(C16), 36.90 (C10), 33.44 (C2), 31.91 (C18), 27.41 (C7), 26.81 (C4), 25.88 (*t*-Bu), 25.06 (C17), 24.59 (C3), 22.63 (C19), 18.22, 18.04 (*t*-Bu), 14.04 (C20), −4.27, −4.61 ($SiCH_3$); exact mass, calcd $C_{32}H_{61}NO_5Si_2$ (M − H_2O, C_4H_9) 520.328, found 520.327.

Acknowledgement is given to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of early phases of this research. We also thank the National Institute of Health for their generous support of this research (Grants CA-19689 and CA-21840). The ^{13}C NMR spectrum used in this investigation was obtained on the departmental CFT-20 instrument provided by NSF Grant 7842. We thank the Purdue University Biological Magnetic Resonance Laboratory (NIH RR01077) for access to the 360-MHz ^1H NMR spectrometer and John Saddler for providing those spectra.

Registry No. **3**, 363-24-6; 8-epi-**3**, 27415-25-4; 11-epi-**3**, 38310-90-6; 8,11-*epi*-**3**, 85548-91-0; **5a**, 51751-83-8; **5b**, 64493-06-7; D-**6b**, 77520-20-8; DL-**6b**, 85548-61-4; DL-**6c**, 85453-04-9; DL-**7a**, 85548-60-3; **7b**, 41138-68-5; DL-**11**, 85548-62-5; D-**11**, 77520-17-3; L-**11**, 77520-12-8; D-**12**, 33375-06-3; L-**12**, 14649-03-7; **13**, 85453-05-0; **14**, 85548-63-6; D-**15**, 85453-06-1; L-**15**, 85548-64-7; **16**, 85548-65-8; **17**, 85548-66-9; **18**, 85453-07-2; D-**19**, 77520-18-4; D-**20**, 85548-67-0; L-**20**, 77493-65-3; L-**20** (enediol), 77493-66-4; **21**, 77520-19-5; D-**22**, 85453-08-3; **23**, 77520-13-9; **24**, 85548-68-1; **25**, 61348-02-5; **27**, 77493-63-1; **28**, 77493-64-2; **29**, 77493-67-5; **30**, 85548-69-2; **31**, 39198-04-4; **32**, 39178-64-8; DL-**33**, 39647-88-6; DL-**33** (hemiphthalate ester), 60457-57-0; D-**33**, 39647-93-3; L-**33**, 42541-99-1; L-**34**, 60498-28-4; L-**35**, 41138-67-4; **36**, 85548-70-5; **37**, 85453-09-4; **38**, 85453-10-7; **39**, 85453-11-8; **40**, 85453-12-9; **41a**, 85479-31-8; **41b**, 85479-32-9; **41c**, 85479-33-0; D-**43**, 77520-21-9; D-**44**, 77493-68-6; L-**46**, 77493-69-7; D-**47**, 77493-70-0; L-**48**, 85610-67-9; D-**49**, 85548-71-6; **50**, 77494-45-2; **51**, 85548-73-8; **52**, 85453-13-0; **53**, 85453-14-1; **54**, 85453-15-2; **54a**, 85453-16-3; **55a**, 85453-17-4; **55b**, 85453-18-5; **56**, 85453-19-6; **57**, 85453-20-9; **58**, 85453-21-0; **59**, 77494-46-3; **60**, 77520-22-0; **61**, 85453-22-1; **62**, 85548-74-9; **63**, 85479-34-1; **64**, 85548-75-0; **65**, 85453-23-2; **66**, 106-95-6; **67**, 85453-24-3; **68**, 85453-25-4; **69**, 85548-76-1; **70**, 77506-98-0; **71**, 85548-77-2; **72**, 85453-26-5; **73**, 85548-78-3; **74**, 85453-27-6; **76**, 85453-28-7; **77**, 85453-29-8; **78**, 85479-28-3; **79a**, 85453-30-1; 8β-**79b**, 85548-79-4; 8α-**79b**, 85610-68-0; **80**, 85453-31-2; **81**, 85453-32-3; **82**, 85453-33-4; **83**, 85453-34-5; **84**, 85453-35-6; **85**, 85453-36-7; **86**, 85453-37-8; **87**, 85548-80-7; **88**, 85453-38-9; **88b**, 85453-39-0; **89a**, 85453-40-3; **89b**, 85548-81-8; **90**, 85453-41-4; **91**, 85453-42-5; **92**, 85453-43-6; **93a**, 85453-44-7; **93b**, 85548-82-9; **94**, 85453-45-8; **95a**, 85453-46-9; **95b**, 85548-83-0; **97**, 85453-47-0; **99**, 85453-48-1; **102**, 85453-77-6; **104**, 85453-49-2; **105**, 85453-50-5; **106**, 85453-51-6; **107**, 85453-52-7; **108**, 77506-99-1; **109**, 85453-53-8; **110**, 77494-47-4; **111**, 85453-54-9; **112**, 85453-55-0; **113**, 85453-56-1; **114**, 85453-57-2; **115**, 85453-58-3; **116**, 85453-59-4; **117**, 85453-60-7; **118**, 85453-61-8; **119**, 85453-62-9; **120**, 77494-48-5; **121**, 85548-84-1; **122**, 85453-63-0; **123**, 85453-64-1; **124**, 85453-65-2; **125**, 85453-66-3; **126**, 85453-67-4; **127**, 85453-68-5; **128**, 85453-69-6; **129**, 85453-70-9; **130**, 85453-71-0; **131**, 85548-85-2; **132**, 85453-72-1; **133**, 85453-73-2; **135**, 66602-10-6; **136**, 31753-17-0; **137**, 31753-19-2; 8-epi-**137**, 85548-90-9; **138**, 13345-50-1; **139**, 85453-74-3; **139** (bis(isopropyldimethylsilyl) ether), 85453-78-7; **140**, 57021-16-6; **141**, 85548-86-3; **142**, 85548-87-4; **143**, 85548-88-5; **144**, 85453-75-4; **145**, 85610-69-1; **146**, 85548-89-6; **147**, 85453-76-5; cyclopentadiene, 542-92-7; cyclopentadiene monoepoxide, 7129-41-1; 2,2,2-trichloroethyl chloroformate, 17341-93-4; hexanoyl chloride, 142-61-0; acetylene, 74-86-2; (*Z*)-7-hydroxy-5-heptenenitrile, 85453-79-8.

Supplementary Material Available: Experimental details for the resolution of DL-**11** and DL-**33** and the preparation of the compounds not described in the Experimental Section as well as a table of X-ray data of **70** (75 pages). Ordering information is given on any current masthead page.

