290 (3.25); ^{1}H NMR ($CDCl_3$) δ 1.54 (3 H, s, CH_3), 1.40–1.60 (6 H, m, methylenes), 2.26 (δ_A) and 3.34 (δ_B) (2 H, ABq, J = 18 Hz, $COCH_2$), 2.72 (1 H, s, OH, exchangeable with D_2O), 2.50 (δ_A) and 2.78 (δ_B) (2 H, ABq, J = 13 Hz, $ArCOCH_2$), 7.60 (3 H, m, Ar H), 8.19 (1 H, d, J = 7 Hz, Ar C_8 H); MS, m/e (relative intensity) 270 (M^+, 24), 211 (72), 210 (100), 195 (24), 193 (13), 183 (12), 173 (21). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.59; H, 6.86.

Rearrangement of 15a: Preparation of (3a*SR*,11b*SR*)-3a-Methyl-1,2,3,3a-tetrahydropentaleno[6a,1-*a*]-naphthalene-4,7(6*H*)-dione (16a). A mixture of 100 mg (0.37 mmol) of the hydroxy diketone **15a** and 20 mg of *p*-TsOH·H_2O in 40 mL of dry benzene was refluxed for 4 h under N_2, as described for **7b** to afford a greenish yellow solid which was purified by chromatography on silica gel (5 g) by elution with CH_2Cl_2 to furnish 85 mg (91%) of the rearranged product **16a**: mp 154 °C; IR ($CHCl_3$) 2960, 2870, 1710–1695 (br), 1635, 1600, 1450, 1375, 1305, 1120, 1025, 1000, 910, 860 cm^{-1}; UV (C_6H_{12}) λ_{max} 240 nm (log ϵ 3.75); UV (C_2H_5OH) λ_{max} 228 nm (log ϵ 4.13), 247 (4.15), 417 (4.07); ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.97 (3 H, s, CH_3), 1.28–2.50 (6 H, complex m, methylenes), 3.78 (δ_A) and 3.91 (δ_B) (2 H, ABX, J_{AB} = 16.17 Hz, J_{AX} = J_{BX} = 1.83 Hz, $COCH{=}CCH_2$), 7.35–7.67 (3 H, m, Ar H), 8.02 (1 H, dd, $J_{8,9}$ = 8.90 Hz, Ar C_6 H); MS, m/e (relative intensity) 252 (M^+, 51), 237 (30), 224 (68), 210 (82), 181 (70), 165 (41), 149 (100). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.93; H, 6.14.

Hydrogenation of the Enedione 16a to 13a. A solution of the enedione **16a** (50 mg, 0.2 mmol) in 10 mL of EtOH containing a catalytic amount of 70% aqueous $HClO_4$ was hydrogenated at room temperature and atmospheric pressure in the presence of Pd/C (10%, 100 mg) for 15 h. The solution was neutralized with solid $NaHCO_3$ and filtered. Removal of the solvent and chromatographic purification of the resultant material over alumina (2 g) with petroleum ether (bp 60–80 °C) as the eluent afforded **13a** as a white solid (40 mg, 80%; mp 92 °C) which was found to be identical with the aforementioned sample (IR and VPC).

(3a*RS*,5a*RS*,11b*SR*)-3a-Methyl-1,2,3,3a,4,5,5a,6(7*H*)-octahydropentaleno[6a,1-*a*]naphthalene (18a). Method A. To a mixture of 235 mg (1.76 mmol) of $AlCl_3$ and 35 mg (0.88 mmol) of $LiAlH_4$ in 10 mL of dry ether at 0–10 °C was added dropwise 120 mg (0.5 mmol) of the cyclopentenone **8a** in 15 mL of dry ether. The reaction mixture was left overnight, decomposed with saturated Na_2SO_4 solution, acidified with 6 N HCl, and extracted with ether. The ether extract was washed with water and dried (Na_2SO_4). The solvent was removed to furnish a colorless liquid, the IR spectrum of which indicated the absence of a C=O group. The ^{1}H NMR (CCl_4) spectrum exhibited two methyl singlets at δ 0.82 and 0.70 in a ratio of ca. 4:1, indicating the presence of **17a** and **18a**. The olefinic proton signal of **17a** appeared as a multiplet at δ 5.17 along with very weak signals of an olefinic proton multiplet at δ 5.3–5.65 possibly due to the double bond isomeric olefin of **17a**. The crude compound was hydrogenated in 7 mL of ethanol in presence of 100 mg of 10% Pd/C to afford **18a** as a colorless liquid: 95 mg (84%); bp 110–115 °C (0.1 mmHg); IR (neat) 2960, 2925, 1445, 725 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.70 (3 H, s, CH_3), 1.50–2.00 (13 H, complex m, methylenes and methine), 1.87–2.17 (2 H, m, Ar CH_2), 6.84–7.10 (4 H, m, Ar H). Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.23; H, 10.04.

Method B. A mixture 120 mg (0.5 mmol) of ketone **13a** and 2 mL of hydrazine hydrate (98%) in 5 mL of diethylene glycol was heated for 2.5 h at 120–130 °C (graphite bath) under nitrogen. It was cooled, 500 mg (9.0 mmol) of KOH was added, and the temperature was gradually raised to 220 °C. The reaction mixture was kept at that temperature for 3 h with continuous distillation of excess hydrazine hydrate and water under a steady stream of dry nitrogen. After cooling, the reaction mixture was poured into ice–water, extracted with ether, washed with water, and dried (Na_2SO_4). The solvent was removed to afford 80 mg (71%) of **18a** as a colorless liquid identical with the sample described above (VPC).

Registry No. (±)-**1a**, 60059-27-0; (±)-**1b**, 60059-28-1; (±)-**1c**, 67661-85-2; (±)-**3a**, 60103-66-4; (±)-**3b**, 60103-67-5; (±)-**3c**, 67661-86-3; (±)-**7a**, 78284-40-9; (±)-**7b**, 83633-86-7; (±)-**7c**, 83633-87-8; (±)-**8a**, 83679-74-7; (±)-**8b**, 83633-88-9; (±)-**8c**, 83633-89-0; (±)-**12a**, 83633-90-3; (±)-**12b**, 83633-91-4; (±)-**12c**, 83633-92-5; (±)-**13a**, 83633-93-6; (±)-**13b**, 83679-75-8; (±)-**13c**, 83633-94-7; (±)-**14a**, 83679-76-9; (±)-**14b**, 83679-77-0; (±)-**14c**, 83679-78-1; (±)-**15a**, 83633-95-8; (±)-**16a**, 83633-96-9; (±)-**17a**, 83633-97-0; (±)-**18a**, 83633-98-1; HBF_4, 16872-11-0; $HClO_4$, 7601-90-3; BF_3·OEt_2, 109-63-7; H_2SO_4, 7664-93-9.

Acid-Catalyzed Intramolecular C-Alkylation in β,γ-Unsaturated Diazomethyl Ketones. 3.[1] A Simple Synthetic Route to Hexahydro-4,9a-ethano-1*H*-fluoren-11-ones, Hexahydro-6*H*-pentaleno[6a,1-*a*]indan-4-ones, and Hexahydrocyclobuta[*j*]fluoren-2(1*H*)-ones

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C-Alkylation rearrangements of the tetrahydrofluorene diazoacetyl derivatives **1a–e** with tetrahydrofluoboric acid in nitromethane and toluene-*p*-sulfonic acid in boiling benzene are shown to give, in good to excellent yields, the hydroxycyclopentanones **3a–e** and the tetrahydro-6*H*-pentaleno[6a,1-*a*]indan-4-ones **4a–e**, respectively. These undergo stereospecific catalytic hydrogenation to the respective bridged cyclopentanones **14a–e** and the hexahydroindan-4-ones **15a–e**. The cyclization of the diazo ketones **1c–e** with trifluoroacetic acid in chloroform gives the respective angularly fused unsaturated cyclobutanones **2c–e**, which undergo highly stereoselective catalytic hydrogenation to the corresponding trans angularly substituted hexahydrofluorene–cyclobutanone compounds **16c–e**.

