Thermolysis of Benzopyranone–Indenone Adducts. 2.[1a] Some New Aspects of the Mechanism

Dirk J. Vanderzande,[2a,b] Eric G. Kiekens,[2a,b] Henri J. Martens,*[2c] and Georges J. Hoornaert*[2b]

Department of Chemistry, K.U. Leuven, Celestijnenlaan 200 F, 3030 Leuven, Belgium, and Limburgs Universitair Centrum, Universitaire Campus, 3610 Diepenbeek, Belgium

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Thermolysis of benzopyranone–indenone adducts 1, probably proceeding via *o*-quinodimethanes **10**, gives C-nor-D-homo steroids **4**, benzo[*c*]fluorenones **5**, and traces of benzo[*b*]cyclopropa[*lm*]fluorenones **6**. Evidence is presented for the intervention of a biradical intermediate **12** leading to compounds of type **5**. A consecutive and common intermediate **15** is introduced to explain the formation of identical products on thermolysis of the regioisomeric adducts 1 and 2. For synthetic use leading to compounds of type **4**, suitable substituents or groups must be chosen to avoid biradicals **12** or competitive reactions as observed for **1h**, which yields benz[*a*]anthracenone **24** on thermolysis.

In recent years the *o*-quinodimethane systems have been under active investigation from both theoretical[3] and synthetic organic view points.[4] The facile intramolecular Diels–Alder reaction of *o*-quinodimethane systems leading to complex carbocyclic and heterocyclic compounds has proven to offer interesting prospects.[4] Also concerted 1,5-sigmatropic shifts of unsaturated groups in *o*-quinodimethane and analogous systems enjoy considerable theoretical interest.[5]

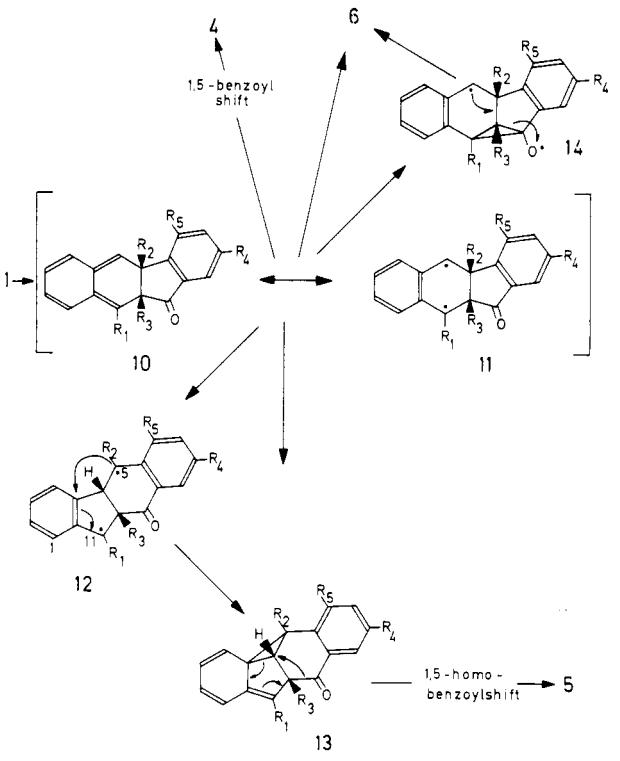
In a previous paper[1a] we reported the formation of C-nor-D-homo steroid **4**, benzo[*c*]fluorenone **5**, and benzo[*b*]cyclopropa[*lm*]fluorenone **6** on thermolysis of benzopyranone adducts 1 (Charts I and II). The formation of the products **4–6** was rationalized by mechanisms proceeding via an intermediate *o*-quinodimethane system **10** (Scheme I). This *o*-quinodimethane system was trapped with tetracyanoethylene and *N*-phenylmaleimide.[1b]

We wish to report some unpredicted results in the thermolysis of specific benzopyranone adducts which reveal certain new aspects of the mechanism.

Results and Discussion

Thermolysis of the regioisomeric benzopyranone–indenone adducts **1a** and **2a** gives almost the same product distribution (Table I). According to the mechanism of Scheme I, we would expect only the products **4a**, **5a**, and **6a** on thermolysis of the adduct **1a**. Compounds **7a**, **8a**, and **9a** are the products predicted for the thermolysis of the adduct **2a**. A similar observation can be made for the adducts **2c** and **1d**, which yield also products normally expected for the thermolysis of **1c** and **2d**, respectively.

Scheme I



The results obtained with **1a** and **2a** suggest a rapid equilibrium between these two adducts via a retro-Diels–Alder reaction involving the benzopyranone and the indenone. This implies that a mixture of the adducts should be recovered on incomplete thermolysis. However, in both reactions only the starting material was recovered. Also the results of the thermolysis of the regioisomeric adducts **1c** and **2c** are not consistent with such a rapid equilibrium; the product distribution in the thermolysis of **1c** and **2c** is clearly different (Table I).

The product distributions of Table I are in agreement with a common intermediate **15** (Scheme II) in the thermolysis of regioisomeric adducts **1** and **2**. In the intermediate **15** bond breaking can occur between C_1 and C_3, leading to the intermediate **12**, or between C_2 and C_3, affording 12_A.[6] If the equilibrium of all intermediates

(1) (a) Vanderzande, D. J.; Ceustermans, R. A.; Martens, H. J.; Toppet, S. M.; Hoornaert, G. J. *J. Org. Chem.* **1983**, *48*, 2188. (b) Vanderzande, D. J. Ph.D. Dissertation, K. U. Leuven, Leuven, Belgium, 1986.

(2) (a) Predoctoral Fellow of the "Instituut tot Aanmoediging van Wetenschappelijk Onderzoek in Nijverheid en Landbouw" (IWONL), Belgium. (b) Leuven. (c) Diepenbeek.

(3) (a) McCullough, J. *J. Acc. Chem. Res.* **1980**, *13*, 270. (b) Steiner, R. P.; Miller, R. D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 1820. (c) Bell, T. W.; Bowes, C. M.; Sondheimer, F. *Tetrahedron Lett.* **1980**, 3299.

(4) (a) Oppolzer, W. *Synthesis* **1978**, 793. (b) Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3. (c) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, *45*, 1463.

(5) (a) Field, D. J.; Jones, D. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1909 and references cited therein. (b) Sato, T.; Itô, S. *Tetrahedron Lett.* **1979**, 1051. (c) Alder, R. W.; Grimme, W. *Tetrahedron* **1981**, *37*, 1809 and references cited therein. In our opinion the literature, concerning 1,5-migrations of unsaturated groups, gives indications for the following hypothesis:[5a,c] on migration of an unsaturated group the major process on the way to the transition state is the formation of a new σ-bond at the expense of the π-bonds, the old σ-bond being almost broken;[5c] the interaction of the π-system of the migrating group with the diene system being an interaction of the HOMO of the latter with the LUMO of the former.[5a]

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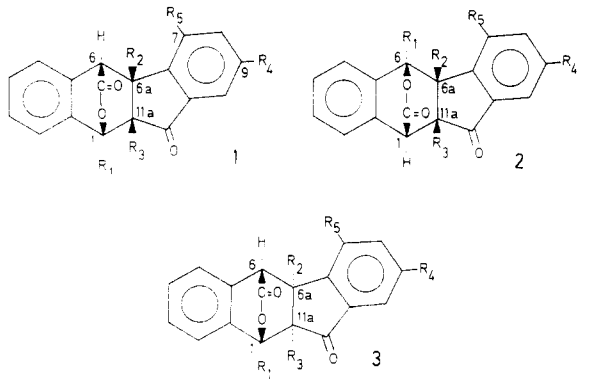
Table I. Product Distribution on Thermolysis of the Regioisomeric Benzopyranone-Indenone Adducts 1 and 2

thermolyzed adduct	1a						1c and 3c						1d					
products in agreement with Scheme I	yes			no			yes			no			yes			no		
yield, %	2	53	8	0	2	8	47	33	10	0	0	0	28	57	0	0	6	7
product	**4a**	**5a**	**6a**	**7a**	**8a**	**9a**	**4c**	**5c**	**6c**	**7c**	**8c**	**9c**	**4d**	**5d**	**6d**	**7d**	**8d**	**9d**
yield, %	2	55	10	0	3	10	0	51	0	19	10	9						
products in agreement with Scheme I	no			yes			no			yes			no			yes		
thermolyzed adduct	**2a**						**2c**						(**2d**)[a]					