Thermolysis of Benzopyranone–Indenone Adducts: A New Route to the C-Nor-D-Homo Steroid Skeleton

Dirk J. Vanderzande,[1a,b] Roger A. Ceustermans,[1a,b] Henri J. Martens,*[1c] Suzanne M. Toppet,[1b] and Georges J. Hoornaert*[1b]

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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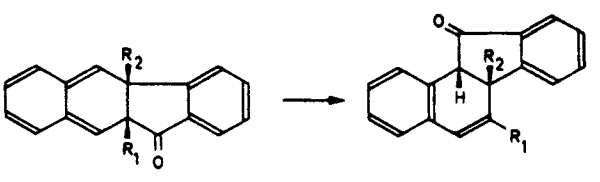
Generation of *o*-quinodimethane systems and their rearrangement reactions during thermolysis of benzopyranone–indenone adducts **9** have been studied. Three products have been obtained: a C-nor-D-homo steroid, **12**, a benzo[*c*]fluorenone, **13**, and a benzo[*b*]cyclopropa[*lm*]fluorenone, **14**. Their formation and relative distribution on thermolysis of different adducts **9** has been rationalized by mechanisms proceeding via an intermediate *o*-quinodimethane system, **17**, the presence of which has been established by trapping with tetracyanoethylene.

In previous papers we reported the photochemical transformation of truxones to C-nor-D-homo steroid systems.[2] One of the possible mechanisms for this transformation included the intermediacy of *o*-quinodimethane systems like **1** that could rearrange to C-nor-D-homo steroid systems **2** by a 1,5-sigmatropic benzoyl shift

Scheme I



1 **2**

(Scheme I). Therefore we investigated also the possibility of generating these *o*-quinodimethane systems via a nonphotochemical reaction. *o*-Quinodimethanes are now un-

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

(2) (a) G. Jammaer, H. Martens, and G. Hoornaert, *J. Org. Chem.*, **39**, 1325 (1974); (b) R. Ceustermans, H. J. Martens, and G. J. Hoornaert, *ibid.*, **44**, 1388 (1979).

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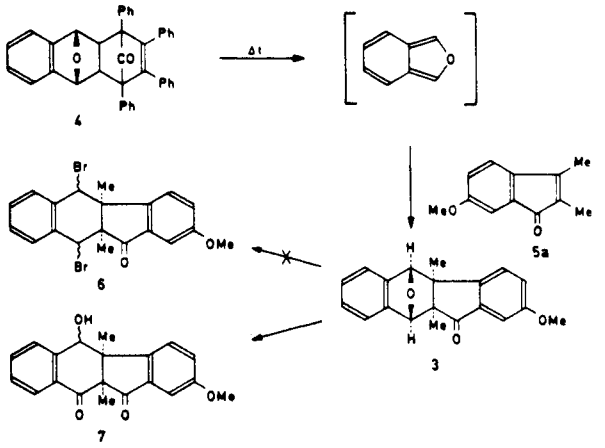
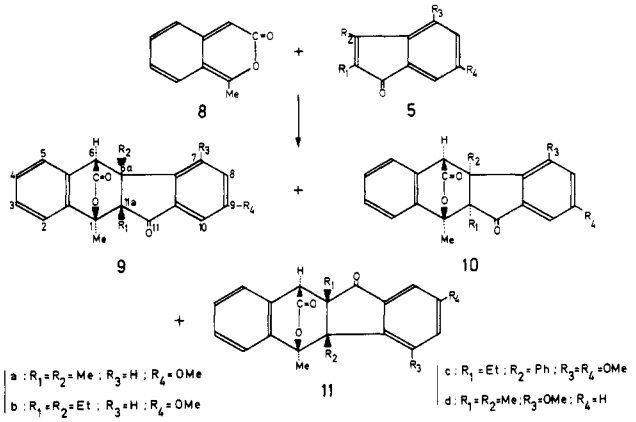
Scheme II



Scheme III



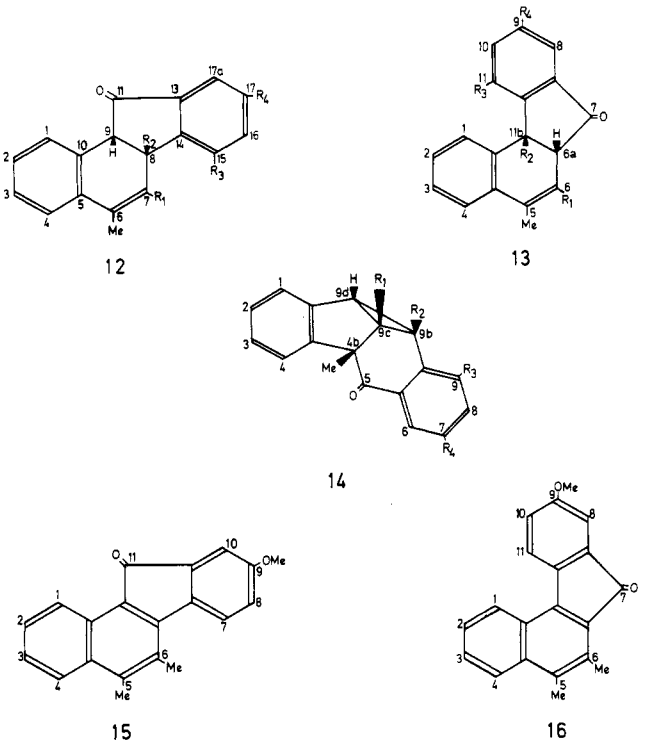
der active investigation from both theoretical[3a-c] and synthetic organic viewpoints.[3d-f] We report in this paper our results concerning the mechanism of the thermal rearrangement of some *o*-quinodimethane systems and the use of these rearrangements in the construction of steroid skeletons.

Results and Discussion

The first entry to *o*-quinodimethane systems 1 we have explored was the isobenzofuran–indenone adduct **3**. Isobenzofuran was generated in situ by thermolysis of the adduct **4**[4] and trapped with an excess of indenone **5a** to give the adduct **3** in good yields (Scheme II). Along with the exo adduct **3**, minor amounts of the endo adduct were formed (exo–endo ratio was 3:1). In order to obtain the brominated product **6**, which would be a suitable precursor to the *o*-quinodimethane system,[5] we treated the adduct **3** with the triphenylphosphine–bromine adduct, a reagent that is reported to cleave the oxygen bridge in similar compounds.[6] However, the only product that we could isolate was the oxidized compound **7**.

In a parallel approach we used benzopyranone adducts that are reported to yield *o*-quinodimethane systems on photolysis.[7] Benzopyranone **8**, formed by the heating of

Chart I



o-acetylphenylacetic acid in dehydrating conditions,[8] reacts in situ with the indenone **5a** to form mainly the Diels–Alder adduct **9a** (95%), about 1% of the adduct **10a**, and minor amounts of the adduct **11a** (Scheme III).

Thermolysis of the adduct **9a** in diphenyl ether at 250 °C affords three products: the C-nor-D-homo steroid **12a** (47%), the benzo[*c*]fluorenone **13a** (33%), and the benzo[*b*]cyclopropa[*lm*]fluorenone **14a** (10%) (Chart I). These products are thermally stable in the reaction conditions.

