spectrum, m/e 164 (M^+), 146 ($M^+ - H_2O$), 128 ($M^+ - 2H_2O$), 91. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.07; H, 7.30.

***cis*-2,3-*O*-Isopropylidene-1,2,3,4-tetrahydronaphthalene (57).** The pure *cis*-2,3-diol **55** or the product mixture obtained above was treated with 2,2-dimethoxypropane and *p*-toluenesulfonic acid to give the desired acetonide **57** as an off-white solid which was recrystallized from aqueous ethanol: mp 76 °C; mass spectrum, m/e 204 (M^+), 189 ($M^+ - CH_3$), 129 ($M^+ - CH_3 - CH_3COOH$). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.60; H, 7.81.

2,3-Dihydroxynaphthalene (58). A sample of diepoxide **1b** (50 mg, 0.31 mmol) was dissolved in 5 mL of xylene and sealed in a thick-walled Pyrex tube. The tube was then heated inside a steel "bomb" at 190 °C for 1 day. The solvent was removed under vacuum, and the residue was purified by preparative TLC on silica gel with ether as the eluent. The melting point and NMR spectrum of the separated product (50%) were consistent with those of an authentic sample of 2,3-dihydroxynaphthalene (Aldrich).

Acknowledgment. This investigation was supported at the University of New Orleans by Grant CA-18346 of the National Cancer Institute and by NSF Grant CHE78-00615 and at Baylor College of Medicine by National Institute of Health Grant GM-16216,24092 and Training Grant GM-02055. We gratefully acknowledge the work done by Dr. M. Takaku on the reaction of *anti*-dioxide **1a** with methoxide ion. We are also indebted to Professor E. Vogel (Universität Köln, Germany) for a gift of dioxide **1b** (used for comparison purposes) and Professor N. S. Bhacca (LSU, Baton Rouge) for assistance in obtaining NMR data. Appreciation is also expressed to Ms. Karen Deogracias for her assistance in the preparation of the manuscript and Ms. Bernette Landreyt and Dr. Eleanor Elder for library aid. We also thank Dr. Kurt Loening of Chemical Abstracts Service for his advice on the nomenclature employed in this paper.

Registry No. **1a**, 58717-74-1; **1b**, 58692-14-1; **2**, 17180-88-0; **3a**, 83731-25-3; **3b**, 69153-87-3; **4a**, 83731-26-4; **4b**, 83731-27-5; **4c**, 83731-28-6; **4d**, 83731-29-7; **4e**, 83731-30-0; **7**, 83731-31-1; **9**, 10075-62-4; **10**, 83780-84-1; **11**, 76561-86-9; **16**, 69222-28-2; **17**, 69222-27-1; **20a**, 83731-32-2; **20b**, 83731-33-3; **20c**, 83731-34-4; **21a**, 83780-85-2; **21b**, 69483-35-8; **22a**, 83731-35-5; **22b**, 83731-36-6; **23**, 83731-37-7; **24**, 83731-38-8; **25a**, 83731-39-9; **25b**, 83731-40-2; **26**, 83780-86-3; **27a**, 83731-41-3; **27b**, 83731-42-4; **28**, 83731-43-5; **29a**, 69532-85-0; **30a**, 83731-44-6; **30b**, 83780-87-4; **31**, 83731-45-7; **32**, 83731-46-8; **33a**, 83731-47-9; **34**, 83731-48-0; **35**, 10075-76-0; **36a**, 83731-49-1; **37**, 83780-88-5; **40a**, 83731-50-4; **41a**, 10075-72-6; **42a**, 83780-89-6; **43a**, 83780-90-9; **43b**, 83731-51-5; **45**, 83731-52-6; **46**, 83731-53-7; **47**, 83731-54-8; **48**, 571-58-4; **49**, 83780-91-0; **50**, 54226-01-6; **51**, 83780-92-1; **52**, 3029-30-9; **53**, 41597-55-1; **54**, 83731-55-9; **55**, 35583-15-4; **55** bis(trifluoroacetate), 83731-56-0; **55** β,β-1,4-dibromobis(trifluoroacetate), 83731-57-1; **56**, 83731-58-2; **57**, 83731-59-3; **58**, 92-44-4; naphthalene, 91-20-3; 1,4-dihydronaphthalene, 612-17-9; *trans*-1,2-dihydro-1,2-dihydroxynaphthalene, 771-16-4.

Acid-Catalyzed Intramolecular C-Alkylation in β,γ-Unsaturated Diazomethyl Ketones. 2.[1] A Simple New Synthetic Route to Octahydro-4,10a-ethanophenanthren-12-ones and Octahydropentaleno[6a,1-*a*]naphthalen-4-ones

