.4 Hz), 3.88 (s, 2H), 6.02 (s, 2H), 7.29 (s, 1H), 7.32 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.49, 27.13, 27.17, 29.74, 30.06, 31.61, 50.28, 101.36, 101.41, 102.24, 122.07, 129.63, 133.23, 139.78, 144.92, 148.13, 148.69, 150.79, 185.78; MS *m*/*z* (relative intensity) 294 (M^+, 100), 279 (18), 266 (29), 251 (27), 237 (21), 223 (22), 165 (29), 152 (24). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.41; H, 6.11.

Preparation of α-(Trifluoroacetoxy)benzocyclobutenones 27a−c. General Procedure. To a boiling solution of an α-halocyclobutenone **9a**, **19b**, or **20b** (0.5 g) in benzene (30 mL) was added a solution of silver trifluoroacetate (1.1 equiv) in benzene (10 mL). The mixture was refluxed for 30 min. After filtration, from precipitated silver halide, the solvent was removed and the solid obtained was purified by recrystallization.

2-(Trifluoroacetoxy)-3,4,5,6-tetrahydro-8,9-diisopropoxycyclobuta[*l*]phenanthren-1(2*H*)-one (27a): white crystals; mp 161−162 °C (EtOH); yield 0.43 g (71%); IR 1790 (vs), 1750 (vs), 1610 (w), 1550 (m) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37−1.42 (m, 12H), 1.81−2.07 (m, 4H), 2.68−2.76 (m, 1H), 2.86−2.93 (m, 1 H), 3.01−3.15 (m, 2H), 4.60−4.66 (m, 1H), 4.69−4.75 (m, 1H), 6.86 (s, 1H), 7.42 (s, 1H), 7.44 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.72, 21.87, 21.89, 22.00, 22.58, 25.87, 27.42, 71.60, 72.71, 87.16, 108.27, 110.66, 120.41, 128.01, 130.71, 142.38, 143.11, 150.45, 150.88, 151.50, 179.30; MS *m*/*z* (relative intensity) 450 (M^+, 75), 353 (49), 311 (41), 269 (100), 107 (80). Anal. Calcd for $C_{24}H_{25}F_3O_5$: C, 63.99; H, 5.59. Found: C, 63.81; H, 5.48.

2-(Trifluoroacetoxy)-3,4,5,6-tetrahydrocyclobuta[9,10]phenanthro[2,3-*d*][1,3]dioxol-1(2*H*)-one (27b): white crystals; mp 204−206 °C dec (toluene); yield 0.42 g (77%); IR 1790 (vs), 1750 (vs), 1620 (w), 1580 (w) (C═O, C═C) cm^{-1}; MS *m*/*z* (relative intensity) 378 (M^+, 20), 281 (100), 165 (13), 152 (11). Anal. Calcd for $C_{19}H_{13}F_3O_5$: C, 60.32; H, 3.46. Found: C, 60.19; H, 3.31.

2-(Trifluoroacetoxy)-2,3,4,5,6,7-hexahydro-1*H*-cyclobuta[5,6]cyclohepta[7,8]naphtho[2,3-*d*][1,3]dioxol-1-one (27c): white crystals; mp 205−207 °C dec (toluene); yield 0.43 g (79%); IR 1800 (vs), 1760 (vs), 1630 (w), 1595 (w) (C═O, C═C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60−1.70 (m, 4H), 1.90−1.93 (m, 2H), 2.91−2.94 (m, 2H), 3.17−3.21 (m, 2H), 6.11 (s, 2H), 6.91 (s, 1H), 7.46 (s, 1H), 7.50 (s, 1H); ^{13}C NMR ($CDCl_3$) δ

26.07, 26.52, 30.00, 30.68, 31.79, 87.51, 101.94, 102.22, 102.38, 122.12, 131.80, 134.32, 142.44, 149.58, 149.61, 150.02, 151.01, 156.49, 156.92, 178.96, 180.04; MS *m/z* (relative intensity) 392 (M^+, 23), 295 (100), 165 (6). Anal. Calcd for $C_{20}H_{15}F_3O_5$: C, 61.23; H, 3.85. Found: C, 61.19; H, 3.77.

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Supporting Information Available: ORTEP representation of the X-ray structure of **9a** (10 pages).[11] This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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