The assignment of the endo structure to the Diels–Alder adducts **9a** and **11a** is based on the high-field absorptions of the aromatic protons (6.6–7.3 ppm) and the aromatic methoxyl function (3.66 ppm) compared to these adsorptions in the exo adduct **10a** (7.1–7.6 and 3.86 ppm). The nearly parallel aromatic rings in the endo adducts are responsible for this shielding. Differentiation between the possible regio-Diels–Alder adducts has been made on the basis of the aromatic induced solvent shift[9] (ASIS) $\Delta(=\delta_{CDCl_3}-\delta_{C_6D_6})$ of 6-H and 1-Me: $\Delta = 0.21$ and 0.15 ppm for 6-H and $\Delta = 0.10$ and 0.08 ppm for 1-Me in isomers **9a** and **10a** compared to $\Delta = -0.12$ and 0.42 ppm for the corresponding hydrogen and methyl group in the regioisomer **11a**.

The C-nor-D-homo steroid structure was assigned to product **12a** on the basis of the ^1H NMR chemical shift of 1-H (7.66 ppm in $CDCl_3$), which can be explained by the deshielding influence of the carbonyl group.[2a] The ^1H NMR data of the product **13a** show the following details: a chemical shift of 7.78 ppm for 11-H with a solvent shift $\Delta = 0.41$ ppm; a quintet multiplicity for the 5-Me and an easy H–D exchange of 6a-H leading to a quartet for the 5-Me; a solvent shift $\Delta = -0.02$ ppm for the 6-Me is observed; hydrogenation of the 5–6 double bond leads to a product with a doublet ($J = 7$ Hz) for 6a-H. Comparison

(3) (a) J. J. McCullough, *Acc. Chem. Res.*, **13**, 270 (1980); (b) R. P. Steiner, R. D. Miller, H. J. Dewey, and J. Michl, *J. Am. Chem. Soc.*, **101**, 1820 (1979); (c) T. W. Bell, C. M. Bowes, and F. Sondheimer, *Tetrahedron Lett.*, **21**, 3299 (1980); (d) W. Oppolzer, *Synthesis*, 793 (1978); (e) T. Kametani and H. Nemoto, *Tetrahedron*, **37**, 3 (1981); (f) K. C. Nicolaou, W. E. Barnette, and P. Ma, *J. Org. Chem.*, **45**, 1463 (1980).
(4) L. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965).
(5) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).
(6) J. de Wit and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **92**, 281 (1973).
(7) (a) D. W. Jones and G. Kneen, *J. Chem. Soc., Chem. Commun.*, 1038 (1972); (b) D. W. Jones and G. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 175 (1975).
(8) J. M. Holland, and D. W. Jones, *J. Chem. Soc. C*, 536 (1970).
(9) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

Table I. Comparison of the ^1H NMR Data of the Compounds 15 and 16[a]

	15		16	
	δ	Δ	δ	Δ
1-H	8.79	−0.64	8.26	0.04
5-CH_3	2.34	0.19	2.53	0.35
6-CH_3	2.40	0.23	2.72	−0.03

[a] δ in ppm, $CDCl_3$; $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$.

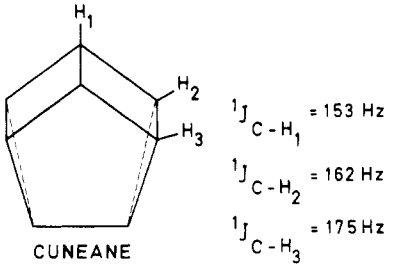
Table II. Comparison of the ^{13}C NMR Data of the Compounds 12b, 13b, and 13c

	12b	13b	13c
$CH_3C=$	14.8	14.3	14.4
$CH_3CH_2C=$	13.6; 22.6	12.4; 26.6	11.5; 26.7
CH_3CH_2C	8.8; 29.3	9; 36.1	

[a] δ in ppm, $CDCl_3$.

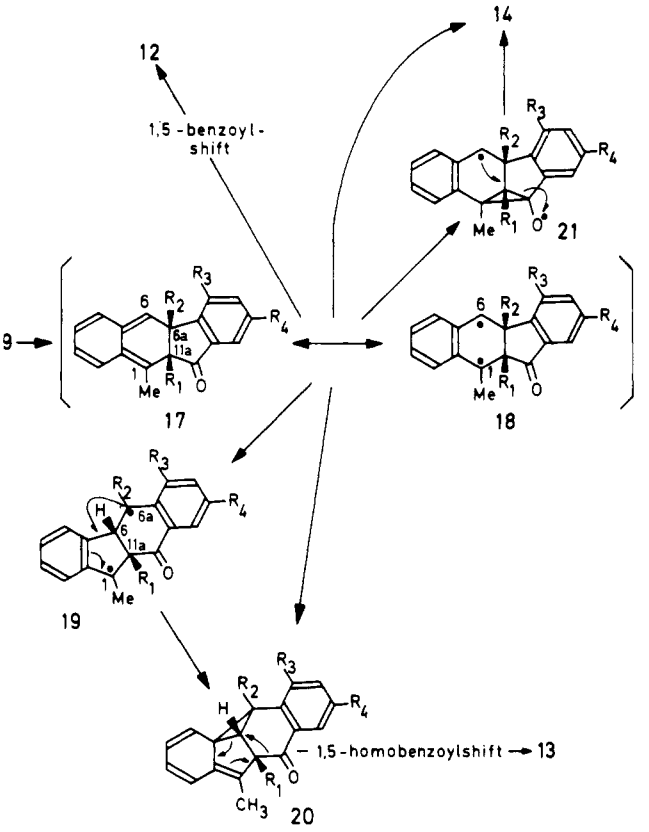
of these data with those of 12a confirms the proposed structure **13a**. The proposed cis junction of the B and C for the products **12a** and **13a** is confirmed by the appearance of a NOE of ±20% (for the proton α to the carbonyl group) on irradiation of the methyl group on the junction. Further evidence for the structure of **12a** and **13a** can be found in their conversion to the oxidized products **15** and **16** simply by heating a diphenyl ether solution at 250 °C in the presence of oxygen. Structures **15** and **16** can be easily differentiated by the ^1H NMR data of 1-H, 5-CH_3, and 6-CH_3 (Table I). Especially, the low-field absorption of 1-H at 8.79 ppm is characteristic for structure **15** and not in agreement with structure **16**.[10]

The ^1H NMR spectrum of compound **14a** shows three methyl groups on a quaternary carbon and one tertiary proton at 2.67 ppm. The latter absorption and the IR absorption at 1680 cm^{-1} (C=O in six-membered ring) are in good agreement with literature values[11] for compounds with the same skeleton. In the ^{13}C NMR spectrum, the corresponding tertiary carbon absorbs at 51.8 ppm and is characterized by $^1J_{CH}$ = 170 Hz. This indicates a serious ring strain comparable to that of a cyclopropane ring carbon in the cage compound cuneane.[12]



Thermolysis of **9b** yields **12b** (23%) and **13b** (49%). As this thermolysis was performed on a small scale, no effort has been made to isolate and purify minor compunds. Assignment of structure **12b** has been made by comparison of ^1H and ^{13}C NMR data of **12a** and **12b**. The very high abundance (100%) of the M − Et peak in the mass spectra of **12b** and **13b** indicates that the ethyl group is located on a quaternary carbon capable of stabilizing a positive charge. Comparison of the ^{13}C NMR spectra of **12b** and **13b** shows a γ effect for the methylene carbon atoms of

Scheme IV



the two ethyl groups in **12b** relative to **13b** (Table II). This indicates that the two ethyl groups are in a γ position to each other in **12b** and not in **13b**, which is in agreement with the proposed structures.