In the preceding paper[1] we demonstrated that under certain conditions intramolecular acid-catlyzed cyclization of β,γ-unsaturated diazo ketones such as the hexahydrophenanthrene diazoacetyl derivatives leads, in excellent

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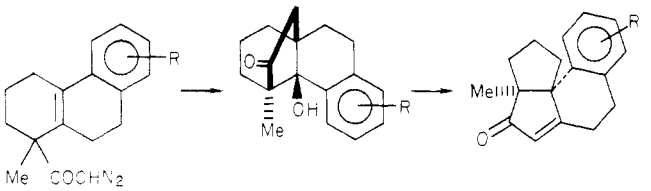
preparative yields, to the corresponding rearranged bridged-ring hydroxycyclopentanones which undergo further acid-induced rearrangement to the fused-ring cyclopentenones (eq 1). In our earlier paper[2] we described



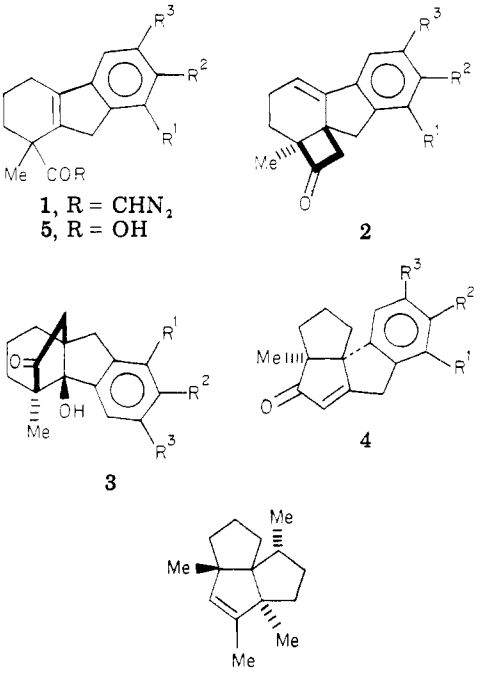
R = H or OMe (1)

that, depending upon the acid-solvent combinations, the decomposition of the tetrahydrofluorene diazoacetyl derivative **1a** (Chart I) gives the angularly fused styrenoid cyclobutanone **2a** or the hydroxycyclopentanone **3a** in good to excellent yields. The cyclobutanone **2b** was also prepared[2] from the methoxy-substituted diazo ketone **1b**. However, the method used for the formation of the rearranged cyclopentenones from the hexahydrophenanthrene substrates (eq 1) was not applicable[3] to the attempted transformation of **3a** to the cyclopentenone **4a**. In view of the current interest in the synthesis of a growing class of compounds isolated from natural sources and some of their transformation products which possess the tricyclo[6.3.0.0^{4,8}]undecane skeleton,[4] e.g., isocomene,[4a,b] we embarked upon a program to explore the potential of the hexahydrofluorene diazo ketones **1a–e** for synthesis of the new pentaleno-annulated systems **4a–e**. As an extension of our previous work[2] we have also investigated acid-catalyzed reactions of these diazo ketones toward the syntheses of the new cyclobutanones **2c–e** and the bridged hydroxycyclopentanones **3a–e**. We now report the realization of these objectives[3] as well as further transformations of some of these compounds to new cyclobutanone, bridged cyclopentanone, and pentaleno-annulated polycyclic systems.

Preparation of the Diazo Ketones

The starting diazo ketones **1c–e** were prepared in 82–90% yields from the corresponding unsaturated acids **5c–e** via the sequential treatment of the dry sodium salt of the respective acid with oxalyl chloride in benzene and an excess of diazomethane in diethyl ether in the presence of triethylamine by following the standard method[2] used for the preparations of **1a** and **1b**. The syntheses of the acids **5d**[5] and **5e**[6] have been reported earlier from this laboratory while the acid **5c**[7] was prepared through cyclodehydration of the epimeric keto esters **10**, adopting the general sequence (**6** → **7** → **8** → **9** → **10** → **13** → **5c**) of reactions used for the acids **5a**[8a] and **5b**[8b] from Hagemann's ester **6**, Chart II; see the Experimental Section). It should be noted that alkylation of **6** with *p*-methoxybenzyl chloride gave a mixture of C-3 and C-1 alkylated[9] products **7** and **11** in a ratio of ~10:1 from which the latter could be

Chart I[a]



1, R = CHN_2
5, R = OH

2

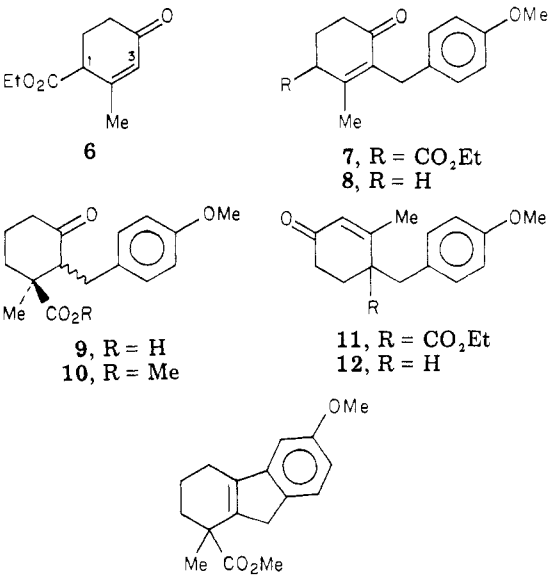
3

4

isocomene

[a] For **1-4**: **a**, $R^1 = R^2 = R^3 = H$; **b**, $R^1 = R^3 = H$, $R^2 = OMe$; **c**, $R^1 = R^2 = H$, $R^3 = OMe$; **d**, $R^1 = OMe$, $R^2 = R^3 = H$; **e**, $R^1 = Me$, $R^2 = R^3 = H$.

Chart II



6

7, R = CO_2Et
8, R = H

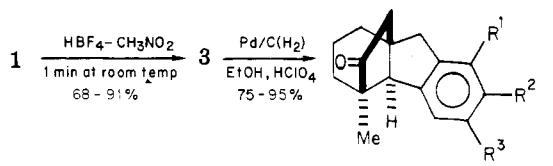
9, R = H
10, R = Me

11, R = CO_2Et
12, R = H

13

(1) Part 2: Satyanarayana, G. O. S. V.; Roy, S. C.; Ghatak, U. R. *J. Org. Chem.*, preceding paper in this issue.
(2) Ghatak, U. R.; Sanyal, B.; Satyanarayana, G. O. S. V.; Ghosh, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1203.
(3) A preliminary communication of a part of this work has been reported: Satyanarayana, G. O. S. V.; Kanjilal, P. R.; Ghatak, U. R. *J. Chem. Soc., Chem. Commun.* **1981**, 746.
(4) (a) Zalkow, L. H.; Harris, R. N., III; Van Derveer, D.; Bertrand, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 456. Zalkow, L. H.; Harris, R. N., III; Burke, N. I. *J. Nat. Prod.* **1979**, *42*, 96. (b) Bohlmann, F.; Le Van, N.; Pickardt, J. *Chem. Ber.* **1977**, *110*, 3777. (c) Bohlmann, F.; Zdero, C. *Phytochemistry* **1979**, *18*, 1747. (d) Bohlmann, F.; Zdero, C.; Bohlmann, R.; King, R. M.; Robinson, H. *Ibid.* **1980**, *19*, 579. (e) Seto, H.; Saski, T.; Uzawa, J.; Setsuo, T.; Yonehara, H. *Tetrahedron Lett.* **1978**, 4411. (f) Kaneda, M.; Takahashi, R.; Iitaka, Y.; Shibata, S. *Ibid.* **1972**, 4609; Kaneda, M.; Iitaka, Y.; Shibata, S. *Acta Crystallogr., Sect. B* **1974**, *B30*, 358. (g) Corbett., R. E.; Lauren, D. R.; Weavers, R. T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1774. (h) Elvidge, J. A.; Lows, D. R. J.; Mc Guinness, J. D.; Davis, A. M.; Shannon, P. V. R. *Ibid.* **1979**, 1250. (i) Kiyoharu, H.; Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Helv. Chim. Acta* **1981**, *64*, 1347.
(5) Ranu, B. C.; Sarkar, M.; Chakraborti, P. C.; Ghatak, U. R. *J. Chem. Soc., Perkin Trans. 1* **1982**, 865.
(6) Ghatak, U. R.; Chakraborti, P. C. *J. Org. Chem.* **1979**, *44*, 4562.
(7) An extremely low-yield synthesis of **5c** has been reported recently from this laboratory[5] by a Diels–Alder cycloaddition route.
(8) (a) Ghatak, U. R.; Dasgupta, R.; Chakravarty, J. *Tetrahedron* **1974**, *30*, 187. (b) Ghosh, S.; Dasgupta, R.; Chakravarty, J.; Ghatak, U. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 804.
(9) (a) Nasipuri, D.; Mitra, K.; Venkataraman, S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1836. (b) White, J. D.; Sung, W. L. *J. Org. Chem.* **1974**, *39*, 2323.

Scheme I[a]



14

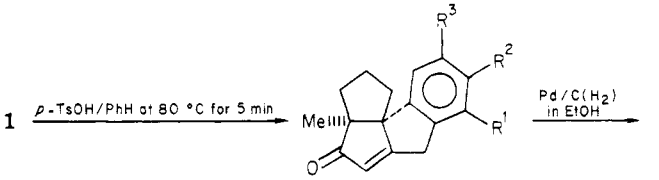
[a] a, $R^1 = R^2 = R^3 = H$; b, $R^1 = R^3 = H$, $R^2 = OMe$; c, $R^1 = R^2 = H$, $R^3 = OMe$; d, $R^1 = OMe$, $R^2 = R^3 = H$; e, $R^1 = Me$, $R^2 = R^3 = H$.

easily eliminated in the subsequent stages. As anticipated, cyclization of **10** to **13** led to problems. Unlike the corresponding demethoxy and the *m*-methoxy analgoues the keto ester **10** on attempted cyclizations with H_2SO_4 in benzene or polyphosphoric acid (PPA)[8] gave complex mixtures. Finally, an acceptable, though not altogether ideal, system of cyclization conditions was realized. Thus, treatment of **10** with PPA in xylene[10] at 120 °C for 3 h afforded the desired cyclized ester **13** in 53% yield which on alkaline hydrolysis followed by chromatography gave the crystalline acid **5c** in 63% yield. Recently, Hook and Mander reported[11] that in the absence of a suitable para-activating group in the aromatic moiety 2-benzylcyclohexane-1,4-diones failed to afford the corresponding tetrahydrofluorenones by cyclodehydration.