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Received April 27, 1982

The utility of acid-catalyzed intramolecular C-alkylation and alkylation–rearrangements of the rigid diazomethyl ketones **1a–c** pertaining to a new and simple efficient synthesis of the respective octahydro-4a-hydroxy-4,10a-ethanophenanthren-12-ones **7a–c** and 3a-methylhexahydropentaleno[6a,1-*a*]naphthalen-4-ones **8a–c** are described. The most thoroughly studied case was that of **1a**, which clearly revealed that in a polar solvent, nitromethane, and with strong protic acids or boron trifluoride etherate the hydroxycyclopentanone **7a** is the major product arising through the Wagner–Meerwein shifts of the initially generated respective cyclobutanone carbinyl cation. While strong protic acids (aqueous $HClO_4$ or aqueous HBF_4) in nonpolar solvents (benzene or chloroform containing ethanol stabilizer) exclusively produce the unsaturated cyclobutanone **3a**, solvents of intermediate polarities with HBF_4 or boron trifluoride etherate gave all three possible products, **3a**, **7a**, and **8a**. The structure of the products formed in the acid-catalyzed reactions of **1b,c** also depends upon the catalyst–solvent combinations as well as the reaction conditions and the nature of the substrates. The hydroxycyclopentanones **7a–c** underwent facile rearrangement with toluene-*p*-sulfonic acid or iodine in refluxing benzene, leading to the respective pentaleno-annulated ketones **8a–c** in excellent yields. These were also obtained from the respective unsaturated cyclobutanones **3b,c**. The benzylic ketone **15a**, prepared in good yield through oxidation of **7a**, rearranged to the respective enedione **16a** in excellent yield. Catalytic hydrogenolysis of the hydroxycyclopentanones **7a–c** afforded the respective bridged ketones **12a–c** exclusively. The stereochemistry of **12a** and **12b** has been established by the X-ray method. The unsaturated cyclopentanones **8a–c** undergo stereospecific hydrogenation to the respective cis AB cyclopentanones **13a–c** whereas lithium–liquid ammonia reduction of **8a,c** gives the respective diastereoisomeric cyclopentanones **13a,c** and **14a,c** in a ratio of ca. 1:9 from which the major isomers were easily separated. The ketone **8b** on similar reduction, however, gave an inseparable mixture of **13b** and **14b** in a ratio of ca. 1:2. The stereochemistries of the epimeric ketones **13a–c** and **14a–c** were assigned from the significant difference in the chemical shifts of the 3a-methyl group in these diastereoisomeric pairs. The cyclopentenone **8a** has been transformed into the parent hydrocarbon **18a**.

Intramolecular olefinic participation in the acid-induced decomposition of γ,δ-unsaturated α-diazomethyl ketones[2] has been extensively studied by Mander and his coworkers[3] and by ourselves[4] for simple elaboration of the

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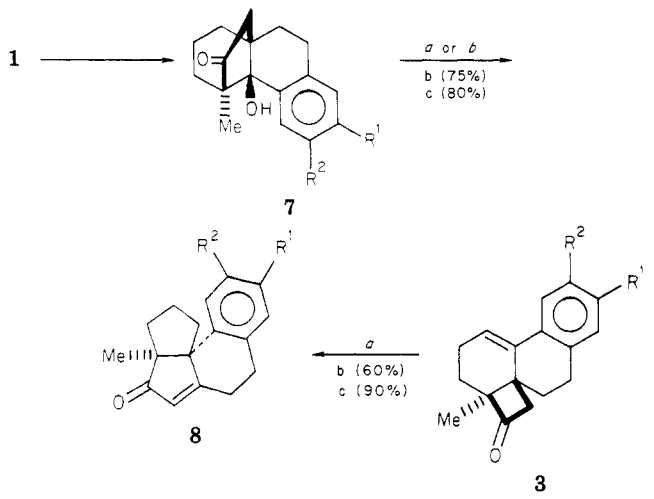
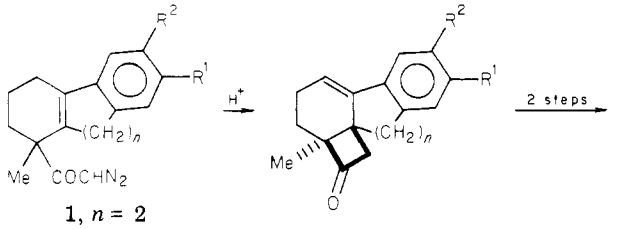
Scheme I[c]



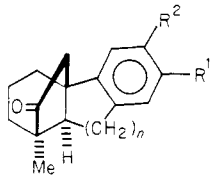
[a] p-TsOH-benzene (refluxed). [b] I_2-benzene (refluxed). [c] a, $R^1 = R^2 = H$; b, R^1 = OMe, $R^2 = H$; c, $R^1 = H$, R^2 = OMe.

difficulty accessible bicyclo[3.2.1]octanone moiety incorporated in polycyclic systems toward the synthesis of some complex diterpenoids. In 1974 we[5] introduced a highly efficient new synthesis of angularly fused cyclobutanones, for example, **3a,b** and **4a,b** by strong protic acid-catalyzed



1, $n = 2$
2, $n = 1$

3, $n = 2$
4, $n = 1$



(1)

5, $n = 2$
6, $n = 1$

a, $R^1 = R^2 = H$; b, R^1 = OMe, $R^2 = H$; c, R^2 = OMe, $R^1 = H$

intramolecular C-alkylation of the β,γ-unsaturated α-diazomethyl ketones **1a,b** and **2a,b** in relatively nonpolar solvents. The usefulness of this simple new cyclobutanone annulation reaction for stereospecific angular alkylation has also been demonstrated through their transformations[6] to the bridged cyclopentanones **5a–c** and **6a,b**. More recently, a similar cyclobutanone annulation reaction has been successfully exploited for the synthesis of some D-nor steroids[7] and the monoterpene, filifolone.[8] Following our preliminary communication,[5] Smith reported[9] acid-catalyzed cyclizations in a few relatively flexible β,γ-unsaturated diazomethyl ketones using $BF_3{\cdot}OEt_2$ in nitromethane and found the respective cyclopentenones to be the only annulation products. Recently this group has published[10] results of their extensive studies on the related cyclopentenone annulation reactions. In our detailed recent studies[1] on the cyclobutanone annulation we have clearly demonstrated that it is *not the structure alone which controls the nature of the products* in the acid-catalyzed reaction of β,γ-unsaturated diazomethyl ketones, e.g., **1a**, *but the choice of the acid catalyst and solvent is also critical* in deciding the nature of the products. Using appropriate acid catalysts and polar solvents, we have transformed the diazo ketone **1a**, to the rearranged bridged hydroxy ketone **7a** and subsequently to the pentalenoannulated tetralin **8a** in excellent preparative yields (see Scheme I). As a consequence, we thought it necessary to undertake further investigations to evaluate the effects of various solvents and acid catalysts in determining the nature of the products formed in the acid-induced intramolecular alkylation–rearrangement conditions on the selected β,γ-unsaturated diazo ketones **1a–c** with the objective of developing preparative routes to the respective bridged-ring (e.g., **7b,c**) and pentaleno-annulated (**8b,c**) systems. In this paper we report the results of these studies and subsequent transformations of the resulting products to some new bridged-ring and condensed-pentalenone derivatives. In the subsequent paper[11] we will present a detailed account of our efforts to extend the cyclobutanone, bridged-ring, and cyclopentenone annulation reactions to a few related tetrahydrofluorene systems (e.g., **2a,b** and other aromatic substituted derivatives).