In order to obtain information about the fate of the substituents R_1 and R_2 during thermolysis, we synthesized the adduct **9c**. Structural proof for this adduct was obtained through comparison of the NMR data with those of the other adducts already mentioned. Thermolysis of **9c** yielded 61% of the benzo[*c*]fluorenone **13c**; only minor amounts of other products were observed. The position of the substituents has been secured by comparison of the NMR data with that of **13b**. Especially the ^{13}C NMR data of the ethyl group are informative. The data of Table II indicate that the ethyl group in **13c** is located on carbon atom 6 of the double bond.

When thermolysis of the adduct **9a** was performed in the presence of an excess of tetracyanoethylene, the *o*-quinodimethane **17** could be trapped as a Diels–Alder adduct. This trapping inhibited the formation of all other products, indicating that the *o*-quinodimethane **17** could be an intermediate in the formation of **12–14**. Thermolysis of the exo isomer **10a** yielded the same products in exactly the same ratio, as could be expected since both adducts should react via the *o*-quinodimethane **17**. Scheme IV is one explanation for the formation of the products **12–14**.

o-Quinodimethanes are known to have a biradical character, with a small HOMO–LUMO gap, which results in high reactivity in pericyclic reactions.[3a] The formation of the C-nor-D-homo steroid **12** can be regarded as a suprafacial 1,5-benzoyl shift of the *o*-quinodimethane **17**. There are several recent reports of such 1,5-shifts in thermal rearrangements of *o*-quinodimethane systems.[13]

(10) (a) K. S. Ng, J. L. Roberts, P. S. Rutledge, M. A. Wilson, and P. D. Woodgate, *Aust. J. Chem.*, **29**, 2683 (1976); (b) R. H. Martin, N. De Fay, and F. Geerts-Evrard, *Tetrahedron*, **20**, 1505 (1964).
(11) I. Murata and Y. Sugihara, *Chem. Lett.*, 625 (1972).
(12) L. Cassar, P. F. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92**, 6366 (1970).
(13) (a) D. J. Field and D. W. Jones *J. Chem. Soc., Perkin Trans. 1*, 1909 (1980); (b) W. R. Dolbier, Jr. K. E. Anapolle, L. McCullagh, K. Matsui, J. M. Riemann, and D. Rolison, *J. Org. Chem.*, **44**, 2845 (1979).

The biradicaloid character of **17** (illustrated through the resonance structure **18**) creates also the possibility of rearrangements of the radical centers. A 1,2-shift of the 6a–11a bond in **18** leads to the biradical **19**, with a radical center on 6a-C stabilized by some captodative action[14] of the substituents on the adjacent aromatic ring (an electron-accepting carbonyl group ortho and an electron-donating methoxyl group para). Rearrangement of **19** to **20**, followed by a 1,5-homobenzoyl shift can lead to the benzo[*c*]fluorenone **13**. However, the formation of **20** can also be envisaged as a one-step $_{\pi}2_a + _{\sigma}2_a$ process starting from **17**.

The formation of **14** can be described as an extension of the oxadi-π-methane rearrangement, for which several photochemical examples have been described.[15] For the normal photochemical oxadi-π-methane rearrangement, a concerted $_{\sigma}2_a + _{\pi}2_a$ and a stepwise reaction, with bonding between the carbonyl carbon and the migration terminus in the initial step, are possible.[16] Regarding the stabilization of the benzylic radical in the intermediate **21**, a stepwise mechanism seems more attractive in our case than a concerted $_{\pi}4_a + _{\sigma}2_a$ process.

The observation that no C-nor-D-homo steroid **12c** is formed in the thermolysis of adduct **9c** can be rationalized by steric hindrance between R_2 = Ph and R_3 = OMe during the rotation of the 6a-C–aryl bond, which must occur during the 1,5-benzoyl shift of **17c** to **12c**. The hypothesis of steric hindrance as the main reason for the absence of **12c** in the thermolysis of **9c** is confirmed by the results of the thermolysis of adduct **9d**. This yields only 22% C-nor-D-homo steroid **12d**, 52% benzo[*c*]fluorenone **13d**, and 18% **14d**; changing the position of the methoxyl function in the adduct **9a** alters the ratio **12**/**13** from 1.4 to 0.4.

Further investigations on the scope of this thermolysis in the synthesis of carbocyclic and heterocyclic compounds are in progress.

Experimental Section

All melting points are uncorrected. Infrared spectra were taken on the Perkin-Elmer Model 297 spectrometer as potassium bromide disks. Proton nuclear magnetic resonance spectra were obtained on a Varian EM 390 or a Varian XL 100 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). 2,3-Dimethyl-6-methoxyindenone (**5a**), 2,3-diethyl-6-methoxyindenone (**5b**), 2-ethyl-3-phenyl-4,6-dimethoxyindenone (**5c**), and 2,3-dimethyl-4-methoxyindenone (**5d**) were synthesized according to earlier described methods.[17]

Synthesis of the Isobenzofuran–2,3-Dimethyl-6-methoxyindenone Adduct (3). A solution of 26 mmol of 2,3-dimethyl-6-methoxyindenone (**5a**) and 26 mmol of adduct **4**[4] in 140 mL of diglyme was refluxed for 15 min. After cooling, the solvent was removed in vacuo. The residue was chromatographed on silica gel with benzene–hexane, which afforded a mixture of exo and endo adducts in a ratio 3 to 1. Pure exo adduct **3** was obtained by recrystallization from methanol (17.7 mmol, 68%): mp 158 °C; IR ($CHCl_3$) 1710 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.80 (3, s, CH_3), 0.92 (3, s, CH_3), 3.81 (3, s, OCH_3), 5.00 (1, s, CH), 5.20 (1, s, CH), 7.10–7.58 (7, m, Ar H); mass spectrum, *m/e* (relative intensity) 306 (4.9), 188 (100), 173 (5.6), 118 (59.4).

No pure endo adduct could be isolated: ^1H NMR ($CDCl_3$) δ 1.56 (3, s, CH_3), 1.64 (3, s, CH_3), 3.60 (3, s, OCH_3), 5.08 (2, s, 2 CH) and 6.54–7.58 (7, m, Ar H).