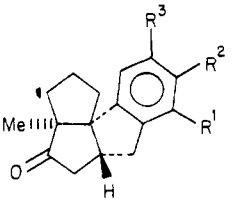
Acid-Catalyzed Reactions of the Diazo Ketones and Some Selected Chemical Transformations of the Resulting Products

Having previously ascertained[2] the optimal condition for the preparation of **3a** from the relatively easily available diazo ketone **1a**, the diazo ketones **1b–e** were submitted to a cyclization–rearrangement reaction with an excess of aqueous HBF_4 (48%) in freshly distilled nitromethane at room temperature for ca. 1 min to afford the respective hydroxycyclopentanones **3b–e** in excellent yields (Scheme I). The IR and ^1H NMR spectra of these compounds (see the Experimental Section) are in complete agreement with the assigned structures. The tentative stereochemical assignments[12] of these compounds are based upon their mode of formation by analogy to the respective hexahydrophenanthrene systems.[1,2] The catalytic hydrogenolysis of the benzylic hydroxy group in **3a,c–e** in the presence of Pd/C (10%) in ethanol containing a catalytic amount of $HClO_4$ (70%) afforded the bridged cyclopentanones **14a,c–e** as the only isolable products, in excellent yields. In contrast, **3b** on reduction under identical conditions gave a mixture of products, possibly arising through acid-catalyzed rearrangement from which **14b** could not be separated. However, hydrogenolysis of **3b** with Pd/C (10%) in ethanol in the absence of acid-catalyst, for 20 h afforded the desired product **14b** in 90% yield after chromatography. Analyses of these compounds by VPC and ^1H NMR indicated their stereochemical homogeneity. The stereochemistry of the newly generated benzylic asymmetric center in **14a–e** has been tentatively assigned from their mode of formation involving inversion of configuration by analogy.[1]

Scheme II[a]



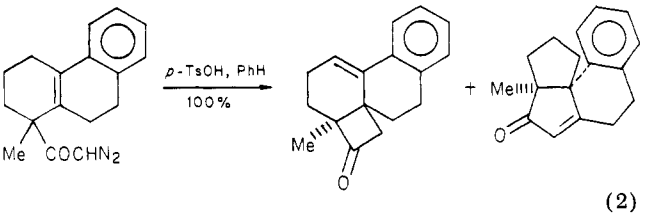
4a, $R^1 = R^2 = R^3 = H$ (75)
b, $R^1 = R^3 = H$; $R^2 = OMe$ (47)
c, $R^1 = R^2 = H$; $R^3 = OMe$ (81)
d, $R^1 = OMe$; $R^2 = R^3 = H$ (60)
e, $R^1 = Me$; $R^2 = R^3 = H$ (70)



15a, $R^1 = R^2 = R^3 = H$ (100)
b, $R^1 = R^3 = H$; $R^2 = OMe$ (100)
c, $R^1 = R^2 = H$; $R^3 = OMe$ (81)
d, $R^1 = OMe$; $R^2 = R^3 = H$ (94)
e, $R^1 = Me$; $R^2 = R^3 = H$ (86)

[a] Numbers in parentheses are percent yields.

As mentioned earlier,[3] in contrast to the respective octahydrophenanthrene analogue, attempted rearrangement of the hydroxycyclopentanone **3a** to the cyclopentenone **4a** with *p*-TsOH in boiling benzene gave a complex mixture of products[13] in which **4a** could not be detected. In an attempt toward the direct transformation of the diazo ketones **1a–e** to the cyclopentenones **4a–e** we searched for new cyclization–rearrangement conditions. The reactions of the diazo ketone **1a** with $BF_3{\cdot}OEt_2$ in benzene and chloroform for 5 min at room temperature afforded mixtures of rearranged cyclopentenone **4a** and the hydroxycyclopentanone **3a** along with other minor uncharacterized products (VPC) in 43:46:2:9 and 32:62:6 ratios, respectively. In our previous paper we have described[1] the direct transformation of the hexahydrophenanthrene diazo ketone by short treatment with *p*-TsOH in boiling benzene to a mixture of the unsaturated cyclobutanone and the rearranged cyclopentenone in a ratio of 55:45 (eq 2).

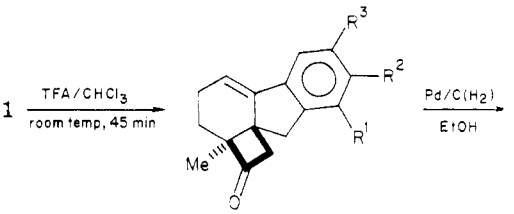


(2)

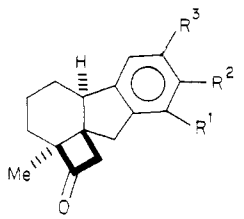
Encouraged by this success, the above cyclization–rearrangement reaction was next studied with the tetrahydrofluorene diazo ketone **1a**. In contrast to the hexahydrophenanthrene analogue, **1a** on short treatment with

(10) Guy, A.; Guette, J. P. *Synthesis* **1980**, 222.
(11) Hook, J. M.; Mander, L. N. *J. Org. Chem.* **1980**, *45*, 1722.
(12) Examination of Dreiding models clearly indicates that although the assigned stereostructure of **3b–e** incorporates a *trans*-bicyclo[3.3.0]-octanone system, it is relatively less strained with respect to that of the alternative C-4a epimeric structure due to the presence of the bridged 1,3-cyclohexane moiety for which a boat conformation is preferred as observed (X-ray) in the corresponding hydrophenanthrene analogues.
(13) One crystalline compound has been isolated in ca. 30% yield the structure of which is under investigation.

Scheme III[a]



2c, $R^1 = R^2 = H$; R^3 = OMe (78)
d, R^1 = OMe; $R^2 = R^3$ = H (78)
e, R^1 = Me; $R^2 = R^3$ = H (94)



16c, $R^1 = R^2 = H$; R^3 = OMe (80)
d, R^1 = OMe; $R^2 = R^3$ = H (95)
e, R^1 = Me; $R^2 = R^3$ = H (91)

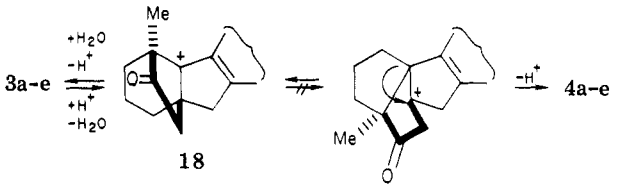
[a] Numbers in parentheses are percent yields.

an excess of *p*-TsOH in boiling benzene gave the cyclopentenone **4a** almost exclusively (95% yield of 96% purity by VPC) which could be easily purified by chromatography (Scheme II). Its IR absorption at 1695 and 1630 cm^{-1} indicated the presence of the cyclopentenone group and an aromatic (also C=C) moiety. The UV spectrum (in EtOH) showed a maximum at 228 nm (log ϵ 4.2) which is in accord with the predicted value of 226 nm according to Woodward's rules.[14] The ^1H NMR spectrum (at 60 MHz) of **4a** exhibited a methyl singlet at δ 1.06 and a broad vinyl proton singlet at δ 5.90. The reactions of diazo ketones **1b–e** under identical conditions with *p*-TsOH in boiling benzene afforded the respective rearranged cyclopentenones **4b–e** in good to excellent yields after purification through chromatography. Catalytic hydrogenation of **4a–e** in the presence of Pd/C (10%) in ethanol gave the corresponding saturated ketones **15a–e** in excellent yields. VPC and ^1H NMR properties of the saturated ketones indicated their stereochemical homogeneities. The assigned stereochemistry at the newly generated asymmetric center in **15a–e** is based on steric considerations and strong diamagnetic shielding of the methyl group, which appeared at δ 0.73–0.75 in the ^1H NMR spectra in these compounds similar to that observed in the respective six-membered ring-B analogues.[1] Lithium–liquid ammonia reduction,[1] for example, of **4e** again gave practically a single diastereomer **15e** in good yield.

We have also prepared the new angularly substituted cyclobutanones **2c–e** from the respective diazo ketones **1c–e** (Scheme III). While in our earlier work[2] we used a mixture of $HClO_4$ (70%) and trifluoroacetic acid (TFA) in chloroform or HBF_4 (48%) in chloroform under the optimum conditions for cyclizations of **1a** and **1b**, respectively, to the corresponding cyclobutanones **2a** (84%) and **2b** (73%), we have now found that TFA in chloroform is also equally effective or even better for cyclobutanone formation from the tetrahydrofluorene diazo ketones **1a,b** or their analogues. Thus, treatment of the diazo ketones **1c–e** with an excess of TFA in chloroform at room temperature gave the corresponding unsaturated cyclobutanones **2c–e** in excellent yields. Catalytic hydrogenation of the styrenoid bond in **2c–e** in the presence of Pd/C (10%) in ethanol proceeded with high stereoselectivity, affording the respective crystalline cyclobutanones **16c–e** in excellent yields. VPC and ^1H NMR properties indicated their stereohomogeneity. The stereochemical assignments to **16c–e** are based on analogy with that observed[2] with **2a,b**.

Discussion

The present work again indicates the sensitivity[15] of the reactions of β,γ-unsaturated diazo ketones toward acid–solvent couples and the reaction conditions. The results of the cyclization reactions of the diazo ketones **1a–e** can be formulated by the same sequence as that postulated for the corresponding hexahydrophenanthrene analogues.[1,2] Under appropriate reaction conditions it is possible to control the course of the reactions of **1a–e** leading to **2a–e**, **3a–e**, or **4a–e**. It is certain that, unlike the respective hexahydrophenanthrene analogues,[1,2] the rearrangement of the initially formed highly strained cyclobutanone carbinyl cation to **17** and **18** (eq 3) must be more facile.