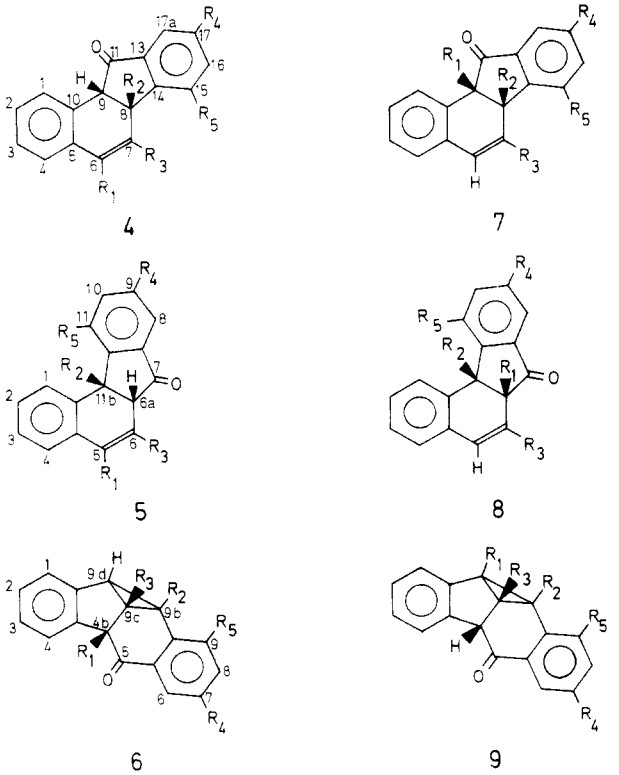
[a] Adduct **2d** was not available.

Chart I

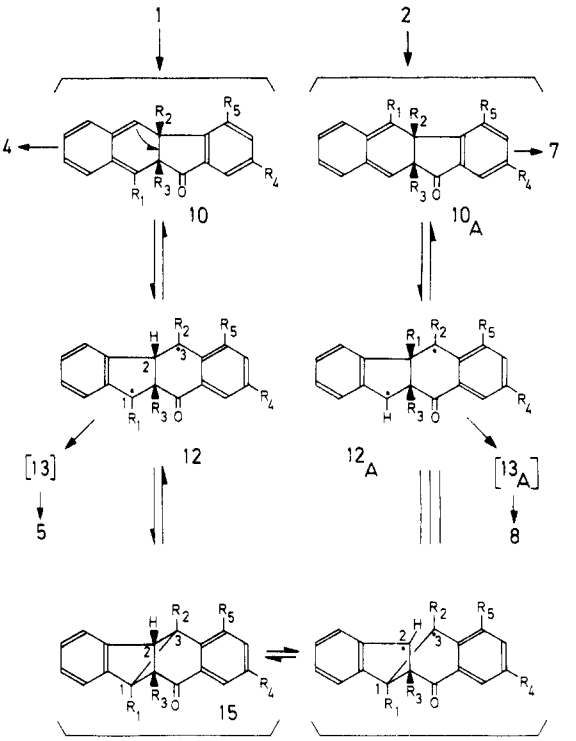


	R_1	R_2	R_3	R_4	R_5
a	Me	Ph	Et	OMe	OMe
b	H	Me	Me	OMe	H
c	Me	Me	Me	OMe	H
d	Ph	Me	Me	OMe	H
e	Me	Me	Me	OMe	OMe
f	Me	Me	Me	H	OMe
g	Me	H	Me	OMe	H
h	Me	CH_2Br	Me	OMe	H

Chart II



Scheme II



occurs very rapidly, one would obtain the same product distribution starting either from adduct **1** or from adduct **2** as is observed for **1a** and **2a**. The observation that compounds of type **7–9** are not isolated in the thermolysis of **1c** indicates that the conversion **12** → **5** occurs rapidly compared to the interconversion of the intermediates. The fact that neither **4c** nor **6c** but only **5c** is obtained from adduct **2c** means that the conversion **10** → **12** determines the amount of **5c** being formed from **10c**.

We focused further investigations on the biradical intermediate of type **12**. In a first attempt we tried to trap it with thiocresol. Thiols have been widely exploited in

(6) (a) Salisbury, L. E. *J. Org. Chem.* **1978**, *43*, 4987. (b) Salisbury, L. E. *J. Org. Chem.* **1978**, *43*, 4991. An intermediate similar to **15** has here been proposed in the rearrangement of **31** to **32**.

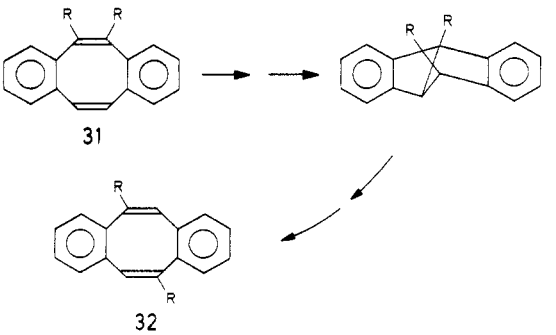
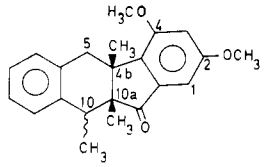


Table II. Ratio (5/4) of the Compounds 4 and 5[a]

thermolyzed adduct	R_1	R_2	R_3	R_4	R_5	ratio 5/4
1b	H	Me	Me	OMe	H	0.3[b]
1c	Me	Me	Me	OMe	H	0.7[b]
1d	Ph	Me	Me	OMe	H	2.0[b]
1f	Me	Me	Me	H	OMe	2.1[c]
1e	Me	Me	Me	OMe	OMe	2.9[c]
1a	Me	Ph	Et	OMe	OMe	26.5[c]

[a] **4**, formed via the intermediate **10** (1,5-CO shift); **5**, formed via the biradical intermediate **12**. [b] Increasing stabilization of **12** due to R_1. [c] Increasing stabilization of **12** due to R_2 or R_4.

the trapping of biradicals[6a] and of free radicals.[7] However in our case, we were unable to detect any amount of a trapped biradical **12**. Instead we isolated a high yield of the reduced *o*-quinodimethane system **16a,b**.