Reaction of Adduct 3 with Triphenylphosphine–Bromine Adduct. To a solution of 0.65 mmol of triphenylphosphine in 5 mL of benzonitrile, cooled in an ice bath, was added slowly 0.67 mmol of bromine dissolved in 5 mL of benzonitrile. After the solution was stirred for 15 min at 0 °C, 0.65 mmol of adduct **3** was added in one portion and stirring was continued for 6 h at 0 °C. Ether was added to the reaction mixture, and the ether phase was separated, washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated in vacuo. The mixture was purified by preparative TLC on silica gel with benzene–ethyl acetate (90:10), which afforded 0.31 mmol of **7** (48%): IR ($CHCl_3$) 1700–1680 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.48 and 1.71 (2 × 3, 2 × s, $2CH_3$), 3.73 (3, s, OCH_3), 4.30 (1, d, J = 10 Hz, OH), 4.96 (1, d, J = 10 Hz, CH), 6.92–7.88 (7, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 18.1 and 20.3 ($2CH_3$), 55.8 (OCH_3), 57.0 and 57.6 (2 quaternary carbon), 71.9 (CHOH), 105.1, 125.5, 125.8, 127.0, 128.4, 130.5, 134.7, 136.5, 145.1 and 149.4 (Ar C), 160.9 ($COCH_3$), 198.7 (C=O in 6-membered ring), 212.1 (C=O in 5-membered ring); mass spectrum, *m/e* (relative intensity) 322 (6.0), 189 (100), 133 (5.1), 105 (15.8).

Procedures for the Synthesis of Benzopyranone–Indenone Adducts. *o*-Acetylphenylacetic acid[8] (20 mmol), indenone **5a** or **5d** (15 mmol), and acetic anhydride (50 mL, freshly distilled 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 14.3 mmol of benzopyranone–indenone adduct **9a** or **9d** (95%). The adduct was recrystallized from methanol. In the case of the synthesis of **9a** further purification of the mother liquor by HPLC yielded apart from adduct **9a** also adducts **10a** (0.15 mmol, 1%) and **11a** (0.1 mmol, 0.6%). For the indenones **5b** and **5c** the same procedure was used with the following modification: the whole procedure was repeated three times for **5b** and five times for **5c** with freshly added acetic anhydride and *o*-acetylphenylacetic acid. This yielded 7.3 mmol of adduct **9b** (91%) and 4.6 mmol of adduct **9c** (57%). All adducts were recrystallized from methanol–toluene (4:1).

Adduct 9a: mp 230 °C; IR 1740 cm^{-1} ($\nu_{C=O}$ ester) 1698, ($\nu_{C=O}$ ketone); ^1H NMR [$CDCl_3/\Delta(= \delta_{CDCl_3} - \delta_{C_6D_6})$] δ 1.44/0.21 (3, s, 11a-CH_3), 1.62/0.28 (3, s, 6a-CH_3), 2.08/0.1 (3, s, 1-CH_3), 3.66/0.78 (3, s, 9-OCH_3), 3.97/0.21 (1, s, 6-H), 6.6–7.3 (7, m, Ar H); mass spectrum, *m/e* (relative intensity) 348 (11.7), 304 (1.8), 289 (4.4), 188 (100.0), 173 (7.3), 160 (62.0), 145 (7.0), 132 (41.6); calcd for M^+ 348.13614, found 348.1367. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.42; H, 5.79.

Adduct 10a: mp 185 °C; IR 1747 cm^{-1} ($\nu_{C=O}$ ester), 1700 ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 0.91/0.25 (3, s, 11a-CH_3), 1.09/0.43 (3, s, 6a-CH_3), 2.06/0.08 (3, s, 1-CH_3), 3.86/0.71 (3, s, 9-OCH_3), 4.01/0.15 (1, s, 6-H), 7.1–7.6 (7, m, Ar H); mass spectrum *m/e* (relative intensity) 348 (10.0), 304 (0.3), 289 (1.3), 188 (100), 173 (6.0), 160 (34.0), 145 (5.6), 132 (20.0); calcd for M^+ 348.13614, found 348.1384.

Adduct 11a: mp 209 °C; IR 1740 cm^{-1} ($\nu_{C=O}$ ester), 1705 ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 1.42/0.18 (3, s, 11a-CH_3), 1.61/0.26 (3, s, 6a-CH_3), 2.08/0.42 (3, s, 6-CH_3), 3.69/0.80 (3, s, 9-OCH_3), 4.00/–0.12 (1, s, 1-H), 6.7–7.35 (7, m, Ar H); mass spectrum *m/e* (relative intensity) 348 (8.5), 289 (1.1), 188 (100), 173 (7.0), 160 (30.2), 145 (5.4), 132 (19.4); calcd for M^+ 348.13614, found 348.1365.

Adduct 9b: mp 165 °C; IR ($CHCl_3$) 1760 cm^{-1} ($\nu_{C=O}$ ester), 1710 ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 1.00/0.08 (3, t, J = 8 Hz, 11a-CH_2CH_3), 1.31/0.14 (3, t, J = 8 Hz, 6a-CH_2CH_3), 2.00–2.42 (4, m, 2 CH_2CH_3), 2.10/0.04 (3, s, 1-CH_3), 3.66/0.73 (3, s, 9-OCH_3), 4.16/0.02 (1, s, 6-H), 6.53–7.57 (7, m, Ar H); mass spectrum, *m/e* (relative intensity) 376 (9.5), 332 (1.5), 303 (6.5), 216 (90.2), 160 (100), and 132 (90.0); calcd for M^+ 376.16744, found 376.1675.

Adduct 9c: mp 233 °C; IR 1752 cm^{-1} ($\nu_{C=O}$ ester), 1700 ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 0.36/–0.18 (3, t, J = 8 Hz, 11a-CH_2CH_3), 1.96 (2, m, 11a-CH_2CH_3), 2.1/0.04 (3, s, 1-CH_3), 3.62/0.75 (3, s, 7-OCH_3), 3.70/0.67 (3, s, 9-OCH_3), 5.08/–0.14 (1, s, 6-H), 6.38/0.18 (1, d, J = 2 Hz, 8-H), 6.47/0.04 (1, d, J = 2 Hz,

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10-H), 6.47 (1, d, J = 8 Hz, 2-H), 6.8–7.5 (7, m, Ar H), 8.14/–0.47 (1, d, J = 8 Hz, 5-H); mass spectrum, m/e (relative intensity) 454 (5.0), 294 (100), 279 (30.0), 132 (10.0); calcd for M^+ 454.1780, found 454.1775.

Adduct 9d: mp 209 °C; IR 1734 cm^{-1} ($\nu_{C=O}$ ester), 1701 ($\nu_{C=O}$ ketone); ^1H NMR ($CDCl_3/\Delta$) δ 1.45/0.16 (3, s, 11a-CH_3), 1.70/0.10 (3, s, 6a-CH_3), 2.05/0.07 (3, s, 1-CH_3), 3.98/0.76 (3, s, 7-OCH_3), 4.53/–0.06 (1, s, 6-H), 6.7–7.4 (7, m, Ar H); mass spectrum, m/e (relative intensity) 348 (14.7), 304 (2.9), 289 (6.6), 188 (33.1), 173 (9.6), 160 (100), 145 (4.6), 132 (73.2); calcd for M^+ 348.13614, found 348.1365.