(3)

The failure of the attempted rearrangement of the hydroxycyclopentanone **3a** to the cyclopentenone **4a** under acidic conditions, clearly rules out the reversibility of the intermediate cations **17** and **18**. Although the hydroxy ketone **3a** undergoes acid-catalyzed rearrangement possibly through the cation **18**, so far we have not been able to characterize the products.[13]

Conclusion

Although the acid-catalyzed intramolecular alkylation reactions of β,γ-unsaturated diazo ketones are extremely complex in nature,[15] in the present work we have been able to demonstrate that by proper selection of the reaction conditions it is possible to generate from the relatively easily accessible tetrahydrofluorene diazo ketones the three types of products in excellent preparative yields. The most important advantage the present method offers, of course, is the fact that the synthesis of a variety of complex new strained polycyclopentanoid,[16] angularly fused cyclobutanone, and bridged cyclopentanone systems, the fabrication of which would otherwise require a long sequence of synthetic transformations, can be efficiently accomplished in a single operation. Furthermore, it is quite obvious that with the proper choice of the starting diazo ketone substrates this route may provide a facile synthetic entry to natural products containing the pentalene moiety. The experiments on the scope of this new reaction of the tricyclo[6.3.0.$0^{4,8}$]undecane systems for the projected synthesis of isocomene[17] and the related natural products are

(14) Woodward, R. B. *J. Am. Chem. Soc.* **1941**, *63*, 1123. Woodward, R. B. *Ibid.* **1942**, *64*, 76.

(15) For a discussion see: Smith, A. B., III; Dieter, R. K. *Tetrahedron* **1981**, *37*, 2407.

(16) For some recent synthesis of strained polycyclopentanoids see: (a) Ten Hoeve, W.; Wynberg, H. *J. Org. Chem.* **1980**, *45*, 2930. (b) Dauben, W. G.; Walker, D. M. *Tetrahedron Lett.* **1982**, *23*, 77 and references cited therein.

in progress in this laboratory.[18]

Experimental Section

For general directions see part 2.[1] Unless otherwise stated, VPC analyses were performed on a 20 × $^1/_8$ in. 10% UCW-982 column at a column temperature of 185 °C with N_2 as the carrier gas.

Preparation of the Unsaturated Acid 5c. Alkylation of 6 with *p*-Methoxybenzyl Chloride. Hagemann's ester (**6**; 40 g, 0.23 mol) was alkylated with *p*-methoxybenzyl chloride (31 g, 0.2 mol) in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol, prepared from 7.8 g (0.2 mol) of potassium, by following the procedure described[8a] previously for alkylation with benzyl chloride. The light yellow, viscous, liquid, alkylated product (40 g, 61%) distilled at 190–200 °C (0.2 mmHg) and consisted of **7** and **11** in a ratio of 10:1 as was apparent from the integration of the broad olefinic proton singlet at δ 5.80 for **11** and the unresolved broad three-protons singlets at δ 1.91 and 3.67 for the C-2 Me and ArOMe of **11** and **7**. This mixture was fractionated twice [bp 190–192 °C (0.2 mmHg)] to afford an analytical sample of **7** in which no olefinic proton could be detected by ^{1}H NMR: IR (neat) 2940, 2840, 1730, 1665, 1610, 1580, 1250, 1180, 1035, 840 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.22 (3 H, t, J = 6 Hz, $CO_2CH_2CH_3$), 1.91 (3 H, s, $=CCH_3$), 2.0–2.50 (4 H, m, methylenes), 3.17 (1 H, br t, J = 5 Hz, $EtO_2C-CH-C=C$), 3.55 (2 H, br s, Ar CH_2), 3.67 (3 H, s, Ar OCH_3), 4.10 (2 H, q, J = 6 Hz, $CO_2CH_2CH_3$), 6.83 (4 H, AB q, J = 9 Hz, ArH). Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.64; H, 7.50.

2-(*p*-Methoxybenzyl)-3-methylcyclohex-2-en-1-one (8). The 10:1 mixture of the keto esters **7** and **11** (112 g, 0.37 mol) was refluxed with a solution of KOH (112 g, 2.0 mol) in 112 mL of water and 800 mL of ethanol under nitrogen for 12 h. The cooled reaction mixture was carefully acidified with an excess of 6 N HCl, and most of the ethanol was removed by distillation in vacuo. The residue was diluted with water and extracted with Et_2O. The ethereal extract was washed with aqueous 5% Na_2CO_3 and water and dried (Na_2SO_4). Removal of the solvent and distillation of the residue at 150–155 °C (0.25 mmHg) afforded 75 g (88%) of a mixture of **8** and **12** in a ratio of ~15:1[19] as revealed from the integrations of the olefinic proton singlet at δ 5.75 for **12** with that of the unresolved broad methyl singlet at δ 1.90 for the isomeric ketones. The $ArOCH_3$ singlet for **12** appeared at δ 3.70 at the base of the major singlet at δ 3.66 for **8**. A part of this product was fractionated twice at 148–150 °C (0.2 mmHg) to afford a practically pure sample of **8**: IR (neat) 2940, 2840, 1660, 1625, 1610, 1585, 1510, 1450, 1380, 1300, 1250, 1110, 1040, 835 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.90 (3 H, s, CH_3), 1.96–2.53 (6 H, m, methylene), 3.50 (2 H, br s, Ar CH_2), 3.66 (3 H, s, Ar OCH_3), 6.79 (4 H, AB q, J = 9 Hz, Ar H). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.04; H, 7.94.

2-(*p*-Methoxybenzyl)-3-methyl-3-carbomethoxy-1-oxocyclohexane (10). To a solution of 57.2 g (0.25 mol) of the aforementioned 15:1 mixture of the unsaturated ketones **8** and **12** in 540 mL of ethanol was added a solution of 57.5 g (0.88 mol) of KCN in 300 mL of water. The mixture was gently refluxed for 14 h, whereupon the color gradually turned to greenish brown. When the mixture cooled, a solution of 80 g (1.43 mol) of KOH in 250 mL of water was added and refluxing continued for another 96 h. The reaction mixture was acidified with ice-cold 6 N HCl and extracted with ethyl acetate. The ethyl acetate extract was washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was washed with ether (2 × 50 mL) to yield a yellowish solid acid: 50 g (73%); mp 120–130 °C. A part of this was recrystallized three times from ethyl acetate to afford a pure epimer of **9** as a colorless solid: mp 131–132 °C; IR (KBr) 2930, 2840, 1725, 1700, 1600, 1585, 1440, 1260, 930 cm^{-1}. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.50; H, 7.23. The corresponding methyl ester **10** (diazomethane) was obtained as a colorless oil: ^{1}H NMR (CCl_4) δ 1.07 (3 H, s, CH_3), 1.50–2.57 (7 H, complex m, methylenes and methine), 2.77–3.27 (2 H, m, Ar CH_2), 3.67 (3 H, s, CO_2CH_3), 3.70 (3 H, s, Ar OCH_3), 6.83 (4 H, AB q, J = 8 Hz, Ar H).

The crude acid **9** (40 g, 0.145 mol) was refluxed with methanol (75 mL), concentrated H_2SO_4 (10 mL), and boric acid (2 g) for 12 h. The neutral fraction afforded an epimeric mixture of **10** as a light yellow liquid: 30 g (93% based upon the recovered acid); bp 200–210 °C. The C-1 CH_3 and COOMe singlets for two epimers appeared at δ 1.07 and 1.32 and at δ 3.60 and 3.67, respectively, in a ratio of ~60:40. Acidification of the alkaline washings followed by extraction with ether gave 8 g (20%) of the recovered acid **9**.

6-Methoxy-1-methyl-1,2,3,4-tetrahydrofluorene-1-carboxylic Acid (5c). To a well-stirred homogeneous solution of PPA (prepared from 18 g of phosphorus pentoxide and 6 mL of 89% w/w phosphoric acid) in 15 mL of dry xylene was added 6 g (21 mmol) of the keto ester **10** all at once at 120 °C. The reaction mixture was further stirred for 3 h at that temperature, decomposed with crushed ice, and extracted with Et_2O. The ethereal extract was washed with water and dried (Na_2SO_4). Removal of the solvent afforded a brown gummy mass which was purified by evaporative distillation at 195–200 °C (0.1 mmHg) to furnish 3 g (53%) of pure **13** (homogeneous in VPC): IR ($CHCl_3$) 2910, 2840, 1725, 1660, 1600, 1585 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.41 (3 H, s, CH_3), 1.43–2.57 (6 H, m, methylenes), 3.18–3.37 (2 H, m, Ar CH_2), 3.60 (3 H, s, $COOCH_3$), 3.73 (3 H, s, Ar OCH_3), 6.43–7.10 (3 H, m, ArH).

A mixture of 3 g (11.03 mmol) of the ester **13** in 30 mL of diethylene glycol and 3 g (54 mmol) of KOH in 10 mL of water was heated at 180 °C for 4 h under nitrogen. The usual workup and removal of the solvent afforded a gummy solid which was purified by chromatography on silica gel (40 g) by elution with ether–petroleum ether (bp 60–80 °C) (1:4) to furnish 1.77 g (63%) of the pure acid **5c**. It was crystallized from ether–petroleum ether (bp 60–80 °C) (1:4); mp 126–127 °C. On admixture with a sample prepared by a different route[5] the melting point was 126 °C: UV λ_{max} 260 nm (log ε 4.0), 293 (3.64); IR (KBr) 2960, 2920, 1690, 1625, 1580, 1480, 1440, 1340, 1290, 1210, 1180, 1035, 845, 810, 800 cm^{-1}.