Results and Discussion

Cyclization and Rearrangements of the Diazo Ketones 1a–c to 3a–c, 7a–c, and 8a–c. As reported earlier,[1] reactions of the diazo ketones **1a–c** in weakly polar solvents such as $CHCl_3$ (containing 1% EtOH stabilizer) or benzene in the presence of strong protic acids [aqueous $HClO_4$ (70%) or aqueous HBF_4 (48%)] gave the respective styrenoid cyclobutanones **3a–c** in excellent yields. In contrast, when the diazo ketone **1a** was subjected to cyclization with aqueous HBF_4 or $BF_3{\cdot}OEt_2$ in a strongly polar solvent (nitromethane), the bridged hydroxy ketone **7a** was the predominant product (ca. 90% by VPC) (Table I). The conditions and the quantitative evaluations of the products in the acid-catalyzed reactions of **1a** are outlined in Table

(1) Part 1: Ghatak, U. R.; Sanyal, B.; Satyanarayana, G. O. S. V.; Ghosh, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1203.

(2) For comprehensive recent reviews on the acid-catalyzed decomposition of unsaturated diazo ketones see: (a) Ghatak, U. R. *Curr. Sci.* **1981**, *50*, 927. (b) Smith, A. B., III; Dieter, R. K. *Tetrahedron* **1981**, *37*, 2407. (c) Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 361.

(3) (a) Beames, D. J.; Klose, T. R.; Mander, L. N. *Chem. Commun.* **1971**, 773. (b) Klose, T. R.; Mander, L. N. *Aust. J. Chem.* **1974**, *27*, 1287. (c) Beames, D. J.; Mander, L. N.; Turner, J. V. *Ibid.* **1974**, *27*, 1977. (d) Hook, J. M.; Mander, L. N.; Urech, R. *J. Am. Chem. Soc.* **1980**, *102*, 6628 and references cited therein.

(4) (a) Chakrabortty, P. N.; Dasgupta, R.; Dasgupta, S. K.; Ghosh, S. R.; Ghatak, U. R. *Tetrahedron* **1972**, *28*, 4653. (b) Ghatak, U. R.; Chakrabarty, S.; Rudra, K. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1957. (c) Ghatak, U. R.; Alam, S. K.; Chakraborti, P. C.; Ranu, B. C. *Ibid.* **1976**, 1669. (d) Ghatak, U. R.; Ray, J. K. *Ibid.* **1977**, 518. (e) Ghatak, U. R.; Chakraborti, P. C. *J. Org. Chem.* **1979**, *44*, 4562. (f) Ghatak, U. R.; Roy, S. C. *J. Chem. Res., Synop.* **1981**, 5; *J. Chem. Res., Miniprint* **1981**, 159. (g) Ranu, B. C.; Sarkar, M.; Chakraborti, P. C.; Ghatak, U. R. *J. Chem. Soc., Perkin Trans. 1* **1982**, 865.

(5) Ghatak, U. R.; Sanyal, B. *J. Chem. Soc., Chem. Commun.* **1974**, 876.

(6) (a) Ghatak, U. R.; Sanyal, B.; Ghosh, S. *J. Am. Chem. Soc.* **1976**, *98*, 3721. (b) Ghatak, U. R.; Alam, S. K.; Ray, J. K. *J. Org. Chem.* **1978**, *43*, 4598. (c) Ghatak, U. R.; Ghosh, S.; Sanyal, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2881.

(7) Ceccherelli, P.; Curini, M.; Tingoli, M.; Pellicciari, R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1924.

(8) Hudlicky, T.; Kutchan, T. *Tetrahedron Lett.* **1980**, *21*, 691.

(9) (a) Smith, A. B., III *J. Chem. Soc., Chem. Commun.* **1975**, 274. (b) Smith, A. B., III. Branca, S. J.; Toder, B. H. *Tetrahedron Lett.* **1975**, 4225. (c) Smith, A. B., III; Dieter, R. K. *J. Org. Chem.* **1977**, *42*, 396.

(10) (a) Smith, A. B., III; Toder, B. H.; Branca, S. J.; Dieter, R. K. *J. Am. Chem. Soc.* **1981**, *103*, 1996. (b) Smith, A. B., III; Dieter, R. K. *Ibid.* **1981**, *103*, 2009. (c) Smith, A. B., III; Dieter, R. K. *Ibid.* **1981**, *103*, 2017.

(11) Roy, S. C.; Satyanarayana, G. O. S. V.; Ghatak, U. R. *J. Org. Chem.*, following paper in this issue.