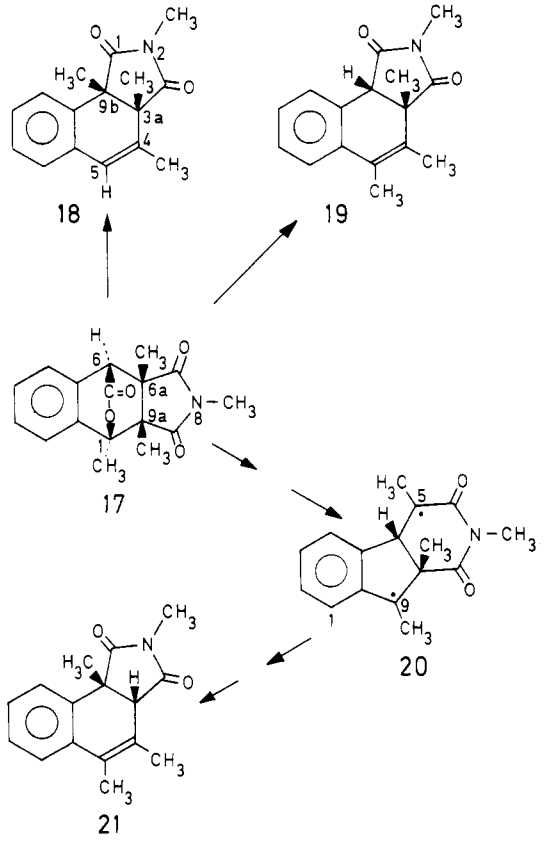
16 a,b

a: β-CH_3 ; b: α-CH_3

In another approach we tried to stabilize the biradical **12** by changing the substituents R_1, R_2, R_4, and R_5 (Table II). Taking into account the results with **1c** and **2c** we can assume that the conversion **10** → **12** determines the amount of **5** being formed from **10**, on thermolysis of **1b,c,f**. Under this condition and if changes in the substituent pattern have no large effect on the 1,5-C=O shift leading to **4**, then the ratio of **5** to **4** can be used to measure the relation between the stabilization of **12** and the increased formation of **5**. In this context it is important to note that the migratory aptitudes of various unsaturated groups in 1,5-sigmatropic rearrangements are rationalized in terms of a migration, involving an interaction of the HOMO of the diene system with the LUMO of the migrating group. The favorable geometry and the small energy gap $E_{C=O}{}^{\pi*}-E_{diene}{}^{HOMO}$ will make this interaction the most important one in the pericyclic process.[5] Since R_1 = Me and R_1 = Ph raise the HOMO of the diene system, we may assume that this will even slightly accelerate the 1,5-C=O shift leading to **4**. Comparison of the **5**:**4** ratios for the thermolysis of **1b–d** in Table II allows one to conclude that an increasing stabilization of the R_1–C–radical center of **12** favors considerably the formation of **5**. The same observation can be made when comparing the results of the adducts **1e**, **1f**, and **1a**: an increasing stabilization of the R_2–C–radical center of **12** favors the formation of **5**. Here we may assume that the 1,5-C=O migration will proceed faster in the order **10f** < **10e** < **10a**. Indeed a methoxyl group meta of the carbonyl function in **10** lowers the LUMO of the benzoyl moiety;[8] furthermore the steric hindrance arising from a phenyl substituent is smaller on rotation than from a methyl substituent.[9] Consequently the steric hindrance at the hinge of the 1,5-C=O migration is smaller in **10a** compared to **10e**.

Another aspect of this type of reaction is revealed by the ratios of **4c** to **5c** (=1.4) and **7c** to **5c** (=0.4) for the thermolysis of the adducts **1c** and **2c**, respectively (Table I). This indicates an appreciable retardation of the 1,5-C=O migration to a methyl-substituted migration terminus in $\mathbf{10_A}$ (formation of **7**) compared to the 1,5-C=O migration to a hydrogen-substituted terminus in **10** (formation of **4**). However steric effects at the migration terminus seem not to be too decisive, if we take into account the results obtained on thermolysis of the adduct **17** (Scheme III). This thermolysis affords only the products **18** (migration to the methyl-substituted terminus; 62%) and **19** (migration to the hydrogen substituted terminus; 38%). The complete absence of a product of type **21**—which could arise via an intermediate of type **20**—confirms again the correlation between the formation of products of type **5** (**21**) and the stabilization of the radical centers in intermediates of type **12**. The biradical **20** is comparable to the latter intermediate but its radical center on C_5 will be less stabilized.[10]

Scheme III



The results for the thermolysis of the adducts **1g** and **1h** deviate to some extent from the normal pattern. Adduct **1g** yields the C-nor-D-homo steroid **4g**, which is readily air-oxidized to the benzo[*a*]fluorenone **23** (38%) (Chart III). A competitive 1,5-hydrogen migration explains the formation of compound **22** (14%); the high

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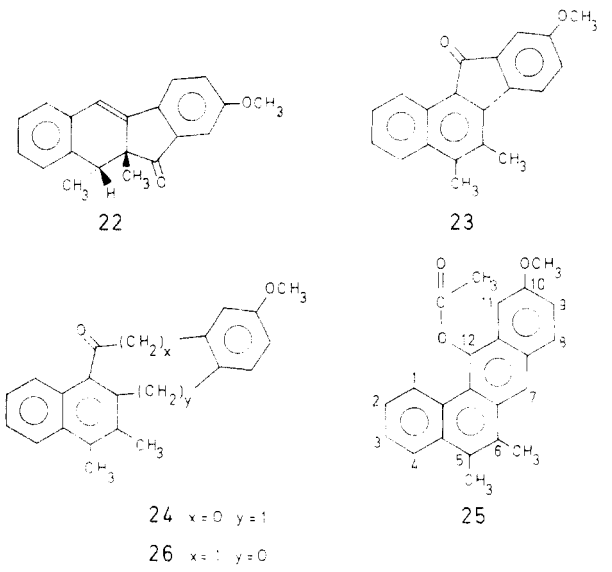
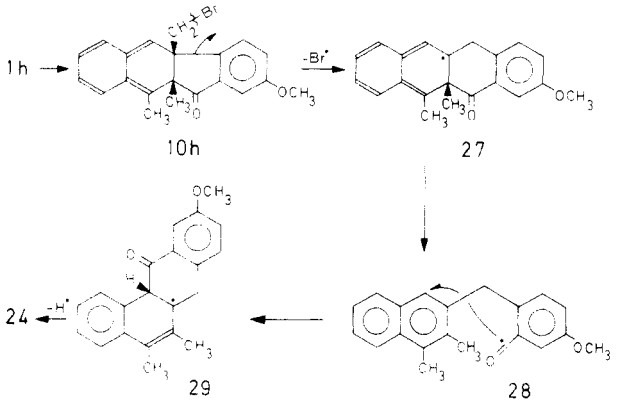
(9) (a) Rieker, A.; Kessler, H. *Tetrahedron Lett.* **1969**, *16*, 1227. (b) Mannschreck, A.; Ernst, L. *Chem. Ber.* **1971**, *104*, 228.
(10) (a) Ingold, K. U. "Free Radicals"; Kochi, J. K., Ed; McGraw-Hill: New York, 1973; Vol. I, p 92. (b) Abell, P. I. "Free Radicals"; Kochi, J. K., Ed.; 1973; Vol. II, pp 98–99.

Chart III



Scheme IV



amount (31%) of the cyclopropane **6g** is probably due to the lower steric hindrance in the cyclopropane ring. Thermolysis of the adduct **1h** affords only a benz[*a*]anthracenone **24**, which is not stable over long periods. It can be converted to a stable acylated benz[*a*]anthracenol **25** in an overall yield of 75% starting from **1h**.

The ^{1}H NMR spectrum of the benz[*a*]anthracenone **24** shows a low-field doublet absorption at 9.80 ppm, integrating for one hydrogen, with an aromatic solvent-induced shift Δ ($=\delta_{CDCl_3} - \delta_{C_6D_6}$) = −0.63 ppm. This low-field absorption is characteristic for the 1-H and it is in good agreement with the value (9.85 ppm) for the $\delta_{1\text{-H}}$ in a similar benz[*a*]anthracenone derivative.[11] Further evidence for the assigned structure **24** was obtained from a NOE experiment. Irradiation of the 5- and 6-methyl groups in the acylated product **25** gave a NOE of 22% for the 4-H (d × d) and 17% for the 7-H (s). This excludes an alternative chrysenone structure **26** for the original product. A possible mechanism for the formation of **24** is given in Scheme IV. The lability of the CH_2–Br bond in **10h** is held responsible for the absence of the normal reaction pathways.

Conclusion

This study discloses the synthetic use of a 1,5-C=O migration in an intermediate *o*-quinodimethane system arising during the thermolysis of benzopyranone adducts. However the scope of the reaction to, e.g., C-nor-D-homo steroids is limited due to the formation of biradicals of type **12** which lead to products of type **5**. The substituent pattern must be chosen in such a way that these biradicals are disfavored so that the pathway via the 1,5-CO shift is preferred.

Experimental Section

All melting points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 297 spectrometer in potassium bromide disks. Nuclear magnetic resonance spectra were obtained on a Varian EM 390, a Bruker WM 250, or a Bruker WP 80 spectrometer. For the mass spectra an AEI-MS-9 spectrometer was used; the ionization energy was 70 eV, and samples were injected directly at a temperature between 100 and 200 °C. Silica gel for preparative layer and column chromatography was Merck Type 60 (70–230 mesh or 230–400 mesh).