Thermolysis of Adduct 9a. A solution of 1.03 mmol of adduct **9a** and 1 mmol of hydroquinone, dissolved in 30 mL of diphenyl ether, was degassed by subsequent freeze–thaw cycles and thermolyzed in the dark at 250 °C during 2 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. The reaction mixture was chromatographed on silica gel with toluene–tetrachloromethane (1:1) and gave first a fraction characterized as benzo[*b*]cyclopropa[*lm*]fluorenone **14a** (31.5 mg, 10%), followed by the benzo[*c*]fluorenone **13a** (103.3 mg, 33%); further elution gave the C-nor-D-homo steroid **12a** (147.2 mg, 47%). The compounds **12a** and **13a** were recrystallized from heptane.

Steroid 12a: mp 146 °C; IR ($CHCl_3$) 1720 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.47 (3, s, 8-CH_3), 1.77 (3, q, J = 0.86 Hz, 7-CH_3), 1.92 (3, q, J = 0.86 Hz, 6-CH_3), 3.56 (1, s, 9-H), 3.76 (3, s, 17-OCH_3), 7.16–7.38 (6, m, Ar H), 7.66 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 1-H); mass spectrum, m/e (relative intensity) 304 (97.0), 289 (100), 274 (15.5), 261 (11.6), 259 (7.0), 246 (8.5), 131 (6.2); calcd for M^+ 304.14632, found 304.1442. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.47; H, 6.58.

Benzo[*c*]fluorenone 13a: mp 141 °C; IR ($CHCl_3$) 1716 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.68/0.19 (3, s, 11b-CH_3), 2.11/0.20 (3, br s, 5-CH_3), 2.23/–0.02 (3, br s, 6-CH_3), 3.17/0.19 (1, m, 6a-H), 3.80/0.62 (3, s, 9-OCH_3), 7.02–7.48 (6, m, Ar H), 7.78/0.41 (1, d, J_o = 8 Hz, 11-H); mass spectrum, m/e (relative intensity) 304 (76.1), 289 (100), 274 (11.7), 261 (11.8), 259 (9.3), 246 (9.0); calcd for M^+ 304.14632, found 304.1447. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.88; H, 6.70.

Benzo[*b*]cyclopropa[*lm*]fluorenone 14a: oil; IR ($CHCl_3$) 1680 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.43/0.30 (3, s, 9b-CH_3), 1.54/0.21 (3, s, 9c-CH_3), 1.66/0.02 (3, s, 4b-CH_3), 2.67/0.33 (1, s, 9d-H), 3.68/0.59 (3, s, 7-OCH_3), 6.8–7.4 (7, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 13.1 (9c-CH_3), 18.9 (4b-CH_3), 21.5 (9b-CH_3), 51.8 (9d-CH), 55.4 (7-OCH_3), 31.2; 47, 60.8 (quaternary C), 108.4, 120.9, 123.4, 124.1, 126.4, 127.8, 129.8, 134.5, 135.9, 143.2, 148, 158.1 (Ar C), 202.1 (C=O); mass spectrum, m/e (relative intensity) 304 (92.8), 289 (100), 274 (21.5), 261 (28.3), 246 (14.7); calcd for M^+ 304.14632, found 304.1459.

Thermolysis of Adduct 9b. A solution of 0.4 mmol of **9b** and 0.5 mmol of hydroquinone, dissolved in 30 mL of diphenyl ether was thermolyzed in the usual way at 250 °C during 3 h. Workup as usual and chromatography on silica gel yielded the indenone **5b** (13 mg, 15%), followed by the benzo[*c*]fluorenone **13b** (65 mg, 49%); further elution gave the C-nor-D-homo steroid **12b** (31 mg, 23%). The products **12b** and **13b** were recrystallized from *n*-heptane.

Steroid 12b: mp 154 °C; IR ($CHCl_3$) 1715 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.40 (3, t, J = 8 Hz, 7-(CH_2CH_3), 0.75 (3, t, J = 8 Hz, 8-CH_2CH_3), 2.00 (2, m, 8-CH_2CH_3), 2.00 (3, s, 6-CH_3), 2.30 (2, m, 7-CH_2CH_3), 3.65 (1, s, 9-H), 3.86 (3, s, 17-OCH_3), 7.12–7.48 (6, m, Ar H), 7.62 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 1-H); ^{13}C NMR ($CDCl_3$) δ 8.8 (8-CH_2CH_3), 13.6 (7-CH_2CH_3), 14.8 (6-CH_3), 22.6 (7-CH_2CH_3), 29.3 (8-CH_2CH_3), 51.5 (8-C), 55.7 (17-OCH_3), 59.7 (9-C), 105.8, 122.6, 123.3, 126.2, 126.7, 127.3, 130.9, 134.9, 138.5, 140.0, 150.9 (Ar C), 159.5 ($COCH_3$), 204.0 (C=O in five-membered ring); mass spectrum, m/e (relative intensity) 332 (34.6), 317 (1.2), 303 (100), 275 (42.3), 274 (38.5), 259 (15.1); calcd for M^+ 332.17762, found 332.1776.

Benzo[*c*]fluorenone 13b: mp 145 °C; IR ($CHCl_3$) 1710 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 0.84 (3, t, J = 8 Hz, 11b-CH_2CH_3), 1.20 (3, t, J = 8 Hz, 6-CH_2CH_3), 2.10 (2, m, 11b-CH_2CH_3), 2.12 (3, s, 5-CH_3), 2.70 (2, m, 6-CH_2CH_3), 3.41 (1, br s, 6a-H), 3.81 (3, s, 9-OCH_3), 6.96–7.42 (6, m, Ar H), 7.76 (1, d, J_o = 8 Hz, 11-H); ^{13}C NMR ($CDCl_3$) δ 9.0 (11b-CH_2CH_3), 12.4 (6-CH_2CH_3), 14.3 (5-CH_3), 26.6 (6-CH_2CH_3), 34.1 (11b-CH_2CH_3), 49.2 (11b-C), 55.7 (9-OCH_3), 58.1 (6a-C), 105.6, 123.0, 123.9, 125.8, 126.6, 126.7, 127.3, 133.8, 135.1, 138.8, 139.0, 151.9, 151.9 (Ar C), 205.2 (C=O in five-membered ring); mass spectrum, m/e (relative intensity) 332 (42.6), 317 (1.8), 303 (100), 288 (4.0), 275 (18.2), 274 (20.5), 259 (6.5); calcd for M^+ 332.17762, found 332.1771.