Table I. Distributions of the Products 3a, 7a, and 8a in the Acid-Catalyzed Reactions of the Diazo Ketone 1a

entry	solvent[a]	acid catalyst[b,c] (amt)	reaction conditions	ratio of the products[e-g] 3a	7a	8a	no. unidentified
1	C_6H_6 or $CHCl_3$ + 1% EtOH	HBF_4 or $HClO_4$[h]	1 h at 0-5 °C and 30 min at room temp	100			
2	$CHCl_3$	$HClO_4$	1 h at 0-5 °C and 30 min at room temp	100			
3	$CHCl_3$ or CH_2Cl_2	HBF_4	1 h at 0-5 °C and 30 min at room temp	38-39	50-52	9-12	
4	C_6H_6	$BF_3 \cdot OEt_2$ (1.1 equiv)[i]	5 min at room temp[d]	20	68	9	3
5	CH_2Cl_2	$BF_3 \cdot OEt_2$ (1.1 equiv)[i]	5 min at room temp	5	83	8	2
6	$CHCl_3$	$BF_3 \cdot OEt_2$ (1.1 equiv)[i]	5 min at room temp	7	82	8	2
7	$CHCl_3$	$BF_3 \cdot OEt_2$ (3.0 equiv)[i]	5 min at room temp	5	55	40	
8[h]	CH_3NO_2	HBF_4 or $BF_3 \cdot OEt_2$ (1.1 equiv)[i]	2 min at room temp[d]	10	90		
9	CH_3NO_2	H_2SO_4 (1.1 equiv)	5 min at room temp[d]	15	75	10	
10	CH_3NO_2	$HClO_4$ (1.1 equiv)	5 min at room temp[d]	5	85	8	2
11	CH_3NO_2	$HClO_4$ (1.1 equiv)	20 h at room temp[d]	6	9	85	

[a] Solvents were dried and freshly distilled. [b] The aqueous perchloric acid ($HClO_4$), tetrafluoboric acid (HBF_4), and sulfuric acid used were 70%, 48%, and 98%, respectively. [c] Unless otherwise stated, 4-5 equiv of the acid catalyst was used with respect to the diazo ketone. [d] Each reaction was carried out with 50 mg (0.19 mmol) of **1a** in 5 mL of the solvent. [e] Isolated crude products were obtained in 90-100% yield. [f] Determined from VPC analysis on a 10% UCW-982 column by using an FID with N_2 as the carrier gas at a column temperature 185 °C; retention times were 4.8, 6.0, and 7.9 min, respectively, for **8a**, **3a**, and **7a**. [g] Average of at least two runs. [h] Reference 1. [i] A 10% solution of $BF_3 \cdot OEt_2$ in the reaction solvent was used.

Table II. Distributions of the Products 3b,c, 7b,c, and 8b,c in the Acid-Catalyzed Reactions of the Diazo Ketones 1b,c

entry	starting material	solvent[a]	acid catalyst[b]	reaction conditions	yield,[e] % 3b,c	7b,c	8b,c
1	1b	C_6H_6	HBF_4	1 h at 0 °C and 30 min at room temp	92		
2	1b	$CHCl_3$	HBF_4	1 h at 0 °C and 30 min at room temp	82		
3	1b	$CHCl_3$	$BF_3 \cdot OEt_2$ (1.1 equiv)	5 min at room temp	75	detected by IR	
4[c]	1b	CH_3NO_2	$BF_3 \cdot OEt_2$ (1.1 equiv)	5 min at room temp	70	detected by IR	
5	1b	CH_3NO_2	H_2SO_4	15-20 s at room temp		79	
6	1b	CH_3NO_2	HBF_4	15-20 s at room temp	45	32	
7	1c	CH_3NO_2	HBF_4	15-20 s at room temp		82	
8	1c	CH_3NO_2	$BF_3 \cdot OEt_2$	5 min at room temp	24[d]	76	
9	1c	CH_3NO_2	H_2SO_4	5 min at room temp	18[d]	70	12

[a] Solvents were dried and freshly distilled. [b] The aqueous tetrafluoboric acid (HBF_4) and sulfuric acid (H_2SO_4) used were 48% and 98%, respectively. [c] Reference 1. [d] Product ratio was determined by VPC analysis on a 10% UCW-982 column by using an FID with N_2 as the carrier gas at a column temperature 190 °C; retention times were 5.2, 7.0, and 8.2 min, respectively, for **8c**, **3c**, and **7c**. [e] Yield of the isolated pure product by column chromatography on neutral alumina.

I. Some of the earlier results[1] on the cyclization-rearrangement reactions of **1a** have also been included in Table I for comparison. The crude product isolated (90–100% yield) from each of the cyclization reactions was subjected to VPC analysis for quantitative evaluations of the products. The results were obtained to the extent of a maximum deviation of ±2.5% in an average of two to three experiments. The structures of **7a** and **8a** have been established by X-ray crystallography.[1]

Encouraged by this initial result we set out to define the generality and limitations of this reaction for the preparation of similar bridged cyclopentanones such as **7b** and **7c** with aromatic methoxysubstituents. A short treatment (15–20 s) of **1c** with aqueous HBF_4 in nitromethane solution at room temperature afforded the corresponding hydroxycyclopentanone **7c** in 82% isolated yield. Repeating this reaction with $BF_3 \cdot OEt_2$ for 5 min gave a mixture of the unsaturated cyclobutanone **3c** and **7c** in a ratio of 24:76 (VPC) (Table II). The *p*-methoxy styrenoid diazo ketone **1b** showed, however, a sharp difference[1] in giving rise to the cyclobutanone **3b** as the major product 45–80%) with aqueous HBF_4 or $BF_3 \cdot OEt_2$ in nitromethane. After an extensive investigation (Table II) we have now finally obtained the desired compound **7b** in 79% yield by reaction of **1b** with H_2SO_4 (98%) in nitromethane. It was not possible to analyze the products by VPC due to the instability of **7b** at the column temperature. However, the products could be separated by column chromatography on neutral alumina. The structural and stereochemical assignments of **7b** and **7c** are based upon their mode of formation by analogy to the demethoxy analogue **7a**. The IR and ^1H NMR spectral data (see the Experimental Section) of **7b** and **7c** are in complete agreement with the assigned structure.