2-Ethyl-3-phenyl-4,6-dimethoxyindenone (**30a**), 2,3-dimethyl-6-methoxyindenone (**30b**), 2,3-dimethyl-4,6-dimethoxyindenone (**30c**), 2-methyl-6-methoxyindenone (**30d**), and 3-(bromomethyl)-2-methyl-6-methoxyindenone (**30e**) were synthesized according to earlier described methods.[12] Further purification of the mother liquor after recrystallization of **30b** yielded the 2,3-dimethyl-4-methoxyindenone (**30f**). The solvents used in the reactions were purified according to known procedures.[13] The aromatic solvent induced shift Δ equals $\delta_{CDCl_3} - \delta_{C_6D_6}$.

Procedures for the Synthesis of Benzopyranone Adducts. *o*-Acetylphenylacetic acid[14] (20 mmol), indenone **30b–f** (15 mmol), and acetic anhydride (40 mL; freshly destilled from quinoline) were refluxed for 7 h under a nitrogen atmosphere. The crude reaction mixture was evaporated under reduced pressure on a water bath. Purification by column chromatography on silica gel with $CHCl_3$ yielded the benzopyranone indenone adduct **1c,e–h**. The adducts **1c** (95%), **1e** (98%), **1f** (98%), **1g** (89%), and **1h** (92%) were recrystallized from methanol. In the case of the synthesis of **1c** further purification of the mother liquor by HPLC yielded apart from the adduct **1c** also the adducts **2c** (0.1 mmol; 0.6%) and **3c** (0.15 mmol; 1%).

For the indenone **30a** the same procedure was used with the following modification: The whole procedure was repeated five times with freshly added acetic anhydride and *o*-acetylphenylacetic acid. Purification of the reaction mixture by column chromatography on silica gel with $CHCl_3$–CCl_4 and a solvent gradient yielded the adducts **1a** (57%), **2a** (31%), and **3a** (4%). All adducts were recrystallized from methanol–toluene (4:1).

If *o*-formylphenylacetic acid[14] (15 mmol) or *o*-benzoylphenylacetic acid[15] (15 mmol) was used instead of *o*-acetylphenylacetic acid, the procedure with the indenone **30b** (20 mmol) yielded the adducts **1b** (96%) and **1d** (90%), respectively. The reaction mixture was chromatographed on silica gel with chloroform–hexane (7:3); after elution of the first fraction (indenone **30b**), chromatography was continued with chloroform–ethylacetate (9:1). The adducts **1b** and **1d** were recrystallized from hexane–toluene (6:4 and 3:7, respectively).

The benzopyranone–trimethylmaleimide adduct **17** was prepared and purified according to a described method.[16]

Adducts 1a, 1c, and 1f: see ref 1.

Adduct 1b: mp 132 °C; IR 1760 ($\nu_{C=O}$ ester), 1700 cm^{-1} ($\nu_{C=O}$ ketone); ^{1}H NMR ($CDCl_3/\Delta$) δ 1.54/0.18 (3, s, 11a-CH_3), 1.61/0.21 (3, s, 6a-CH_3), 3.68/0.75 (3, s, 9-OCH_3), 4.00/0.15 (1, s, 6-H), 5.42/0.19 (1, s, 1-H), 6.67–7.23 (6, m, Ar H), 7.37 (1, d, J = 9 Hz, 7-H); mass spectrum, m/e (relative intensity) 334 (13.0), 290 (0.3), 275 (1.8), 188 (100), 173 (12.0), 145 (9.0), 119 (35.0); calcd for M^+ 334.12049, found 334.1199.

Adduct 1d: mp 215 °C dec; IR 1762 ($\nu_{C=O}$ ester), 1699 cm^{-1} ($\nu_{C=O}$ ketone); ^{1}H NMR ($CDCl_3/\Delta$) δ 1.23/0 (3, s, 11a-CH_3) 1.66/0.25 (3, s, 6a-CH_3), 3.66/0.70 (3, s, 9-OCH_3), 4.02/0.09 (1, s, 6-H), 6.60–7.57 (10, m, Ar H), 8.00–8.17 (2, m, Ar H); mass spectrum, m/e (relative intensity) 410 (2.1), 366 (1.0), 351 (2.2),

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336 (0.6), 222 (100), 194 (52.3), 188 (36.6); calcd for M^+ 410.15179, found 410.1526.

Adduct 1e: mp 234 °C; IR 1750 ($\nu_{C=O}$ ester), 1710 cm^{-1} ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 1.40/0.10 (3, s, 11a-CH_3), 1.67/0.07 (3, s, 6a-CH_3), 2.03/0.03 (3, s, 1-CH_3), 3.63/0.70 (3, s, 9-OCH_3), 3.90/0.77 (3, s, 7-OCH_3), 4.47/–0.06 (1, s, 6-H), 6.30/0.03 (1, d, J = 2 Hz, 10-H), 6.57/0.24 (1, d, J = 2 Hz, 8-H), 6.70–7.20 (4, m, Ar H); mass spectrum, m/e (relative intensity) 378 (3.0), 218 (100), and 203 (10.0); calcd for M^+ 378.1467, found 378.1465.

Adduct 1g: mp 165 °C; IR 1760 ($\nu_{C=O}$ ester), 1710 cm^{-1} ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 1.50/0.20 (3, s, 11a-CH_3), 2.07/0.05 (3, s, 1-CH_3), 3.64/0.41 (1, d, J = 4 Hz, 6a-H), 3.66/0.73 (3, s, 9-OCH_3), 4.17/0.08 (1, d, J = 4 Hz, 6-H), 6.70–7.14 (7, m, Ar H); mass spectrum, m/e (relative intensity) 334 (16.9), 290 (23.7), 275 (27.1), 174 (61.0), 160 (100), 145 (3.0), 132 (59.3); calcd for M^+ 334.12049, found 334.1202.

Adduct 1h: mp 189 °C; IR 1752 ($\nu_{C=O}$ ester), 1703 cm^{-1} ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 1.59/0.24 (3, s, 11a-CH_3), 2.04/0.11 (3, s, 1-CH_3), 3.65/0.75 (3, s, 9-OCH_3), 3.82/0.41 and 3.99/0.28 (2 × 1, 2 × d, J = 11 Hz, 6a-CH_2Br), 4.45/0.08 (1, s, 6-H), 6.68 (1, d, J = 2 Hz, 10-H), 6.68–7.22 (5, m, Ar H), 7.69/0.35 (1, d, J = 8 Hz, 7-H); mass spectrum, m/e (relative intensity) 428 (2.0), 426 (2.0), 347 (4.1), 289 (5.6), 268 (10.1), 266 (10.1), 187 (8.2), 160 (100), 132 (50.6); calcd for M^+ 428.04462 and 426.04662, found 428.0453 and 426.0469.

Adduct 2a: mp 206 °C; IR 1750 ($\nu_{C=O}$ ester), 1700 cm^{-1} ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 0.67/–0.23 (3, t, J = 8 Hz, 11a-CH_2CH_3), 1.40 (2, m, 11a-CH_2CH_3), 2.22/0.05 (3, s, 6-CH_3), 3.68/0.73 (3, s, 7-OCH_3), 3.72/0.65 (3, s, 9-OCH_3), 4.27/–0.21 (1, s, 1-H), 6.44–6.64 (3, m, Ar H), 6.95–7.72 (7, m, Ar H), 8.21/–0.30 (1, br d, J = 8 Hz, 5-H); mass spectrum, m/e (relative intensity) 454 (3.0), 294 (100), 279 (30.0); calcd for M^+ 454.1780, found 454.1783.