Preparation of the Diazo Ketones 1c–e. 1-(Diazoacetyl)-1-methyl-6-methoxy-1,2,3,4-tetrahydrofluorene (1c). To a solution of 775 mg (3.0 mmol) of **5c** in 15 mL of methanol was added dropwise a 10% solution of sodium methoxide in methanol until the solution became alkaline (phenolphthalein). Methanol was removed under reduced pressure, and the last trace of methanol was removed by azeotropic distillation with benzene and finally dried in vacuo (90 °C, 8 mmHg) for 2 h. To the ice-cold stirred suspension of the sodio salt in 75 mL of benzene was added dropwise 1.4 mL (18.13 mmol) of oxalyl chloride containing 0.6 mL of pyridine. The reaction mixture was kept at 0 °C for 30 min and at room temperature for 30 min and finally was warmed to 60 °C for 1 h. The precipitated salt was filtered off, and the filtrate was concentrated under reduced pressure. The reddish brown residue thus obtained was taken up in 50 mL of Et_2O and was added with stirring to ice-cold ethereal diazomethane [from 4 g (40 mmol) of *N*-methylnitrosourea] containing 0.84 mL (6 mmol) of Et_3N. The reaction mixture was allowed to stand overnight. The precipitated salt was filtered off, and the solvent was removed from the filtrate. The yellow residue was filtered through a column of alumina (30 g) by elution with ether–petroleum ether (bp 60–80 °C) (1:1) to furnish 700 mg (82%) of **1c** as a yellowish thick liquid: IR ($CHCl_3$) 2940, 2860, 2115, 1605, 1585, 1360, 1280, 1150, 1050, 775 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.33 (3 H, s, CH_3), 1.57–2.67 (6 H, m, methylenes), 3.20 (br t, 2 H, J = 4 Hz, Ar CH_2), 3.77 (3 H, s, Ar OCH_3), 5.08 (1 H, s, $COCHN_2$), 6.50–7.17 (3 H, m, Ar H).

1-(Diazoacetyl)-1-methyl-8-methoxy-1,2,3,4-tetrahydrofluorene (1d). The crude diazoketone prepared from 510 mg (1.8 mmol) of **5d**[5] as above on filtration through a column of 20 g of alumina afforded 500 mg (91%) of yellow solid which was recrystallized from ether–petroleum ether (bp 60–80 °C) (1:3): mp 122–123 °C dec; IR (KBr) 2920, 2840, 2120, 1610, 1580, 1480, 1450, 1440, 1360, 1340, 1290, 1260, 1230, 1155, 1120, 1070, 1050, 910, 785, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (3 H, s, CH_3), 1.58–2.71 (6 H, m, methylenes), 3.31 (2 H, t, J = 3 Hz, Ar CH_2), 3.91 (3 H,

(17) For synthesis of isocomene see: (a) Pirrung, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 82. (b) Paquette, L. A.; Han, Y.-K. *Ibid.* **1981**, *103*, 1835. (c) Dauben, W. G.; Walker, D. M. *J. Org. Chem.* **1981**, *46*, 1103. (d) Oppolzer, W.; Battig, K.; Hudlicky, T. *Helv. Chim. Acta* **1979**, *62*, 1493.

(18) Ghatak, U. R. *Curr. Sci.* **1981**, *50*, 927.

(19) The relative ease of saponification[9a] of **7** in comparison to the isomeric ester **11** accounted for partial separation of the latter from the mixture.

s, $ArOCH_3$), 5.18 (1 H, s, $COCHN_2$), 6,68–7.38 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2N_2$: C, 72.32; H, 6.43. Found: C, 72.09; H, 6.61.

1-(Diazoacetyl)-1-methyl-8-methyl-1,2,3,4-tetrahydrofluorene (1e). The crude diazo ketone, prepared from 1 g (4.13 mmol) of **5e**[6] by following the aforementioned procedure, was filtered through 25 g of alumina to furnish 0.90 g (82%) of pure **1e** which was crystallized from ether–petroleum ether (bp 60–80 °C) (1:1) mp 102–103 °C; IR (KBr) 2920, 2880, 2110, 1610, 1450, 1355, 1330, 1160, 780, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (3 H, s, CH_3), 1.43–2.63 (9 H, m, methylenes including the $ArCH_3$ at 2.28 as a singlet), 3.13 (2 H, t, J = 3 Hz, Ar CH_2), 5.03 (1 H, s, $COCHN_2$), 6.63–7.03 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}ON_2$: C, 76.66; H, 6.81. Found: C, 76.55, H, 6.90.

Acid-Catalyzed Reactions of the Diazo Ketones 1b–e. Preparation of the Hydroxycyclopentanones 3b–e. (±)-4aβ-Hydroxy-7-methoxy-4α-methyl-2,3,4,4a,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (3b). A solution of 500 mg (1.77 mmol) of the diazo ketone **1b**[2] in 50 mL of CH_3NO_2 at room temperatures was treated with 0.5 mL (3.86 mmol) of 48% aqueous HBF_4 for 1 min. The deep red solution was diluted with water. The organic phase was separated, washed with 5% aqueous Na_2CO_3 and water, and dried ($CaCl_2$). Removal of the solvent and purification of the resultant material by chromatography on alumina (5 g) by elution with petroleum ether (bp 60–80 °C)–ether (2:1) afforded 330 mg (68%) of pure **3b** as a colorless solid, which was recrystallized from petroleum ether (bp 60–80 °C)–ether (1:1): mp 112 °C; IR (KBr) 3490, 2960, 2880, 2840, 1735, 1620, 1610, 1580, 1490, 1440, 1380, 1340, 1320, 1290, 1250, 1135, 1065, 985, 960, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.60 (1 H, s, OH, exchangeable with D_2O), 1.50–1.75 (4 H, m, methylenes), 1.80–2.30 (4 H, m, CH_2 and $COCH_2$), 2.68 (δ_A) and 2.90 (δ_B) (2 H, AB q, J = 16 Hz, Ar CH_2), 3.78 (3 H, s, Ar OCH_3), 6.78–7.37 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.98; H, 7.65.

(±)-4aβ-Hydroxy-6-methoxy-4α-methyl-2,3,4,4a,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (3c). A solution of 250 mg (0.89 mmol) of **1c** in 50 mL of CH_3NO_2 was treated with 0.25 mL (1.93 mmol) of aqueous HBF_4 for 30 s. The usual workup and chromatographic purification over 10 g of alumina with ether–petroleum ether (bp 60–80 °C) as the eluent afforded 220 mg (91%) of pure **3c**. Crystallization from ether–petroleum ether (bp 60–80 °C) (1:1) gave colorless crystals: mp 121–122 °C; Ir (KBr) 3380, 2940, 2840, 1725, 1620, 1580, 1480, 1450, 1300, 1280, 1230, 1065, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (3 H, s, CH_3), 1.40–2.53 (9 H, complex m, methylenes, including the OH signal, exchangeable with D_2O), 2.60–2.83 (2 H, m, Ar CH_2), 3.66 (3 H, s, Ar OCH_3), 6.60–7.26 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.88; H, 7.52.

(±)-4aβ-Hydroxy-8-methoxy-4α-methyl-2,3,4,4a,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (3d). A solution of 250 mg (0.89 mmol) of **1d** in 50 mL of CH_3NO_2 was treated with 0.25 mL (1.93 mmol) of aqueous HBF_4 for 30 s to afford **3d** as a yellowish solid which was purified by filtration through a short column of alumina (8 g) in ether–petroleum ether (bp 60–80 °C) (1:1) to give 220 mg (91%) of pure **3d**. It was recrystallized from ether–petroleum ether (bp 60–80 °C) (1:1): mp 123–124 °C; IR (KBr) 3460, 2940, 2910, 1720, 1580, 1470, 1455, 1365, 1310, 1105, 1080, 1050, 980, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (3 H, s, CH_3), 1.43–2.56 (9 H, complex m, methylenes including the OH at 1.85, exchangeable with D_2O), 2.78 (2 H, s, Ar CH_2), 3.83 (3 H, s, Ar OCH_3), 6.66–7.26 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.11; H, 7.68.

(±)-4aβ-Hydroxy-8-methyl-4α-methyl-2,3,4,4a,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (3e). A solution of 150 mg (0.57 mmol) of **1e** in 40 mL of CH_3NO_2 was treated with 0.25 mL (1.93 mmol) of aqueous HBF_4 during 30 s to give a brownish solid which was purified by chromatography on alumina (8 g) to afford 120 mg (82%) of pure **3e**. It was recrystallized from ether–petroleum ether (bp 60–80 °C) (1:1): mp 132–133 °C; IR (KBr) 3540, 2950, 2920, 2875, 1725, 1590, 1460, 1385, 1265, 1130, 1075, 1050, 1025, 1000, 960, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (3 H, s, CH_3), 1.66 (1 H, s, OH, exchangeable with D_2O), 2.23 (3 H, s, Ar CH_3), 1.45–2.53 (8 H, m, methylenes), 2.75 (2 H, s, Ar CH_2), 6.93–7.33 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.66; H, 7.96.