Recently, we have shown[1] that the hydroxycyclopentanone **7a** undergoes facile rearrangement with *p*-TsOH in boiling benzene to the spirocyclopentenone **8a** in 94% yield. The rearrangement proceeds equally well when *p*-TsOH is replaced by iodine. Interestingly, the diazo ketone **1a** on short treatment (ca. 5 min) with an excess of *p*-TsOH in boiling benzene produced in quantitative yield[12] a mixture of the cyclobutanone **3a** and the spirocyclopentenone **8a** in a ratio of 45:55 (VPC). The methoxy-substituted bridged-hydroxy cyclopentanone derivative **7b** also underwent rearrangement with iodine or *p*-TsOH in refluxing benzene for 15 h to afford the spirocyclopentenone **8b** in 75% yield. Similarly, the hydroxycyclopentanone **7c** or the cyclobutanone **3c** gave the respective rearranged product **8c** in 80% and 92% yields as the only isolable product with *p*-TsOH in boiling

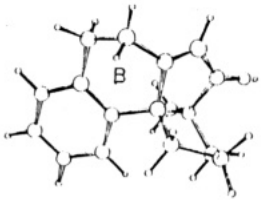


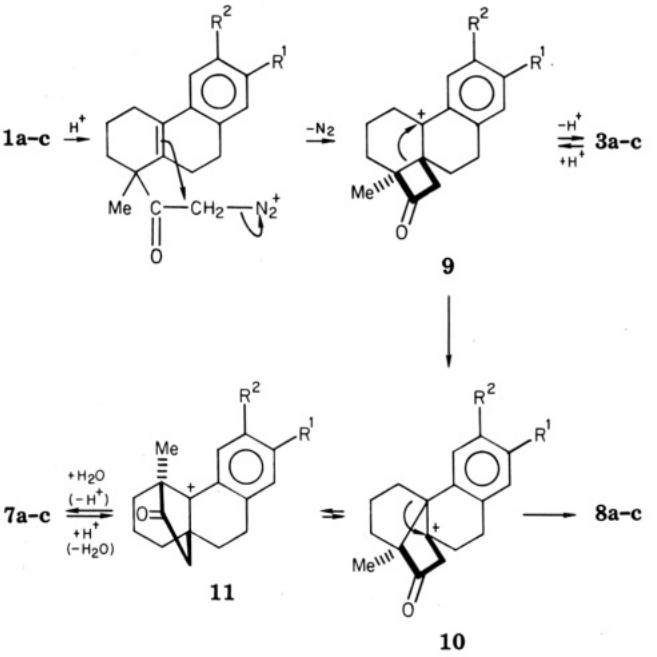
Figure 1. Perspective view of **8a**.

benzene (Scheme I). The spectral data of **8b** and **8c** (see the Experimental Section) are in complete agreement with the assigned structures. The unusual upfield chemical shifts of the methyl singlet in **8a**[1] (δ 0.89), **8b** (δ 0.87), and **8c** (δ 0.90) in the ^{1}H NMR spectra need special mention. A perspective drawing of the final X-ray model[1] of **8a**, shown in Figure 1, revealed that the angular methyl group is under the shielding zone of the aromatic moiety and that the six-membered ring (ring B) has a twist-boat conformation.

Perhaps the most important consequence of this study is the clear indications of the sensitivity of the cyclization and rearrangement reactions of the diazo ketones **1a–c** and the derived products (e.g., **3a–c** or **7a–c**) toward various acid–solvent combinations. In fact, a given set of reaction conditions may not often work as a general method in closely related systems. In conformation of earlier preparative work,[1] the present results recorded in Tables I and II clearly indicate that the strong protic acids $HClO_4$ and HBF_4 in a relatively nonpolar solvents such as $CHCl_3$ (containing EtOH stabilizer) and benzene are the best catalyst–solvent combinations for the cyclobutanone formation (Table I, entries 1 and 2), whereas a highly polar solvent, e.g., nitromethane with HBF_4, $BF_3{\cdot}OEt_2$, or H_2SO_4 as a catalyst at a very short reaction time, is suitable for the formation of the rearranged hydroxycyclopentanones **7a–c**. Interestingly, reaction in nitromethane and $BF_3{\cdot}OEt_2$ or HBF_4 with the diazo ketone **1a** (Table I, entry 8) gives the same mixture of products, a 1:9 ratio of **3a** and **7a**, thus revealing that possibly the same mechanism is operating in all these reactions in nitromethane. The reactions of **1a** with H_2SO_4 or $HClO_4$ in nitromethane also produce **8a** (Table I, entries 9 and 10) which, however, is the major product when the reaction time is extended (entry 11). The results of the cyclizations of **1a** in solvents of intermediate polarity (Table I, entries 3–6), where the rearranged cyclopentenone **8a** is also a product along with **3a** and **7a**, indicate the important role that the solvents play in these reactions. Even the presence of a small amount of EtOH in $CHCl_3$, which possibly changes the polarity of the solvent, dramatically influences the nature of the resulting products in the reaction of **1a** with HBF_4 (Table I, entries 1 and 3). The limited number of experiments with **1c** (Table II, entries 7–9) show behavior of this substrate similar with that of **1a**, particularly in the formations of the rearranged hydroxycyclopentanone **7c** and the cyclopentenone **8c**. Specifically, there is a sharp difference in the nature of the cyclization products between **1a** and **1c** with that of **1b**, particularly with respect to the formation of the hydroxycyclopentanone **7b**. The possible mechanistic pathways for the formation of all three products from the diazo ketones, **1a–c**, can be rationalized as proposed earlier[1] and depicted in Scheme II. The relative inertness of the diazo ketone **1b** toward the formation of the cyclopentenone **8b** (Table II) in comparison to those of **1a** and **1c** (Tables I and II) clearly reflects the importance of the relative stabilities[1] of the *p*-methoxyphenyl cation (**11b**) with respect to the corresponding cations **11a** and **11c** in determining the subsequent rearrangements to the respective cations **10a–c** (Scheme II). The present results also show that the rearranged cyclopentenones **8a–c** are the stablest products[12] among the various intermediates. The key step in the acid-catalyzed transformations of the β,γ-unsaturated diazo ketones such as **1a–c** to the bridged bicyclo[3.2.1]octanones **7a–c** or the pentaleno-annulated products **8a–c** is the facile generation of the cyclobutanone carbinyl cations **9a–c** which undergo Wagner–Meerwein shifts, under controlled conditions. Similar acid-catalyzed rearrangements[13] of cyclobutane or cyclobutanone derivatives derived mostly through [2 + 2] cycloaddition reactions have been productively utilized for the synthesis of bridged bicyclo[3.2.1]octane ring and polycyclopentanoid annulated systems.