Adduct 3a: mp 239 °C; IR 1765 ($\nu_{C=O}$ ester), 1710 cm^{-1} ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ –0.20/–0.20 (3, t, J = 8.4 Hz, 11a-CH_2CH_3), 0.89/–0.02 and 1.73/–0.13 (2 × 1, 2 × m, 11a-CH_2CH_3), 1.98/0.01 (3, s, 1-CH_3), 3.83/0.57 and 3.90/0.60 (2 × 3, 2 × s, 7- and 9-OCH_3), 5.03/–0.24 (1, s, 6-H), 6.53–7.70 (11, m, Ar H); mass spectrum, m/e (relative intensity) 454 (1.0), 381 (1.0), 294 (100), 279 (36.8); calcd for M^+ 454.1780, found 454.1792.

Adducts 2c and 3c: see ref 1.

Thermolysis of the Benzopyranone Adducts: General Procedure. A solution of 1 mmol of the adduct and 1 mmol of hydroquinone,[17] dissolved in 100 mL of diphenyl ether, was degassed by subsequent freeze–thaw cycles and thermolyzed in the dark at 250 °C for x h. The diphenyl ether was removed by chromatography on silica gel with hexane; subsequent elution with $CHCl_3$–CH_3OH (9:1) yielded the reaction mixture.

Thermolysis of Adduct 1a: After thermolysis (6 h) and usual workup, the reaction mixture was chromatographed on silica gel with toluene–tetrachloromethane (1:1); it gave first a fraction characterized as a mixture of the benzo[b]cyclopropa[lm]-fluorenone **6a** and the indenone **30a** (4:6), and the second fraction was a mixture of the benzo[c]fluorenone **5a**[1] and the benzo[b]-cyclopropa[lm]fluorenone **9a**; further elution gave the benzo-[c]fluorenone **8a** (2%) and the C-nor-D-homo steroid **4a** (2%).

Fractionized recrystallization of the second fraction from n-heptane–toluene (7:3) yielded pure compounds **5a** (53%) and **9a** (8%). The first fraction, 1,3-dihydro-1-methoxyisobenzofuran[18] (1.5 mmol) and 5 mL of toluene were refluxed for 4 h under a nitrogen atmosphere. After removal of the solvent, preparative TLC on silica gel with benzene–hexane (7:3) yielded the benzo-[b]cyclopropa[lm]fluorenone **6a** (8%). Compounds **6a** and **9a** were recrystallized from n-heptane and methanol, respectively.

Steroid 4a: oil, IR 1720 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.42 (3, t, J = 7.5 Hz, 7-CH_2CH_3), 2.15 (3, s, 6-CH_3), 2.43 (2, m, 7-CH_2CH_3), 3.61 (3, s, 15-OCH_3), 3.72 (1, s, 9-H), 3.90 (3, s, 17-OCH_3), 6.76 (1, d, J = 3 Hz, 16-H), 6.92–7.46 (10, m, Ar H); mass spectrum, m/e (relative intensity) 410 (70.3), 395 (10.8), 381 (100), 367 (6.8), 366 (10.8), 353 (8.1); calcd for M^+ 410.18818, found 410.1854.

Benzo[b]cyclopropa[lm]fluorenone 6a: mp 152 °C, IR 1690 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.71 (3, t, J = 7.5 Hz, 9c-CH_2CH_3), 1.63 (3, s, 4b-CH_3), 1.16 and 1.77 (2, m, 9c-CH_2CH_3), 3.18 (3, s, 9-OCH_3), 3.73 (3, s, 7-OCH_3), 3.78 (1, s, 9d-H), 6.23 (1, d, J = 2 Hz, 8-H), 6.69 (1, d, J = 2 Hz, 6-H), 6.60–7.67 (9, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 11.6 (9c-CH_2CH_3), 18.6 (q × s, 4b-CH_3), 21.8 (9c-CH_2CH_3), 39.7, 52.6 and 61.4 (C), 46.1 (d, $^1J_{CH}$ = 167.5 Hz, 9d-CH), 55.5 (7-OCH_3), 55.9 (9-OCH_3), 100.1, 105.8, 122.8, 124.2, 125.9, 126.3, 127.4 × 2, 129.5, 128.6, 130.5 (Ar CH), 137.5, 142.0, 142.5, 149.2, 159.3, 159.7 (Ar C), 202.8 (5-C=O); mass spectrum, m/e (relative intensity) 410 (94.1), 395 (22.1), 381 (100), 367 (7.4), 366 (11.0), 353 (22.1); calcd for M^+ 410.18818, found 410.1865.

Benzo[c]fluorenone 8a: oil; IR 1720 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.93 (3, t, J = 7.5 Hz, 6-CH_2CH_3), 1.06 (3, s, 6a-CH_3), 1.90 and 2.24 (2 × 1, 2 × m, 6-CH_2CH_3), 3.74 (3, s, 11-OCH_3), 3.88 (3, s, 9-OCH_3), 6.39 (1, t, J = 1.5 Hz, 5-H), 6.81 (1, d, J = 2.3 Hz, 10-H), 6.94–7.36 (10, m, Ar H); mass spectrum, m/e (relative intensity) 410 (74.5), 395 (8.5), 381 (100), 367 (6.4), 366 (10.6), 353 (17.0); calcd for M^+ 410.18818, found 410.1862.

Benzo[b]cyclopropa[lm]fluorenone 9a: mp 219 °C; IR 1687 cm^{-1} ($\nu_{C=O}$) ^1H NMR ($CDCl_3$) δ 0.98 (3, t, 123.4, 123.6, 7.2 Hz, 9c-CH_2CH_3), 1.22 and 1.73 (2 × 1, 2 × m, 9c-CH_2CH_3), 1.88 (3, s, 9d-CH_3), 3.40 (3, s, 9-OCH_3), 3.68 (3, s, 7-OCH_3), 4.37 (1, s, 4b-H), 6.21 (1, d, J = 2.2 Hz, 8-H), 6.66 (1, d, J = 2.2 Hz, 6-H), 7.00 (1, d, J = 4 Hz, Ar H), 6.40–7.29 (7, m, Ar H), 7.34 (1, d, J = 7.2 Hz, Ar H); ^{13}C NMR ($CDCl_3$) δ 10.5 (9c-CH_2CH_3), 15.6 (9d-CH_3), 22.9 (9c-CH_2CH_3), 39.2, 47.6, and 50.5 (C), 55.2 and 55.3 (7- and 9-OCH_3), 59.1 (d, $^1J_{CH}$ = 138.7 Hz, 4b-CH), 98.6, 104.9, 123.4, 123.6, 124.9, 125.6, 126.2, 127.3, 127.4, 132.2 and 132.9 (Ar CH), 134.1, 138.2, 142.6, 148.5, 158.2, and 158.7 (Ar C), 202.2 (s × d × d, 5-C=O); mass spectrum, m/e (relative intensity) 410 (52.2), 395 (6.7), 381 (100), 367 (5.6), 366 (11.1), 353 (14.4); calcd for M^+ 410.18818, found 410.1866.

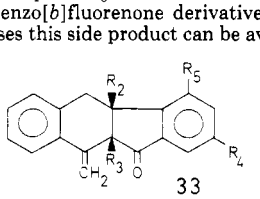
Thermolysis of Adduct 2a. Reaction for 3 h, usual workup, and purification as for the thermolysis of the adduct **1a** yielded a comparable product distribution for **4a** (2%), **5a** (55%), **6a** (10%), **8a** (3%), and **9a** (10%).

Thermolysis of Adduct 1b. Reaction for 2.5 h, workup, and chromatography on silica gel with chloroform–hexane (3:7) and a solvent gradient (toluene–tetrachloromethane) yielded the benzo[c]fluorenone **5b** (14%), followed by the benzo[b]cyclopropa[lm]fluorenone **6b** (18%) and the C-nor-D-homo steroid **4b** (51%); further elution gave unreacted adduct **1b** (12%). The time for thermolysis of **1b** was kept short because **6b** has proven to be unstable on prolonged heating. The products **4b** and **5b** were recrystallized from methanol and n-heptane, respectively.