Catalytic Hydrogenation of the Hydroxycyclopentanones 3a–e to 14a–e. (±)-4α-Methyl-2,3,4,4aα,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (14a). A solution of 100 mg (0.41 mmol) of the hydroxy ketone **3a**[2] in 20 mL of ethanol containing 0.10 mL (1.17 mmol) of 70% $HClO_4$ was hydrogenated in the presence of 100 mg of 10% Pd/C for 24 h. The catalyst was filtered off, and the filtrate was neutralized with powdered $NaHCO_3$. The undissolved material was separated by filtration, and the filtrate was concentrated to afford 70 mg (75%) of **14a** as a colorless solid (homogeneous in VPC) which was recrystallized from petroleum ether (bp 60–80 °C) mp 99–100 °C; IR (KBr) 2930, 2870, 1735, 1460, 1380, 1215, 1005, 960, 770, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.45–1.50 (6 H, m, methylenes), 2.30 (2 H, s, $COCH_2$), 2.66 (2 H, s, Ar CH_2), 2.90 (1 H, br s, Ar CH), 7.01 (4 H, br s, Ar H); MS, m/e (relative intensity) 226 (M^+, 14), 184 (19), 183 (35), 182 (100), 155 (18), 142 (38), 128 (27). Anal. Calcd for $C_{16}H_{18}O$: C, 84.95; H, 8.02. Found: C, 84.79; H, 8.22.

(±)-4α-Methyl-7-methoxy-2,3,4,4aα,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (14b). A solution of 100 mg (0.37 mmol) of **3b** in 20 mL of ethanol was hydrogenated for 20 h in the presence of 60 mg of 10% Pd/C to afford 91 mg (95%) of **14b** (homogeneous in VPC, t_R = 7.2 min at 170 °C) as a colorless thick liquid. The analytical sample was prepared by chromatography on alumina (5 g) by elution with petroleum ether (bp 40–60 °C): IR (neat) 2935, 2860, 1735, 1610, 1580, 1480, 1255, 1030 cm^{-1}; ^1H NMR (CCl_4) δ 1.26 (3 H, s, CH_3), 1.42–3.43 (11 H, complex m, methylenes and methine), 3.75 (3 H, s, Ar OCH_3), 6.42–7.12 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.66; H, 7.98.

When the above hydrogenolysis was carried out in the presence of $HClO_4$ catalyst, the product consisted of two other products (ca. 50%) besides **14b** as revealed from VPC and ^1H NMR.

(±)-4α-Methyl-6-methoxy-2,3,4,4aα,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (14c). A solution of 100 mg (0.37 mmol) of **3c** in 20 mL of ethanol containing 0.1 mL (1.17 mmol) of aqueous $HClO_4$ was hydrogenated for 16 h in the presence of 100 mg of 10% Pd/C to furnish 90 mg (95%) of **14c** (homogeneous in VPC, t_R = 5.15 min at 180 °C) as a colorless thick liquid which was purified by chromatography on 5 g of alumina with ether–petroleum ether (bp 60–80 °C) (1:4) as the eluent: IR ($CHCl_3$) 2910, 2840, 1740, 1600, 1580, 1460, 975, 880 cm^{-1}; ^1H NMR (CCl_4) δ 1.31 (3 H, s, CH_3), 1.44–2.57 (9 H, complex m, methylenes), 2.78 (2 H, br s, Ar CH_2), 3.84 (3 H, s, Ar OCH_3), 6.65–7.27 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.69; H, 7.90.

(±)-4α-Methyl-8-methoxy-2,3,4,4aα,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (14d). A solution of 135 mg (0.50 mmol) of **3d** in 20 mL of ethanol containing 0.2 mL (2.34 mmol) of aqueous $HClO_4$ was hydrogenated for 10 h in the presence of 100 mg of 10% Pd/C to furnish 100 mg (78%) of pure **14d** (homogeneous in VPC, t_R = 5.2 min at 180 °C) which was recrystallized from ether–petroleum ether (bp 60–80 °C) (1:4): mp 110–111 °C; IR (KBr) 2940, 2820, 1740, 1600, 1580, 1420, 1260, 1130, 980, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.46–2.56 (9 H, complex m, methylenes), 2.77 (2 H, br s, Ar CH_2), 3.83 (3 H, s, Ar OCH_3), 6.66–7.26 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.60; H, 7.85.

(±)-4α-Methyl-8-methyl-2,3,4,4aα,9,9a-hexahydro-4β,9aβ-ethano-1*H*-fluoren-11-one (14e). A solution of 128 mg (0.50 mmol) of **3e** in 20 mL of ethanol containing 0.20 mL (2.34 mmol) of aqueous $HClO_4$ was hydrogenated for 12 h in the presence of 100 mg of 10% Pd/C to afford 100 mg (83%) of **14e** (homogeneous in VPC, t_R = 5.5 min at 180 °C) as a colorless solid which was recrystallized from petroleum ether (bp 60–80 °C): mp 105–106 °C; IR (KBr) 2960, 2860, 1735, 1600, 1520, 1460, 1230, 940, 810, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.43–2.54 (9 H, complex m, methylenes), 2.23 (3 H, s, Ar CH_3), 2.76 (2 H, br s, Ar CH_2), 7.00–7.33 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.93; H, 8.30.

Reaction of Diazo Ketone 1a with BF_3·OEt_2 in Benzene. To a solution of the diazo ketone **1a**[2] (50 mg, 0.2 mmol) in anhydrous benzene (10 mL) at room temperature was added a 10% (v/v) solution of BF_3·OEt_2 (0.3 mL, 0.22 mmol). After 5 min the reaction mixture was diluted, washed successively with water, 5% aqueous $NaHCO_3$, and water, and dried (Na_2SO_4). removal of the solvent under reduced pressure afforded a light yellow gum

(50 mg) which was found to be a mixture of **4a** and **3a** along with two other minor compounds in a ratio of 43:46:2:9 by VPC analysis with t_R = 2.57, 3.87, 2.13, 5.48 min, respectively.

Reaction of Diazo Ketone 1a with BF_3·OEt_2 in $CHCl_3$. Treatment of a solution of **1a** (50 mg, 0.2 mmol) in $CHCl_3$ (10 mL, freshly distilled over P_2O_5) with a 10% (v/v) solution of BF_3·OEt_2 in $CHCl_3$ (0.3 mL, 0.22 mmol) under the above conditions gave a mixture of **4a** and **3a** along with another minor compound in a ratio of 32:62:6 (VPC analysis gave t_R = 2.57, 3.87, and 2.13 min, respectively).

Reactions of the Diazo Ketones 1a–e with *p*-TsOH in Boiling Benzene. Preparation of 4a–e. (3a*SR*,11b*SR*)-3a-Methyl-1,2,3,3a-tetrahydro-5*H*-pentaleno[6a,1-*a*]indan-4-one (4a). A mixture of 1 g of *p*-TsOH·H_2O in 100 mL of dry benzene was refluxed with 500 mg (1.98 mmol) of the diazo ketone **1a** for 5 min under nitrogen. The cooled product was washed with 5% aqueous Na_2CO_3 and water and dried (Na_2SO_4). Removal of solvent under reduced pressure afforded 422 mg (95%) of the cyclopentenone **4a** as a light yellow semisolid of 96% purity (VPC). Chromatographic purification on 10 g of alumina with ether–petroleum ether (bp 40–60 °C) (1:1) as the eluent afforded pure **4a** (334 mg, 75%) as a colorless low-melting solid: IR ($CHCl_3$) 2950, 2850, 1695, 1630, 1450, 1370 cm^{-1}; UV λ_{max} 228 nm (log ϵ 4.2); ^1H NMR (CCl_4) δ 1.06 (3 H, s, CH_3), 1.33–2.33 (6 H, m, methylenes), 3.76 (2 H, br s, Ar CH_2), 5.90 (1 H, s, C=CH), 7.16 (4 H, m, Ar H); MS, *m/e* (relative intensity) 224 (M^+, 50), 209 (96), 196 (72), 182 (37), 181 (100), 152 (32). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.56; H, 7.29.

(3a*SR*,5a*SR*)-8-Methoxy-3a-methyl-1,2,3,3a-tetrahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (4b). A mixture of 1 g of *p*-TsOH·H_2O in 100 mL of anhydrous benzene was refluxed for 30 min under nitrogen with a moisture trap. It was cooled to 50–60 °C, 500 mg (1.77 mmol) of the diazo ketone **1b** in 50 mL of anhydrous benzene was added to it, and the mixture was gently refluxed for 5 min. The usual workup afforded a yellow viscous liquid which was found to be a mixture of the cyclopentenone **4b** and two other components in a ratio of 70:15:15 (t_R = 11.25, 15, and 18 min, respectively). Chromatographic separation over silica gel (40 g) afforded 210 (47%) of pure **4b** with ether–petroleum ether (bp 40–60 °C) (1:2): IR ($CHCl_3$) 2830, 2780, 1700, 1640, 1610, 1580, 1100 cm^{-1}; UV λ_{max} 230 nm (log ϵ 4.22); ^1H NMR (CCl_4) δ 1.01 (3 H, s, CH_3), 1.10–2.33 (6 H, m, methylenes), 3.76 (5 H, br s, Ar OCH_3 and Ar CH_2) 5.86 (1 H, br s, C=CH), 6.75 (2 H, m, Ar C_7 H and Ar C_9 H), 7.03 (1 H, d, $J_{9,10}$ = 8 Hz, Ar C_{10} H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.43; H, 7.32.