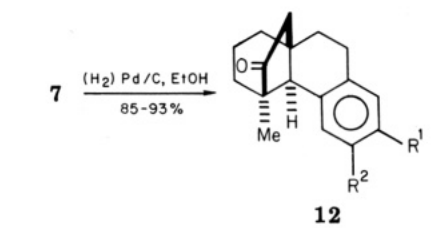
From a synthetic viewpoint it is significant that with appropriate reaction conditions it is possible to adopt the acid-catalyzed cyclizations and cyclization–rearrangement reactions to generate highly complex bridged-ring cyclopentanones **7a–c** and the relatively inaccessible pentaleno-annulated polycyclic systems **8a–c** in excellent prepa-

Scheme II[a]



[a] **a**, $R^1 = R^2 = H$; **b**, R^1 = OMe, R^2 = H; **c**, R^1 = H, R^2 = OMe.

Scheme III[a]

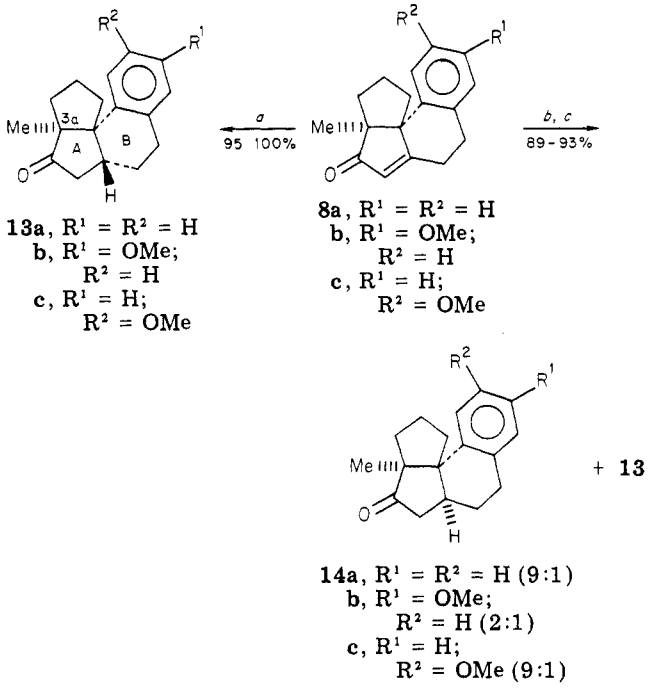


[a] **a**, $R^1 = R^2 = H$; **b**, R^1 = OMe, R^2 = H; **c**, R^1 = H, R^2 = OMe.

(12) Satyanarayana, G. O. S. V.; Kanjilal, P. R.; Ghatak, U. R. *J. Chem. Soc., Chem. Commun.* **1981**, 746.

(13) (a) Hayano, K.; Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Helv. Chim. Acta* **1981**, *64*, 1347. (b) Pirrung, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 82. (c) Tobe, Y.; Hayauchi, Y.; Sakai, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 637. (d) Eaton, P. E.; Jobe, P. G.; Nyi, K. *J. Am. Chem. Soc.* **1980**, *102*, 6636. (e) Duc, K.; Fetizon, M.; Kone, M. *Tetrahedron* **1978**, *34*, 3513. (f) Cargill, R. L.; Jackson, T. E.; Peet, N. P.; Pond, D. M. *Acc. Chem. Res.* **1974**, *7*, 106.

Scheme IV



13a, $R^1 = R^2 = H$
b, R^1 = OMe; R^2 = H
c, R^1 = H; R^2 = OMe

8a, $R^1 = R^2 = H$
b, R^1 = OMe; R^2 = H
c, R^1 = H; R^2 = OMe

+ 13

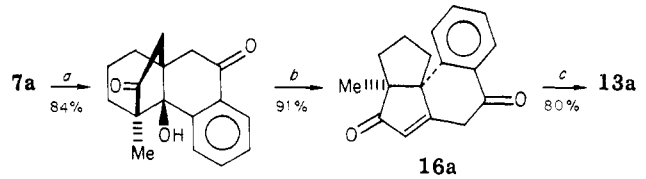
14a, $R^1 = R^2 = H$ (9:1)
b, R^1 = OMe; R^2 = H (2:1)
c, R^1 = H; R^2 = OMe (9:1)

[a] Pd/C (10%)-EtOH, H_2. [b] Li-NH_3(l)-THF, NH_4Cl. [c] Jones reagent.

rative yields through simple starting materials **1a–c**. Although a few cases of such alkylation–rearrangement of diazomethyl ketones, particularly with aryl participation,[14] have been observed earlier, this reaction has not yet been exploited adequately[12,15] for synthetic work.