Steroid 4b: mp 135 °C; IR 1715 cm^{-1} ($\nu_{C=O}$), ^1H NMR ($CDCl_3/\Delta$) δ 1.58/0.31 (3, s, 8-CH_3), 1.85/0.28 (3, s, 7-CH_3), 3.62/0.24 (1, s, 9-H), 3.85/0.60 (3, s, 17-OCH_3), 6.07/0.20 (1, s, 6-H), 6.93–7.47 (6, m, Ar H), 7.64 (1, d × d, J = 9 Hz, J = 3 Hz, 1-H); mass spectrum, m/e (relative intensity) 290 (98.9), 275 (100), 260 (10.9), 247 (10.9), 232 (14.1); calcd for M^+ 290.13067, found 290.1298.

Benzo[c]fluorenone 5b: mp 99.5 °C; IR 1710 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.67/0.24 (3, s, 11b-CH_3), 2.17/–0.06 (3, br s, J = 1.4 Hz, 6-CH_3), 3.15/0.20 (1, br s, J = 1.4 Hz, 6a-H), 3.79/0.62 (3, s, 9-OCH_3), 6.23/0.08 (1, d × q, J = 1.4 Hz, J = 1.4 Hz, 5-H), 6.87–7.47 (6, m, Ar H), 7.63 (1, d, J = 9 Hz, 11-H); mass spectrum, m/e (relative intensity) 290 (88.2), 275 (100), 260 (6.4),

(17) Thermolysis of adducts **1** in the absence of a radical inhibitor (hydroquinone) gives a lower yield but a comparable relative distribution of the products **4–9**. However the amount of side products is not reproducible: e.g., when R_1 = CH_3 in the adducts **1**, the formation of a variable amount of benzo[b]fluorenone derivatives of type **33** can be observed. In most cases this side product can be avoided completely by addition of 0.1 equiv of hydroquinone. In some cases 1 equiv or more is needed to avoid all side reactions (decomposition, tar products, ...). To describe a standard procedure we used always at least 1 equiv of hydroquinone. We believe that this component inhibits radical chain reactions, one of them involving the intermediate **10** and yielding products of type **33**. No appreciable acceleration of the rate-determining decomposition step of adducts **1** was observed on changing the concentration of hydroquinone neither on addition of acid or base.



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(18) Naito, K.; Rickborn, B. *J. Org. Chem.* **1980**, *45*, 4061.

247 (10.0), 232 (13.6); calcd for M^+ 290.13067, found 290.1301.

Benzo[*b*]cyclopropa[*lm*]fluorenone 6b: oil; IR 1685 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.54/0.33 (3, s, 9c-CH_3), 1.64/0.31 (3, s, 9b-CH_3), 2.63/0.32 (1, s, 9d-H), 3.70/0.56 (3, s, 7-OCH_3), 4.04/−0.05 (1, s, 4b-H), 6.80–7.50 (7, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 17.5 (q × t, 9c-CH_3), 20.4 (q × d, 9b-CH_3), 30.5 and 43.5 (9b- and 9c-C), 51.0 (d, $^1J_{CH}$ = 169.4 Hz, 9d-CH), 55.1 (7-OCH_3), 63.0 (d, $^1J_{CH}$ = 138.8 Hz, 4b-CH), 108.0, 121.0, 124.0, 124.1, 126.0, 127.5 and 129.5 (Ar CH), 134.2, 134.7, 142.0, 143.6, and 157.6 (Ar C), 199.5 (5-C=O); mass spectrum, *m/e* (relative intensity) 290 (80.6), 275 (100), 260 (6.1), 247 (10.0), 232 (10.5); calcd for M^+ 290.1306, found 290.1302.

Thermolysis of the Adducts 1c, 2c, and 3c. Reaction of **3c** in identical conditions (10 h) as described for **1c** (2 h),[1] followed by usual workup and chromatography, yielded the same product distribution as for **1c**: **4c** (47%), **5c** (33%), and **6c** (10%). Reaction of **2c** for 2 h, usual workup, and HPLC yielded the benzo[*c*]fluorenone **5c** (51%),[1] the C-nor-D-homo steroid **7c** (19%), the benzo[*c*]fluorenone **8c** (10%), and the benzo[*b*]cyclopropa[*lm*]fluorenone **9c** (9%).

Steroid 7c: oil; IR 1715 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.27/0.16 (3, s, 8-CH_3), 1.41/−0.02 (3, s, 9-CH_3), 2.07/0.27 (3, br s, 7-CH_3), 3.80/0.70 (3, s, 17-OCH_3), 6.28/0.15 (1, br s, 6-H), 6.86–7.54 (7, m, Ar H); mass spectrum, *m/e* (relative intensity) 304 (85), 289 (100), 261 (12); calcd for M^+ 304.14632, found 304.1455.

Benzo[*c*]fluorenone 8c: oil; IR 1715 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.27/0.04 (3, s, 6a-CH_3), 1.51/0.20 (3, s, 11b-CH_3), 1.83/−0.03 (3, br s, 6-CH_3), 3.80/0.66 (3, s, 9-OCH_3), 6.17/0.18 (1, br s, 5-H), 6.95–7.79 (7, m, Ar H); mass spectrum, *m/e* (relative intensity) 304 (96), 289 (100), 261 (15), 246 (15); calcd for M^+ 304.14632, found 304.1451.

Benzo[*b*]cyclopropa[*lm*]fluorenone 9c: oil; IR 1685 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.37/0.33 (3, s, 9d-CH_3), 1.53/0.32 (3, s, 9c-CH_3), 1.62/0.29 (3, s, 9b-CH_3), 3.70/0.63 (3, s, 7-OCH_3), 4.02/−0.08 (1, s, 4b-H), 6.80–7.40 (7, m, Ar H); mass spectrum, *m/e* (relative intensity), 304 (85), 289 (100), 274 (30); calcd for M^+ 304.14632, found 304.1466.

Thermolysis of Adduct 1d. Thermolysis (1 h, 2 equiv of hydroquinone), usual workup, and chromatography on silica gel with chloroform–hexane (4:6) and a solvent gradient yielded a first fraction containing the benzo[*c*]fluorenones **5d** and **8d** (9:1); the second fraction was a mixture of the C-nor-D-homo steroid **4d** and the benzo[*b*]cyclopropa[*lm*]fluorenone **9d** (4:1). Fractionized recrystallization of these two fractions from methanol or toluene–hexane (7:3) yielded pure compounds **5d** and **4d**. Further purification of the two filtrates on silica gel with chloroform–hexane (1:1) gave more **5d** (57%) and the product **8d** (6%), respectively, and more **4d** (28%) and the product **9d** (7%). The products **5d**, **8d**, and **9d** were recrystallized from methanol; the product **4d** was recrystalized from toluene–hexane (7:3).

Steroid 4d: mp 201 °C dec; IR 1716 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.56 (3, s, 7-CH_3), 1.67 (3, s, 8-CH_3), 3.69 (1, s, 9-H), 3.87 (3, s, 17-OCH_3), 6.53 (1, d, J = 9 Hz, 4-H), 6.73–7.47 (10, m, Ar H), 7.63 (1, d, J = 9 Hz, 1-H); ^{13}C NMR ($CDCl_3$) δ 17.4 (q × s, 7-CH_3), 23.9 (q × d, 8-CH_3), 47.1 (8-C), 55.7 (17-OCH_3), 62.6 (d × quintet, 9-CH), 105.5, 122.6, 126.3, 126.7, 127.3, 128.3, 128.6, 128.9, 129.8, and 130.0 (Ar CH), 130.2, 133.0, 134.1, 136.5, 137.5, 139.9,151.4, and 159.4 (Ar C), 203.2 (11-C=O); mass spectrum, *m/e* (relative intensity) 366 (100), 351 (95.0), 338 (4.7), 336 (9.1), 323 (5.8), 308 (6.9), 289 (7.7); calcd for M^+ 366.16197, found 366.1597.