(3a*SR*,5a*SR*)-9-Methoxy-3a-methyl-1,2,3,3a-tetrahyro-6*H*-pentaleno[6a,1-*a*]indan-4-one (4c). A solution of 250 mg (0.89 mmol) of **1c** in 15 mL of benzene was added to a boiling solution of 0.5 g of *p*-TsOH·H_2O in 50 mL of benzene, and the mixture was refluxed for 5 min to furnish 180 mg (81%) of **4c** (homogeneous in VPC and ^1H NMR) which was purified by chromatography on 10 g of silica gel: IR ($CHCl_3$) 2960, 2840, 1700, 1640, 1600, 1440, 1240, 1110, 850 cm^{-1}; UV λ_{max} 230 nm (log ϵ 4.20); ^1H NMR (CCl_4) δ 1.03 (3 H, s, CH_3), 1.43–3.36 (6 H, m, methylenes), 3.73 (5 H, br s, Ar CH_2 and Ar OCH_3), 5.83 (1 H, br s, C=CH), 6.57–7.30 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.18; H, 7.01.

(3a*SR*,5a*SR*)-7-Methoxy-3a-methyl-1,2,3,3a-tetrahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (4d). To a solution of 0.5 g of *p*-TsOH·H_2O in 50 mL of anhydrous benzene refluxed for 30 min with a moisture trap was added 250 mg (0.89 mmol) of **1d** in 15 mL of benzene. The refluxing was continued for another 5 min, and the usual workup gave a yellowish viscous liquid which was found to be a mixture of the cyclopentenone **4d** with another component in a ratio of 90:10 (VPC). Chromatographic separation over 20 g of silica gel with petroleum (bp 40–60 °C) –ether (2:1) as the eluent furnished 150 mg (60%) of pure **4d** as a colorless thick liquid: IR ($CHCl_3$) 2910, 2850, 1705, 1645, 1605, 1585, 1100, 875 cm^{-1}; UV λ_{max} 240 nm (log ϵ 4.12); ^1H NMR (CCl_4) δ 1.03 (3 H, s, CH_3), 1.10–2.60 (6 H, m, methylenes), 3.66 (2 H, br s, Ar CH_2), 3.83 (3 H, s, ArOCH_3), 5.93 (1 H, br s, C=CH), 6.50–7.37 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.38; H, 7.30.

(3a*SR*,5a*SR*)-7-Methyl-3a-methyl-1,2,3,3a-tetrahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (4e). A solution of 135 mg (0.5 mmol) of **1e** in 10 mL of benzene was treated with 0.4 g of *p*-TsOH·H_2O for 5 min as described above. The usual workup and removal of the solvent afforded a yellow thick liquid which was found to be 95% pure **4c** (VPC and ^1H NMR). Purification by chromatography on silica gel (8 g) with ether–petroleum ether (bp 40–60 °C) (1:3) as the eluent afforded 84 mg (70%) of the pure **4e**: IR ($CHCl_3$) 2915, 2840, 1700, 1660, 1600, 1480, 1220, 1110, 950 cm^{-1}; UV λ_{max} 235 nm (log ϵ 4.21); ^1H NMR (CCl_4) δ 1.07 (3 H, s, CH_3), 1.20–2.53 (6 H, m, methylenes), 2.30 (3 H, s, Ar CH_3), 3.70 (2 H, br s, Ar CH_2), 5.92 (1 H, br s, C=CH), 6.87–7.13 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.58; H, 7.49.

Catalytic Hydrogenation of the Cyclopentenones 4a–e. (3a*SR*,5a*RS*,11b*SR*)-3a-Methyl-1,2,3,3a,5,5a-hexahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (15a). A solution of 150 mg (0.67 mmol) of the unsaturated ketone **4a** in 20 mL of ethanol was hydrogenated at room temperature and atmospheric pressure for 30 min in presence of 100 mg of 10% of Pd/C. The catalyst was filtered off, and the solvent was removed to afford **15a** as a homogeneous (VPC) colorless liquid (150 mg, 100%) which on evaporative distillation at 130 °C (0.1 mmHg) furnished the analytically pure sample: IR (neat) 2940, 2860, 1735, 1480, 1455, 1320, 1270, 1105, 1030, 760 cm^{-1}; ^1H NMR (CCl_4) δ 0.73 (3 H, s, CH_3), 1.27–1.77 (7 H, m, methylenes and methine), 1.93–2.10 (2 H, m, $COCH_2$), 2.27–2.73 (2 H, m, Ar CH_2), 7.07 (4 H, s, Ar H). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 9.02. Found: C, 84.86; H, 8.26.

(3a*SR*,5a*RS*,11b*SR*)-8-Methoxy-3a-methyl-1,2,3,3a,5,5a-hexahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (15b). A solution of 200 mg (0.80 mmol) of **4b** in 25 mL of ethanol was hydrogenated in presence of 100 mg of 10% Pd/C for 30 min to afford 200 mg (100%) of **15b** (homogeneous in VPC) which was purified by evaporative distillation at bp 155 °C (0.1 mmHg): IR ($CHCl_3$) 2950, 2865, 1730, 1610, 1585, 1495, 1305, 1250, 1200, 1030 cm^{-1}; ^1H NMR (CCl_4) δ 0.73 (3 H, s, CH_3), 1.23–1.75 (7 H, m, methylenes and methine), 1.87–2.13 (2 H, m, $COCH_2$), 2.27–2.70 (2 H, m, Ar CH_2), 3.72 (3 H, s, Ar OCH_3), 6.55–6.70 (2 H, m, Ar C_7 H and Ar C_9 H), 6.97 (1 H, d, $J_{9,10}$ = 8 Hz, Ar C_{10} H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.42; H, 7.99.

(3a*SR*,5a*RS*,11b*SR*)-9-Methoxy-3a-methyl-1,2,3,3a,5,5a-hexahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (15c). A solution of 85 mg (0.33 mmol) of **4c** in 10 mL of ethanol was hydrogenated for 1 h in presence of 50 mg of 10% Pd/C to give 80 mg (94%) of pure **15c** (homogeneous in VPC): IR ($CHCl_3$) 2920, 2840, 1730, 1600, 1585, 1480, 1360, 1310, 1280, 1200, 960, 825 cm^{-1}; ^1H NMR (CCl_4) δ 0.75 (3 H, s, CH_3), 1.23–2.43 (7 H, m, methylenes), 2.45–2.80 (2 H, m, $COCH_2$), 3.18–3.35 (2 H, m, Ar CH_2), 3.71 (3 H, s, Ar OCH_3), 6.40–7.06 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.62; H, 7.82.

(3a*SR*,5a*RS*,11b*SR*)-7-Methoxy-3a-methyl-1,2,3,3a,5,5a-hexahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (15d). A solution of 85 mg (0.33 mmol) of **4d** in 10 mL of ethanol was hydrogenated for 1 h in presence of 50 mg of 10% Pd/C to furnish 80 mg (94%) of **15d** as a homogeneous (VPC) colorless thick liquid: IR ($CHCl_3$) 2910, 2860, 1725, 1610, 1585, 1480, 1310, 1220, 1050 cm^{-1}; ^1H NMR (CCl_4) δ 0.73 (3 H, s, CH_3), 1.20–1.97 (7 H, m, methylenes), 2.01–2.20 (2 H, m, $COCH_2$), 2.20–3.30 (2 H, m, Ar CH_2), 3.81 (3 H, s, Ar OCH_3), 6.51–7.38 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.52; H, 7.82.

(3a*SR*,5a*RS*,11b*SR*)-7-Methyl-3a-methyl-1,2,3,3a,5,5a-hexahydro-6*H*-pentaleno[6a,1-*a*]indan-4-one (15e). Method A. A solution of 80 mg (0.33 mmol) of **4e** in 10 mL of ethanol was hydrogenated for 1 h in presence of 50 mg of 10% Pd/C to yield 70 mg (86%) of **15e** (homogeneous in VPC) as a colorless thick liquid which was purified by chromatog. over 4 g of silica gel with ether–petroleum ether (bp 60–80 °C) (1:4) as the eluent: IR ($CHCl_3$) 2950, 2860, 1730, 1605, 1485, 1310, 1240, 980 cm^{-1}; ^1H NMR (CCl_4) δ 0.73 (3 H, s, CH_3), 1.20–2.0 (7 H, m, methylenes), 2.10–2.19 (2 H, m, $COCH_2$), 2.20 (3 H, s, Ar CH_3), 2.29–3.30 (2 H, m, Ar CH_2), 6.80–7.00 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.90; H, 8.12.

Method B. Li–NH_3(l) Reduction of 4e. To a stirred solution of 160 mg (0.66 mmol) of the unsaturated ketone **4e** in 10 mL of anhydrous ether and 150 mL of dry liquid ammonia distilled from sodium was added 150 mg (0.021 mol) of small pieces of Li wire during 4 min. Stirring was continued for another 5 min. The

blue color was discharged by solid NH_4Cl, and the ammonia was allowed to evaporate at room temperature. The residue was diluted with water, acidified with 6 N HCl, and extracted with Et_2O. The ether extract was washed with water and dried (Na_2SO_4). Removal of the solvent afforded 140 mg of a gummy viscous liquid [IR ($CHCl_3$) 3480, 1730, 1600 cm^{-1}] which without further purification was dissolved in 10 mL of acetone and was subjected to Jones oxidation to yield 120 mg (75%) of **15e** as a light yellow viscous liquid. This was found to be a single component (VPC, NMR) of about 96% purity. Chromatographic purification over 5 g of silica gel with petroleum ether (bp 60–80 °C) as the eluent afforded the pure **15e**, which was found to be identical with the compound obtained from catalytic hydrogenation (NMR, IR, VPC).