Some Selected Transformations of 7a–c and 8a–c. Catalytic hydrogenation of each of the hydroxycyclopentanones **7a–c** in ethanol containing a catalytic amount of aqueous $HClO_4$ (70%) in the presence of palladium-on-charcoal (10%) at atmospheric pressure and temperature afforded in each case a single crystalline hydrogenolyzed product, **12a–c** in excellent yield (Scheme III). IR and ^1H NMR spectral data are in complete agreement with the assigned structures. The stereochemistry of the newly created benzylic asymmetric center has been unambiguously established by single-crystal X-ray analyses of **12a**[16a] and **12b**[16b] carried out at the x-ray laboratory of the Presidency College, Calcutta. The bridged ketones **12a–c** are potential intermediates for introduction of C-4 and C-10a *cis*-dicarboxylic acid functionalities in the *trans*-hexahydrophenanthrene moiety.[6c,17] Catalytic hydrogenation of the cyclopentenones **8a–c** in the presence of palladium-on-charcoal (10%) proceeded stereospecifically, affording the respective cyclopentanones **13a–c** in almost quantitative yield (Scheme IV). VPC and ^1H NMR properties of these ketones indicated their stereochemical homogeneity. Lithium–liquid ammonia reduction of **8a** and **8c** followed by oxidation of the crude products with Jones reagent afforded a mixture of the diastereoisomeric

Scheme V

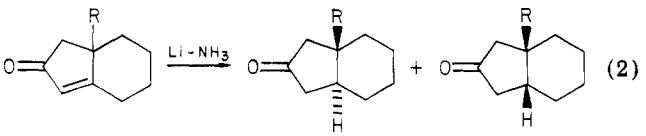


15a 16a

[a] CrO_3-AcOH-H_2O. [b] *p*-TsOH-PhH. [c] Pd/C, H_2, EtOH, $HClO_4$ (70%).

cyclopentanones **13a** and **14a** and of **13c** and **14c** in a ratio of ca. 1:9 as revealed by ^1H NMR or VPC. The crystalline major epimers **14a** and **14c** could be easily separated by column chromatography. The cyclopentenone **8b** on similar reaction gave a mixture of the respective diastereoisomeric ketones **14b** and **13b** in a ratio of ca. 2:1 (^1H NMR) which could not be cleanly separated by chromatography. The stereochemistries depicted in Scheme IV for the **13a,14a**, **13b,14b**, and **13c,14c** pairs were revealed by their widely different chemical shifts of the C-3a methyl group in the ^1H NMR spectra. The methyl singlet in AB-cis ketones **13a–c** appears at δ 0.71, 0.71, and 0.75, respectively, significantly upfield from the values of δ 1.01, 0.97, and 1.01 for the methyl singlet in the epimeric AB-trans ketones **14a–c**. These differences in the chemical shifts of the 3a-methyl singlet in the diasteroisomeric ketones could be easily rationalized by inspection of Drieding molecular models which clearly revealed that in the AB-cis epimers the methyl group is placed in the strong shielding zone of the aromatic ring with a twist-boat ring-B conformation similar to that observed with the cyclopentenones **8a–c** (loc. cit.), whereas in the AB-trans epimers the methyl group only deviates slightly from the plane of the aromatic ring, thereby exhibiting the expected chemical shift for this.

The stereospecificity in the catalytic hydrogenation of **8a–c** is predominantly governed by the steric hindrance exerted by the 3aα-methyl group, resulting in the addition of hydrogen exclusively from the β phase and leading to **13a–c**. The formation of the mixture of AB-trans (**14a–c**) and AB-cis (**13a–c**) isomers in the lithium–liquid ammonia reduction of **8a–c** was not completely unexpected. Although reduction of enones of this type is not known, the effect of the angular methyl group (or other substituents) on the stereochemical results of the simple cyclopentenone has been evaluated as shown in eq 2.[18] The present results



(2)

R = H (99%) R = Me (30%) R = H (1%) R = Me (70%)

clearly show that the heavily substituted cyclopentenones **8a–c** produce predominantly the AB-trans products (**14a–c**) in lithium–liquid ammonia reduction. The hydroxy dione **15a** obtained in 84% yield by benzylic oxidation[19] of **7a** (Scheme V) also underwent smooth rearrangement with *p*-TsOH in boiling benzene to afford the greenish yellow enedione **16a** in excellent yield. The spectral data for **15a** and **16a** (see the Experimental Section) are in complete agreement with the assigned struc-

(14) (a) Johnson, D. W.; Mander, L. N.; Masters, T. J. *Aust. J. Chem.* **1981**, *34*, 1243. (b) Beames, D. J.; Klose, T. R.; Mander, L. N. *Ibid.* **1974**, *27*, 1269.

(15) For synthesis of an intermediate toward aspidosperma alkaloids by a similar reaction see: Takano, S.; Shishido, K.; Sato, M.; Yuta, K.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1978**, 943.

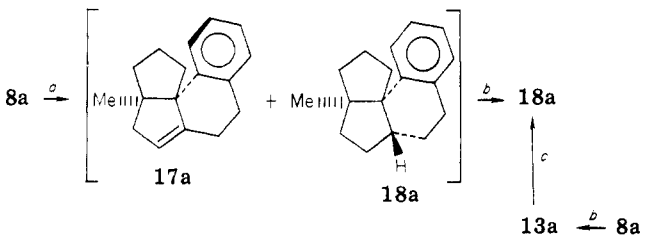
(16) (a) Bandyopadhyay, B. R.; Ghosh, M.; Basak, B. S., unpublished results. (b) Basak, B. S.; Kundu Das, S. C., unpublished results. We thank Professor Basak for informing us of the final X-ray data of **12a** and **12b**.

(17) (a) Ghatak, U. R.; Chakrabarty, S. *J. Org. Chem.* **1976**, *41*, 1089. (b) Ghatak, U. R.; Sarkar, M.; Patra, S. K. *Tetrahedron Lett.* **1978**, 2929.

(18) Dauben, W., private communication cited by: Caine, D. *Org. React.* **1976**, *23*, 104.

(19) Ghatak, U. R.; Chatterjee, N. R.; Banerjee, A. K.; Chakravarty, J.; Moore, R. E. *J. Org. Chem.* **1969**, *34*, 3739.