Benzo[*c*]fluorenone 5d: mp 182 °C; IR 1705 cm^{-1} ($\nu_{C=O}$), ^1H NMR ($CDCl_3/\Delta$) δ 1.80/0.23 (3, s, 11b-CH_3), 2.01/−0.11 (3, s, 6-CH_3), 3.29/0.25 (1, s, 6a-H), 3.82/0.61 (3, s, 9-OCH_3), 6.56 (1, d × d, J = 8 Hz, J = 3 Hz, 4-H), 6.80–7.50 (10, m, Ar H), 7.78 (1, d, J = 8 Hz, 11-H); ^{13}C NMR ($CDCl_3$) δ 21.7 (6-CH_3), 29.3 (11b-CH_3), 45.1 (11b-C), 55.5 (9-OCH_3), 64.6 (d × septet, $^1J_{CH}$ = 127.5 Hz, 6a-CH), 105.4, 123.0, 126.2, 126.3, 126.5, 126.7 × 2, 126.8, 128.4, 129.4, and 130.8 (Ar CH), 129.0, 133.5, 133.9, 137.7, 139.0, 139.3, 152.2, and 159.3 (Ar C), 203.8 (7-C=O); mass spectrum, *m/e* (relative intensity) 366 (100), 351 (86), 338 (2.1), 336 (6.7), 323 (6.5), 308 (7.0), 289 (8.5); calcd for M^+ 366.16197, found 366.1599.

Benzo[*c*]fluorenone 8d: mp 164 °C; IR 1704 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.02 (3, s, 11b-CH_3), 2.19 (3, d, J = 1.5 Hz, 6-CH_3), 3.78 (3, s, 9-OCH_3), 6.50 (1, q, J = 1.5 Hz, 5-H), 6.70–7.50 (12, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 22.4 (q × d, 6-CH_3), 28.7 (q × s, 11b-CH_3), 50.8 (11b-C), 55.5 (9-OCH_3), 68.7 (6a-C), 105.3, 124.0, 124.3, 125.3, 126.3, 126.5, 127.3, 127.6, 129.3, and 129.7 (Ar CH), 132.7, 135.1, 136.8, 139.1, 140.7, 151.7, and 159.4 (Ar C), 204.5 (7-C=O); mass spectrum, *m/e* (relative intensity) 366 (89.7), 351 (100), 338 (18.9), 336 (8.0), 323 (9.0), 308 (6.9), 289 (10.7); calcd for M^+ 366.16197, found 366.1608.

Benzo[*b*]cyclopropa[*lm*]fluorenone 9d: mp 171 °C; IR 1685 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.36/0.22 (3, s, 9b-CH_3), 1.52/0.31 (3, s, 9c-CH_3), 3.72/0.59 (3, s, 7-OCH_3), 4.20/−0.11 (1, s, 4b-H), 6.62–7.53 (12, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 16.1 (q × d, 9c-CH_3), 20.0 (q × s, 9b-CH_3), 33.1 (9b-C), 46.4 (9c-C), 55.3 (7-OCH_3), 58.3 (9d-C), 63.6 (d × quintet, $^1J_{CH}$ = 141 Hz, 4b-CH), 108.0, 121.1, 123.7, 124.7, 126.2, 127.0, 127.4, 128.7, 129.7, and 131.0 (Ar CH), 134.4, 135.4, 137.0, 141.2, 147.5, and 157.8 (Ar C), 200.0 (5-C=O); mass spectrum, *m/e* (relative intensity) 366 (81.7), 351 (100), 338 (21.5), 323 (10.8), 308 (9.7), 289 (12.9); calcd for M^+ 366.16197, found 366.1609.

Thermolysis of the Adduct 1e. Reaction for 6 h (1.5 equiv of hydroquinone), usual workup, and chromatography on silica gel with toluene–tetrachloromethane (1:1) yielded the cyclopropane **6e** (18%); further elution gave the benzo[*c*]fluorenone **5e** (50%) and the C-nor-D-homo steroid **4e** (17%). All products were recrystallized from methanol.

Steroid 4e: mp 190 °C; IR 1715 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.60 (3, s, 8-CH_3), 1.85 (3, s, 7-CH_3), 1.94 (3, s, 6-CH_3), 3.53 (1, s, 9-H), 3.83 (3, s, 17-OCH_3), 3.90 (3, s, 15-OCH_3), 6.71 (1, d, J = 3 Hz, 16-H) 6.86 (1, d, J = 3 Hz, 17a-H), 7.23 (4, s, Ar H); mass spectrum, *m/e* (relative intensity) 334 (70), 319 (100), 304 (26), 291 (14); calcd for M^+ 334.15688, found 334.1569.

Benzo[*c*]fluorenone 5e: mp 153 °C; IR 1710 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.80 (3, s, 11b-CH_3), 2.09 (3, s, 5-CH_3), 2.20 (3, s, 6-CH_3), 3.07 (1, s, 6a-H), 3.77 (3, s, 9-OCH_3), 3.95 (3, s, 11-OCH_3), 6.73 (2, s, 8- and 10-H), 6.83–7.37 (3, m, Ar H), 7.57 (1, d × d, J = 6 Hz, J = 3 Hz, 1 -H); mass spectrum, *m/e* (relative intensity) 334 (84), 319 (100), 306 (13), 304 (21), 291 (14), 289 (6), 276 (7), 261 (7); calcd for M^+ 334.15688, found 334.1553.

Benzo[*b*]cyclopropa[*lm*]fluorenone 6e: mp 156 °C; IR 1688 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.41 (3, s, 9c-CH_3), 1.50 (3, s, 9b-CH_3), 1.63 (3, s, 4b-CH_3), 2.70 (1, s, 9d-H), 3.70 and 3.72 (2 × 3, 2 × s, 7- and 9-OCH_3), 6.37 (1, d, J = 3 Hz, 8-H), 6.62 (1, d, J = 3 Hz, 6-H), 6.70–7.40 (4, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 12.9 (9c-CH_3), 18.9 (4b- and 9b-CH_3), 29.6, 41.1 and 60.7 (4b-, 9b-, and 9c-C), 51.5 (9d-CH), 55.6 (7-OCH_3), 55.9 (9-OCH_3), 100.3, 105.0, 123.0, 124.0, 126.0, and 127.4 (Ar CH), 127.1, 137.4, 143.7, 148.1, 159.4, and 159.7 (Ar C), 203.1 (5-C=O); mass spectrum, *m/e* (relative intensity) 334 (62), 319 (100), 306 (41), 304 (31), 291 (52); calcd for M^+ 334.15688, found 334.1566. Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.02; H, 6.63. Found: C, 78.88; H, 6.58.

Thermolysis of Adduct 1e in the Presence of Thiocresol. A solution of 1 mmol of adduct **1e** dissolved in 50 mL of thiocresol was thermolyzed at 250 °C for 6 h. The major part of the solvent was distilled off under vacuum. Workup and chromatography on silica gel with chloroform–hexane (6:4) yielded one fraction characterized as a mixture of the products **16a** and **16b** (6:4) (95%). HPLC gave a pure fraction of the product **16a**.

Benzo[*b*]fluorenone 16a: oil; IR 1703 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.98 (3, s, 10a-CH_3), 1.38 (3, d, J = 7.5 Hz, 10-CH_3), 1.42 (3, s, 4b-CH_3), 3.05 (1, q, J = 7.5 Hz, 10-H), 3.14 and 3.20 (2 × 1, 2 × d, J = 15 Hz, 5-CH_2), 3.79 (3, s, 2-OCH_3), 3.93 (3, s, 4-OCH_3), 6.69 (2, s, 1- and 3-H), 6.95–7.21 (4, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 13.1 (q × d, 10-CH_3), 16.8 (q × d, 10a-CH_3), 23.4 (q × t, 4b-CH_3), 41.0 (t × quintet, 5-CH_2), 41.1 (10-CH), 47.3 and 56.7 (C), 55.3 (2- and 4-OCH_3), 95.9, 106.5, 125.9, 126.0, 126.3, and 127.6 (Ar CH), 136.5, 136.7, 141.7, 141.8, 157.6, and 160.6 (Ar C), 210.2 (11-C=O); mass spectrum, *m/e* (relative intensity) 336 (92), 321 (45), 218 (100), 203 (28), 175 (11), 118 (97), 117 (52).