Preparation of the Unsaturated Cyclobutanones 2c–e from the Diazo Ketones 1c–e. 7-Methoxy-2aα-methyl-2a,3,4,10-tetrahydrocyclobuta[*j*]fluoren-2(1*H*)-one (2c). A solution of 280 mg (1.0 mmol) of **1c** in 75 mL of $CHCl_3$ at 0 °C was treated with 0.5 mL (6.5 mmol) of TFA for 45 min to afford a gummy solid which was purified by chromatog. on 15 g of neutral alumina with ether–petroleum ether (bp 60–80 °C) (1:8) as the eluent to give 200 mg (78%) of pure **2c**. It was crystallized from petroleum ether bp (40–60 °C): mp 85–86 °C; IR (KBr) 2920, 2840, 1770, 1645, 1600, 1590, 1400, 1340, 1260, 1100, 975, 825 cm^{-1}; UV λ_{max} 260 nm (log ϵ 4.20); ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.67–2.01 (4 H, m, methylenes), 2.20–3.43 (4 H, m, Ar CH_2 and $COCH_2$), 3.80 (3 H, s, Ar OCH_3), 6.27 (1 H, br t, J = 6 Hz, C=CH), 6.66–7.30 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.01.

9-Methoxy-2aα-methyl-2a,3,4,10-tetrahydrocyclobuta[*j*]-fluoren-2(1*H*)-one (2d). A solution of 280 mg (1 mmol) of the diazo ketone **1d** in 75 mL of chloroform at 0 °C was treated with 0.5 mL (6.5 mmol) of TFA for 45 min to afford a yellowish gummy solid. Chromatography on neutral alumina (5 g) with ether–petroleum ether (bp 60–80 °C) (1:6) gave 200 mg (78%) of pure **2d** which was recrystallized from ether–petroleum ether (bp 60–80 °C) mp 127–128 °C; IR (KBr) 2940, 2840, 1780, 1650, 1600, 1580, 1480, 1260, 1165, 1100, 1080, 785 cm^{-1}; UV λ_{max} 260 nm (log ϵ 4.23); ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.37–2.37 (4 H, m, methylenes), 2.93–3.13 (4 H, m, Ar CH_2 and $COCH_2$), 3.83 (3 H, s, Ar OCH_3), 6.27 (1 H, br t, J = 6 Hz, C=CH), 6.60–7.23 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.34; H, 7.34.

9-Methyl-2aα-methyl-2a,3,4,10-tetrahydrocyclobuta[*j*]-fluoren-2(1*H*)-one (2e). A solution of 200 mg (0.75 mmol) of **1e** in 50 mL of $CHCl_3$ at 0 °C was treated with 0.5 mL (6.5 mmol) of TFA for 45 min as above to furnish 170 mg (94%) of **2e** as a light yellow solid which was recrystallized from ether–petroleum ether (bp 40–60 °C) (1:4): mp 91–92 °C; IR (KBr), 2940, 2810, 1775, 1650, 1600, 1585, 1480, 1240, 1050, 950 cm^{-1}; UV λ_{max} 262 nm (log ϵ 4.21); ^1H NMR ($CDCl_3$) δ 1.33 (3 H, s, CH_3), 1.50–2.90 (4 H, m, methylenes), 2.30 (3 H, s, Ar CH_3), 2.91–3.15 (4 H, m, $COCH_2$ and Ar CH_2), 6.23 (1 H, br t, J = 5 Hz, C=CH), 6.95–7.38 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.60; H, 7.52.

Catalytic Hydrogenation of the Unsaturated Cyclobutanones 2c–e. 7-Methoxy-2aα-methyl-2a,3,4,5,5aα,10-hexahydrocyclobuta[*j*]fluoren-2(1*H*)-one (16c). A solution of 125 mg (0.5 mmol) of **2c** in 20 mL of ethanol was hydrogenated for 1 h in presence of 50 mg of 10% Pd/C to afford 120 mg (95%) of a mixture of two isomers in a ratio of 19:1 (VPC, ^1H NMR). Chromatographic purification and fractional crystallization from petroleum ether (bp 40–60 °C) furnished 100 mg (80%) of pure **16c**: mp 90–91 °C; IR (KBr) 2940, 2865, 1775, 1600, 1585, 1480, 1380, 1250, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3 H, s, CH_3), 1.41–3.49 (11 H, complex m, methylenes and methine), 3.81 (3 H, s, Ar OCH_3), 6.51–7.22 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.60; H, 7.79.

9-Methoxy-2aα-methyl-2a,3,4,5,5aα,10-hexahydrocyclobuta[*j*]fluoren-2(1*H*)-one (16d). A solution of 125 mg (0.5 mmol) of the styrenoid cyclobutanone **2d** in 20 mL of ethanol was hydrogenated in presence of 50 mg of 10% Pd/C for 1 h to afford 120 mg (95%) of pure **16d** (VPC, ^1H NMR) which was recrystallized from petroleum ether (bp 60–80 °C) mp 126–127 °C; IR (KBr) 2920, 2840, 1780, 1600, 1590, 1480, 1385, 1265, 1110, 1080, 790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.40–3.47 (11 H, complex m, methylenes and methine) 3.83 (3 H, s, Ar OCH_3), 6.50–7.20 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.43; H, 7.93.

9-Methyl-2aα-methyl-2a,3,4,5,5aα,10-hexahydrocyclobuta[*j*]fluoren-2(1*H*)-one (16e). A solution of 110 mg (0.47 mmol) of **2e** in 20 mL of ethanol was hydrogenated for 1 h in presence of 60 mg of 10% Pd/C to furnish 100 mg (91%) of pure **16e** (VPC, ^1H NMR), which was recrystallized from petroleum ether (bp 60–80 °C): mp 123–124 °C; IR (KBr) 2940, 2860, 1780, 1600, 1490, 1380, 1250, 1120, 1060, 950, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, s, CH_3), 1.35–3.25 (11 H, complex m, methylenes and methine), 2.30 (3 H, s, Ar CH_3), 6.88–7.39 (3 H, m, Ar H). Anal. Calcd for $C_{17}H_{20}O$: C, 79.65; H, 7.86. Found: C, 79.53; H, 7.83.

Registry No. (±)-**1a**, 60059-29-2; (±)-**1b**, 60059-30-5; (±)-**1c**, 83681-18-9; (±)-**1d**, 83649-58-5; (±)-**1e**, 83664-24-8; (±)-**2c**, 83649-59-6; (±)-**2d**, 83649-60-9; (±)-**2e**, 83649-61-0; (±)-**3a**, 78284-39-6; (±)-**3b**, 83649-62-1; (±)-**3c**, 83649-63-2; (±)-**3d**, 83649-64-3; (±)-**3e**, 83649-65-4; (±)-**4a**, 83680-52-8; (±)-**4b**, 83680-53-9; (±)-**4c**, 83649-66-5; (±)-**4d**, 83649-67-6; (±)-**4e**, 83649-68-7; (±)-**5c**, 83649-69-8; (±)-**5c**·Na, 83649-70-1; (±)-**5c** chloride, 83649-71-2; (±)-**5d**, 83649-72-3; (±)-**5e**, 71685-84-2; (±)-**6**, 59323-55-6; (±)-**7**, 83649-73-4; (±)-**8**, 83649-74-5; (±)-**9** (isomer 1), 83649-75-6; (±)-**9** (isomer 2), 83649-76-7; (±)-**10** (isomer 1), 83649-77-8; (±)-**10** (isomer 2), 83649-78-9; (±)-**11**, 83649-79-0; (±)-**12**, 83649-80-3; (±)-**13**, 83649-81-4; (±)-**14a**, 83649-82-5; (±)-**14b**, 83649-83-6; (±)-**14c**, 83649-84-7; (±)-**14d**, 83649-85-8; (±)-**14e**, 83649-86-9; (±)-**15a**, 83680-54-0; (±)-**15b**, 83649-87-0; (±)-**15c**, 83649-88-1; (±)-**15d**, 83649-89-2; (±)-**15e**, 83649-90-5; (±)-**16c**, 83649-91-6; (±)-**16d**, 83649-92-7; (±)-**16e**, 83664-25-9; *p*-methoxybenzyl chloride, 824-94-2.

Magnesium-Induced Cyclizations of 2-(3-Iodopropyl)cycloalkanones. A Cyclopentane Annelation Method[1]

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A process for the stereoselective construction of a cyclopentane ring onto a preexisting cycloalkanone is developed. 2-(3-Iodopropyl)cycloalkanones, obtained by known methods from the parent cyclic ketones, were converted to bicyclo[*x*.3.0]alkan-1-ols in moderate to good yields by magnesium in THF. This cyclization shows a large preference for formation of the cis compounds. Attempts to extend this reaction to the formation of six- and seven-membered rings were largely unsuccessful.

The Barbier alternative[2] to the Grignard reaction involves the simultaneous interaction of an alkyl halide, an aldehyde or ketone, and magnesium metal in an ether solvent. This process has enjoyed some success with allylic

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