Thermolysis of Adduct 9c. A solution of 0.26 mmol of **9c** and 0.34 mmol of hydroquinone, dissolved in 30 mL of diphenyl ether, was thermolyzed as usual at 250 °C during 7 h. Workup as usual and chromatography on silica gel yielded the indenone **5c** (11 mg, 14%), followed by the benzo[*c*]fluorenone **13c** (65 mg, 61%); only minor amounts of other products were observed. The benzo[*c*]fluorenone **13c** was recrystallized from toluene–*n*-heptane (1:1).

Benzo[*c*]fluorenone 13c: mp 209 °C; IR 1720 cm^{-1} ($\nu_{C=O}$), ^1H NMR ($CDCl_3$) δ 0.63 (3, t, J = 8 Hz, 6-CH_2CH_3), 2.12 (3, s, 5-CH_3), 2.18, 2.58 (2, 2 m, 6-CH_2CH_3), 3.4 (1, br s, 6a-H), 3.67 (3, s, 11-OCH_3), 3.84 (3, s, 9-OCH_3), 6.7–7.27 (9, m, Ar H), 7.34 (1, dd, J_o = 7 Hz, J_m = 2 Hz,4-H), 7.47 (1, dd, J_o = 7 Hz, J_m = 2 Hz, 1-H); ^{13}C NMR ($CDCl_3$) δ 11.5 (6-$CHCH_3$), 14.4 (5-CH_3), 26.7 (6-CH_2CH_3), 54.0 (11b-C), 55.7, 55.9 (9-OCH_3 and 11-OCH_3), 67.2 (6a-C), 97.7, 107.1 (5-C and 6-C), 124.1, 126, 126.7 × 2, 127.1, 127.4, 128 × 2, 129.6, 132.5, 136.2, 138.4, 140.8, 141, 145.6, 158.4, 161.2 (Ar C), 204.6 (C=O in five-membered ring); mass spectrum, m/e, (relative intensity) 410 (100), 395 (9), 381 (93), 366 (10), 353 (6); calcd for M^+ 410.1881, found 410.1871. Anal. Calcd for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38. Found: C, 81.59; H, 6.47.

Thermolysis of Adduct 9d. A solution of 1.1 mmol of **9d** and 1 mmol of hydroquinone, dissolved in 30 mL of diphenyl ether, was thermolyzed as usual at 250 °C during 6 h. Workup as usual and chromatography on silica gel yielded the cyclopropane **14d** (60.2 mg, 18%), followed by the benzo[*c*]fluorenone **13d** (174 mg, 52%); further elution gave the C-nor-D-homo steroid **12d** (73.6 mg, 22%). All products were recrystallized from methanol.

Steroid 12d: mp 172 °C; IR 1711 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.63 (3, s, 8-CH_3), 1.83 (3, br s, 7-CH_3), 1.94 (3, br s, 6-CH_3), 3.52 (1, s, 9-H), 3.93 (3, s, 15-OCH_3), 6.87–7.5 (7, m, Ar H); mass spectrum, m/e (relative intensity) 304 (90.5), 289 (100), 274 (23.4), 261 (18.9), 246 (11.7); calcd for M^+ 304.14632, found 304.1453.

Benzo[*c*]fluorenone 13d: mp 156 °C; IR 1705 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.83/–0.01 (3, s, 11b-CH_3), 2.12/0.19 (3, br s, 5-CH_3), 2.22/0.02 (3, b s, 6-CH_3), 3.10/0.20 (1, br s, 6a-H), 4.03/0.66 (3, s, 11-OCH_3), 6.93–7.4 (6, m, Ar H), 7.58/–0.21 (1, dd, J_o = 6 Hz, J_m = 3 Hz, 1-H); mass spectrum, m/e (relative intensity) 304 (86.0), 289 (100), 274 (13.3), 261 (15.0), 246 (11.4). Calcd for M^+ 304.14632, found 304.1453.

Benzo[*b*]cyclopropa[*lm*]fluorenone 14d: mp 181 °C; IR 1680 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.43/0.25 (3, s, 9c-CH_3), 1.51/–0.08 (3, s, 9b-CH_3), 1.65/0 (3, s, 4b-CH_3), 2.71/0.21 (1, s, 9d-H), 3.75/0.55 (3, s, 9-OCH_3), 6.62–7.2 (7, m, Ar H); ^{13}C NMR ($CDCl_3$) δ 13.0 (9c-CH_3), 18.6, 18.9 (4b-CH_3 and 9b-CH_3), 51.7 (9d-CH), 56.0 (9-OCH_3), 30.0, 44.1, 60.8 (quaternary C), 116.5, 118.0, 123.1, 124.0, 126.2, 127.4, 127.8 (Ar CH), 130.3, 137.2, 143.7, 148.1, 158.6 (Ar C) 203.5 (C=O); mass spectrum, m/e (relative intensity) 304 (81.8), 289 (100), 274 (16.8), 261 (26.2), 246 (11.2); calcd for M^+ 304.14632, found 304.1451.

Hydrogenation of Benzo[*c*]fluorenone 13a. A solution of 0.76 mmol of **13a**, dissolved in 60 mL of methanol, was hydrogenated in a Parr apparatus with 230 mg 10% Pd on C during 40 h. Preparative TLC on silica gel with dichloromethane–hexane (3:1) yielded 0.59 mmol of the hydrogenated product (77.6%): IR ($CHCl_3$) 1700 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.03 (3, d, $J_{5\text{-}H}$ = 7 Hz, 5-CH_3), 1.28 (3, d, $J_{6\text{-}H}$ = 7 Hz, 6-CH_3), 1.78 (3, s, 11b-CH_3), 2.42–2.70 (1, m, 6-H), 2.79 (1, d, $J_{6\text{-}H}$ = 7 Hz, 6a-H), 2.87–3.09 (1, m, 5-H), 3.80 (3, s, 9-OCH_3), 7.02–7.80 (7, m, Ar H); mass spectrum, m/e (relative intensity) 306 (33), 291 (100), 278 (6.2), 277 (7.4).

Thermolysis of the C-nor-D-homo Steroid 12a. A solution of 0.36 mmol of **12a**, dissolved in 20 mL of diphenyl ether, was thermolyzed at 250 °C in the dark during 18 h. Preparative TLC on silica gel with benzene–hexane (4:1), after removal of the diphenyl ether as usual, yielded, besides **12a**, a red product; recrystallization from heptane afforded 0.15 mmol of the benzo[*a*]fluorenone **15** (43%): mp 172 °C; IR 1685 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 2.34/0.19, 2.40/0.23 (2 × 3, 2 s, 5-CH_3 and

6-CH_3), 3.79/0.58 (3, s, 9-OCH_3), 6.64/0.06 (1, dd, J_o = 8 Hz, J_m = 2 Hz, 8-H), 6.90–7.48 (4, m, Ar H), 7.68/0.10 (1, d, J_o = 8 Hz, 4-H), 8.79/–0.64 (1, d, J_o = 9 Hz, 1-H); mass spectrum, *m/e* (relative intensity) 288 (100), 273 (18), 245 (5); calcd for M^+ 288.11502, found 288.1144. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.44; H, 5.60.