Benzo[*b*]fluorenone 16b: oil; IR 1703 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.27 (3, s, 10a-CH_3), 1.42 (3, s, 4b-CH_3), 1.45 (3, d, J = 7.4 Hz, 10-CH_3), 2.72 (1, q, J = 7.4 Hz, 10-H), 2.77 and 3.39 (2 × 1, 2 × d, J = 14.2 Hz, 5-CH_2), 3.65 (3, s, 2-OCH_3), 3.83 (3, s, 4-OCH_3), 6.48 (2, s, 1- and 3-H), 6.90–7.23 (4, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 12.6 (q × d, 10-CH_3), 19.3 (q × d, 10a-CH_3), 23.2 (q × t, 4b-CH_3), 39.4 (t × q, 5-CH_2), 42.3 (10-CH), 47.5 and 56.8 (C), 55.2 (2- and 4-OCH_3), 95.3, 106.0 (106.0, 124.3, 125.7, 126.1, and

126.7 (Ar CH), 137.6, 138.2, 140.4, 141.5, 157.2, and 160.4 (Ar C), 209.3 (11-C=O).

Thermolysis of Adduct 1f: For the NMR data of the products, we refer to ref 1; the yields of the thermolysis in similar conditions as for **1e** were **4f** (25%), **5f** (53%), and **6f** (17%).

Thermolysis of Adduct 17: Reaction for 3 h, workup, and chromatography on silica gel with toluene–tetrachloromethane (8:2) yielded the benz[*e*]isoindoledione **18** (62%) followed by the benz[*e*]isoindoledione **19** (38%). The products **18** and **19** were recrystallized from chloroform–methanol (3:7).

Benz[*e*]isoindoledione 18: mp 69 °C; IR 1780, and 1710–1690 cm^{-1} ($\nu_{C=O}$ imide); ^1H NMR ($CDCl_3$) δ 1.37 (3, s, 3a-CH_3), 1.53 (3, s, 9b-CH_3), 2.02 (3, d, J = 1.5 Hz, 4-CH_3), 2.96 (3, s, 2-NCH_3), 6.30 (1, q, J = 1.5 Hz, 5-H), 6.90–7.35 (3, m, Ar H), 7.50 (1, m, 9-H); mass spectrum, m/e (relative intensity) 255 (74), 170 (100), 155 (42); calcd for M^+ 255.1259, found 255.1251.

Benz[*e*]isoindoledione 19: mp 150 °C; IR 1780, 1705 cm^{-1} ($\nu_{C=O}$ imide); ^1H NMR ($CDCl_3$) δ 1.40 (3, s, 3a-CH_3), 1.98 (3, br s, 5-CH_3), 2.05 (3, br s, 4-CH_3), 3.00 (3, s, 2-NCH_3), 3.70 (1, s, 9b-H), 7.15–7.40 (4, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 15.0 and 15.1 (4- and 5-CH_3), 20.8 (q × d, 3a-CH_3), 25.4 (*N*-CH_3), 49.8 (3a-C), 52.8 (d × q × d, 9b-CH), 123.4, 127.1, and 128.4 (Ar CH), 125.5 and 127.3 (4- and 5-C), 130.3 (d × t, Ar 9-CH), 128.7 and 133.5 (Ar 5a- and 9a-C), 175.9 (3-C), 180.2 (1-C); mass spectrum, m/e (relative intensity) 255 (87), 170 (100), 155 (35); calcd for M^+ 255.1259, found 255.1246. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.04; H, 6.68; N, 5.42.

Thermolysis of Adduct 1g. Reaction for 2 h, usual workup, and chromatography on silica gel with chloroform–hexane (1:1) yielded the benzo[*a*]fluorenone **23** (38%) followed by the cyclopropane **6g** (31%); further elution gave the benzo[*b*]fluorenone **22** (14%).

Benzo[*b*]cyclopropa[*lm*]fluorenone 6g: oil; IR 1685 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.43/0.34 (3, s, 9c-CH_3), 1.58/–0.02 (3, s, 4b-CH_3), 2.45/0.37 and 2.94/0.37 (2 × 1, 2 × d, J = 8.5 Hz, 9b- and 9d-H), 3.67/0.56 (3, s, 7-OCH_3); and 6.69–7.32 (7, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 18.1 (q × s, 4b-CH_3), 19.0 (q × d × d, 9c-CH_3), 30.8 (d, $^1J_{CH}$ = 161 Hz, 9b-CH), 42.7 (9c-C), 45.5 (d, $^1J_{CH}$ = 168.5 Hz, 9d-CH), 55.4 (7-OCH_3), 59.4 (4b-C), 108.9, 120.9, 123.3, 124.2, 126.5, 128.1, and 131.1 (Ar CH), 130.6, 135.3, 141.6, 147.7, and 158.4 (Ar C), 201.2 (5-C=O); mass spectrum, m/e (relative intensity) 290 (88), 275 (100), 247 (12); calcd for M^+ 290.13067, found 290.1298.

Benzo[*b*]fluorenone 22: oil; IR 1708 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 0.85/–0.12 (3, d, J = 6.6 Hz, 10-CH_3), 1.11/–0.05 (3, s, 10a-CH_3), 3.19/–0.03 (1, q, J = 6.6 Hz, 10-H), 3.88/0.66 (3, s, 2-OCH_3), 6.87/0.23 (1, s, 5-H), 7.16–7.43 (6, m, Ar H), 7.75/0.38 (1, d, J = 9.3 Hz, 4-H); mass spectrum, m/e (relative intensity) 290 (92), 275 (100), 247 (10); calcd for M^+ 290.13067, found 290.1298.

Benzo[*a*]fluorenone 23: **23** showed the same characteristics as the product previously obtained from the oxidation of **4c**.[1]

Thermolysis of Adduct 1h. After thermolysis (2 h) and usual workup, the reaction mixture was treated with 100 mL of acetic anhydride and 25 mL of triethylamine during 48 h at 50 °C under a nitrogen atmosphere. The mixture was poured into ice–water–K_2CO_3, extracted three times with chloroform, and purified on silica gel with chloroform–hexane (7:3). Recrystallization from toluene yielded 1.5 mmol of the benz[*a*]anthracenol **25** (75%). If the reaction mixture was not treated with acetic anhydride the unstable compound **24** was obtained.

Benz[*a*]anthracenone 24: IR 1640 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 2.39/0.46 (3, s, 6-CH_3), 2.61/0.30 (3, s, 5-CH_3), 3.91/0.44 (3, s, 10-OCH_3), 4.00/0.48 (2, s, 7-CH_2), 7.00–8.18 (6, m, Ar H), 9.80/–0.63 (1, d, J = 8 Hz, 1-H); mass spectrum, m/e (relative intensity) 302 (100), 287 (72), 259 (17).

Benz[*a*]anthracenol 25; mp 204 °C; IR 1755 cm^{-1} ($\nu_{C=O}$ ester); ^1H NMR ($CDCl_3$) δ 2.51 (3, s, 12-$OCOCH_3$), 2.60 (3, s, 5-CH_3), 2.69 (3, s, 6-CH_3), 3.91 (3, s, 10-OCH_3), 7.14 (1, d, J = 2.3 Hz, 11-H), 7.18 (1, d × d, J = 9 Hz, J = 2.3 Hz, 9-H), 7.45 and 7.65 (2 × 1, 2 × t × d, J = 7.1 Hz, J = 1.6 Hz, 2- and 3-H), 7.88 (1, d, J = 9 Hz, 8-H), 7.98 (1, d × d, J = 7.1 Hz, J = 1.6 Hz, 4-H), 8.33 (1, s, 7-H), 9.10 (1, d × d, J = 7.1 Hz, J = 1.6 Hz, 1-H); mass spectrum, m/e (relative intensity) 344 (23), 303 (12), 302 (100), 287 (33); calcd for M^+ 344.14123, found 344.1396.

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