Thermolysis of Benzo[*c*]fluorenone 13a. A solution of 0.17 mmol of **13a**, dissolved in 20 mL of diphenyl ether, was thermolyzed at 250 °C in the dark during 18 h. Preparative TLC on silica gel with benzene–hexane (4:1), after removal of the diphenyl ether as usual, yielded besides **13a**, a red product; recrystallization from heptane afforded 0.13 mmol of the benzo[c]fluorenone **16** (77%): mp 193 °C; IR 1690 cm^{-1} ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 2.53/0.35 (3, s, 5-CH_3), 2.72/–0.03 (3, s, 6-CH_3), 3.86/0.66 (3, s, 9-OCH_3), 6.87/0.15 (1, dd, J_o = 8 Hz, J_m = 3 Hz, 10-H), 7.10–7.56 (3, m, Ar H), 7.73/0.25 (1, d, J_o = 8 Hz, 11-H), 7.9/0.18 (1, m, 4-H), 8.26/0.04 (1, m, 1-H); mass spectrum, *m/e* (relative intensity) 288 (100), 273 (40), 245 (17); calcd for M^+ 288.11502, found 288.1151. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 82.92; H, 5.69.

Trapping the *o*-Quinodimethane with Tetracyanoethylene. A solution of 1.00 mmol of **9a**, 0.5 mmol of hydroquinone, and 5.96 mmol of tetracyanoethylene dissolved in 15 mL of diphenyl ether was degassed and thermolyzed in the dark at 250 °C during 5 h. Preparative TLC on silica gel with benzene, after removal of the diphenyl ether as usual, yielded 0.74 mmol (74%) of the *o*-quinodimethane–tetracyanoethylene adduct and 0.07 mmol (7%) of the indenone **5a**; no other products were isolated. Identification of the *o*-quinodimethane–tetracyanoethylene adduct: mp 253–256 °C dec; IR 2240 cm^{-1} ($\nu_{C\equiv N}$), 1705 ($\nu_{C=O}$); ^1H NMR ($CDCl_3/\Delta$) δ 1.60/0.30 (3, s, 11a-CH_3), 1.96/0.36 (3, s, 6a-CH_3), 2.36/0.22 (3, s, 1-CH_3), 3.66/0.76 (3, s, 9-OCH_3), 4.00/0.50 (1, s, 6-H), 6.63–7.4 (7, m, Ar H); mass spectrum, *m/e* (relative intensity) 432 (28), 304 (100), 289 (51), 276 (11), 188 (33); calcd for M^+ 432.1586, found 432.1586. Anal. Calcd for $C_{27}H_{20}N_4O_2$: C, 74.99; H, 4.66; N, 12.95. Found: C, 75.36; H, 5.01; N, 12.60.

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Registry No. *exo*-**3**, 85749-62-8; *endo*-**3**, 85798-63-6; **4**, 85798-64-7; **5a**, 55288-46-5; **5b**, 85749-63-9; **5c**, 85762-04-5; **5d**, 55288-49-8; **7**, 85749-64-0; **9a**, 85749-65-1; **9b**, 85749-66-2; **9c**, 85749-67-3; **9d**, 85749-68-4; **10a**, 85798-65-8; **11a**, 85749-70-8; **12a**, 85749-70-8; **12b**, 85749-71-9; **12d**, 85749-72-0; **13a**, 85749-73-1; **13a** dihydro derivative, 85749-74-2; **13b**, 85749-75-3; **13c**, 85749-76-4; **13d**, 85749-77-5; **14a**, 85749-78-6; **14d**, 85749-79-7; **15**, 85749-80-0; **16**, 85749-81-1; *o*-acetylphenylacetic acid, 36073-90-2; tetracyanoethylene, 670-54-2; *o*-quinodimethane–tetracyanoethylene adduct, 85749-82-2; cuneane, 20656-23-9.

Resolution and Absolute Configuration of Bicyclo[3.3.0]octa-2,6-diene-2-carboxylic Acid

James K. Whitesell,* Mark A. Minton, and Steven W. Felman

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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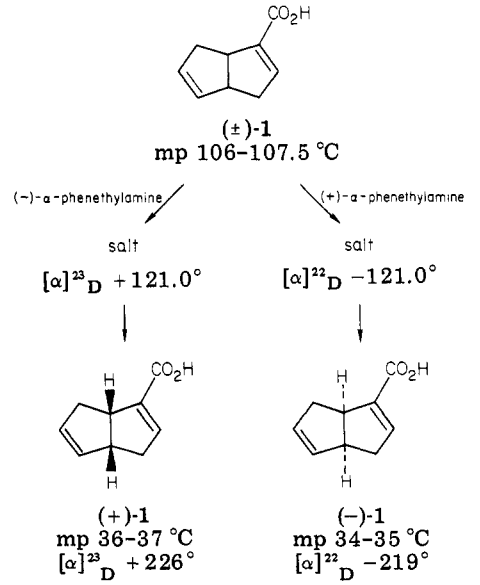
An efficient resolution of the title acid (1) by using (+)- and (–)-α-phenethylamine is described. The (+) acid was determined to be 1*S* by chemical correlation through (+)-*cis*-bicyclo[3.3.0]octan-2-one (3) with (+)-*cis*-bicyclo[3.3.0]oct-7-en-*endo*-2-ol (4) where the absolute configuration is known to be 1*R*. The 1*R* configuration for (–)-3 was consistent with the negative Cotton effect observed for this ketone.

We have been involved for some time in exploiting the bicyclo[3.3.0]octane framework for the synthesis of terpenoid and other natural products.[1] Recently[2] we detailed convenient syntheses for two, isomeric diene acids with this framework which have been particularly useful to us in our synthetic studies. For one of these, bicyclo[3.3.0]octa-2,6-diene-2-carboxylic acid (1), we have been able to effect an exceptionally efficient resolution and to correlate one of the enantiomers with known chirality in order to establish the absolute configuration in this series (see Scheme I).

Resolution of the acid was effected through the salts formed with the enantiomers of α-phenethylamine. Progress of the separation of the diastereomeric salts thus formed could not be followed by melting point determinations since the salts melted with decomposition. However, optical rotation was found to be quite sensitive to the degree of separation as the diastereomeric salts had nearly equal magnitude but opposite rotations (+121° for the (+) acid and (–) amine and –131° for the (–) acid and (–) amine). The degree of resolution could also be followed, though less conveniently, by conversion of the salt to the acid and then to the methyl ester by using diazomethane. The methyl group absorptions of the enantiomers in the

Scheme I



(1) See for example: Whitesell, J. K.; Matthews, R. S.; Minton, M. A.; Helbling, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3468–3472.
(2) Whitesell, J. K.; Minton, M. A.; Flanagan, W. G. *Tetrahedron* **1981**, *37*, 4451–4455.

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