Scheme VI



[a] $LiAlH_4$-$AlCl_3$ in Et_2O. [b] Pd/C, H_2, EtOH. [c] NH_2-$NH_2 \cdot H_2O$, diethylene glycol, KOH.

tures. Catalytic hydrogenation of **16a** in ethanol containing a small amount of $HClO_4$ (70%) in the presence of Pd/C (10%) catalyst afforded the saturated ketone **13a** in 80% yield, identical with the sample obtained by reduction of **8a**.

To complete the synthesis of the parent hydrocarbon, benzotricyclo[7.3.0.0^{1,6}]dodecane[20] (**18a**, Scheme VI), we subjected unsaturated ketone **8a** to reduction with $LiAlH_4$–$AlCl_3$.[21] The product appeared to be a mixture containing the olefin **17a** and the saturated hydrocarbon **18a** in a ratio of ca. 4:1 (^1H NMR) along with a very minor amount of possibly the double bond isomers of **17a**. The crude mixture on catalytic hydrogenation afforded a single (VPC) epimer, **18a**, in 84% yield. The same hydrocarbon was also obtained in 71% yield by Wolff–Kishner reduction of the saturated ketone **13a**, thereby revealing an identical stereochemical outcome in the catalytic hydrogenation of both the cyclopentenone **8a** and the unsaturated hydrocarbon **17a**.

Conclusion

The present work conclusively established that acid-catalyzed cyclization of rigid β,γ-unsaturated diazomethyl ketones proceeds via the initial formation of the respective cyclobutanone carbinyl cation which may undergo Wagner–Meerwein shifts leading to the respective rearranged products, depending mainly upon the reaction conditions. Besides providing a simple route to angularly fused cyclobutanones, this method can be utilized for efficient synthesis of angularly bridged octahydrophenanthrenes and pentaleno-annulated tetralin systems having quaternary carbon centers[22] which are otherwise relatively inaccessible. We are presently investigating the synthetic applications of these intermediates toward natural products having angularly substituted hydrophenanthrene and pentalene moieties.

Experimental Section

The compounds described are all racemates. Melting points, taken in an open capillary, are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 298 spectrometer. UV spectra were recorded on a Beckman DU, a Shimadzu UV-Vis 210A, or a Cary 17D spectrometer for solutions in 95% ethanol. ^1H NMR spectra were taken (at 60 MHz) on a Varian Associates Model T-60A spectrometer, and chemical shifts are reported in δ from internal Me_4Si standard. Mass spectra were recorded on a Hitachi RM-60 mass spectrometer. Analytical VPC was performed on a Hewlett-Packard Model 5730A chromatograph equipped with an FID and using a 20 × $^1/_8$ in. 10% UCW-982 column at 185 °C with N_2 as the carrier gas. Elemental analyses were performed by Mr. P. P. Bhattacharyya of this laboratory. Unless otherwise mentioned, the chloroform used in all reactions was proanalysis (E. Merck) grade containing ethanol as stabilizer. Dry chloroform was prepared immediately before use by distillation over phosphorus pentoxide. Nitromethane was distilled just before use. Aqueous perchloric acid ($HClO_4$), tetrafluoroboric acid (HBF_4), and sulfuric acid (H_2SO_4) were 70%, 48% and 98% solutions, respectively. Column chromatography was performed on neutral aluminum oxide "standardized for chromatographic analysis according to Brockmann" (M/s. Sarabhai M. Chemicals).

Acid-Catalyzed Cyclization Studies of the Diazomethyl Ketone 1a with Various Catalysts and Solvents. General Conditions. (a) With HBF_4 in Benzene. To a cold (ca. 5 °C) magnetically stirred solution of diazo ketone **1a** (50 mg, 0.19 mmol) in 25 mL of benzene was added dropwise HBF_4 (0.1 mL, 0.77 mmol). The mixture was stirred for 1 h in the cold followed by an additional 30 min at 20–25 °C. The usual workup[1] afforded the product, 45 mg (100%). The product was subjected to VPC analysis (Table I).

Under identical conditions reaction of **1a** (50 mg) in 20 mL of dry $CHCl_3$ with $HClO_4$ (0.1 mL, 1.17 mmol) or in 20 mL of dry CH_2Cl_2 with HBF_4 (0.25 mL, 1.92 mmol) afforded the crude products in 90% and 100% yields, respectively (Table I).

(b) With $BF_3 \cdot OEt_2$ in Dry Benzene. A solution of **1a** (50 mg, 0.19 mmol) in 50 mL of dry benzene was treated with a 10% (v/v) solution of freshly distilled $BF_3 \cdot OEt_2$ (0.27 mL, 0.2 mmol) in dry benzene at room temperature (25–30 °C) for 5 min. The benzene solution was washed successively with water, 5% aqueous Na_2CO_3, and water and then dried (Na_2SO_4). Evaporation of the solvent under reduced pressure afforded 45 mg (100%) of a light yellow gum which was subjected to VPC analysis (Table I).

Repeating the above reaction of **1a** with dry CH_2Cl_2 or $CHCl_3$ under identical conditions afforded 95–100% of the crude reaction products which were subjected to VPC analysis (Table I).

(c) With an Excess of $BF_3 \cdot OEt_2$ in Dry $CHCl_3$. A solution of **1a** (50 mg, 0.19 mmol) in dry $CHCl_3$ was treated at room temperature with a 10% (v/v) solution of $BF_3 \cdot OEt_2$ (0.81 mL, 0.6 mmol) as described above. The crude product (41 mg, 90%) was subjected to VPC analysis (Table I).

(d) With H_2SO_4 in Nitromethane. Treatment of **1a** (50 mg, 0.19 mmol) in 5 mL of dry nitromethane with a 10% (v/v) solution of H_2SO_4 (0.11 mL, 0.2 mmol) in nitromethane at room temperature for 5 min followed by the usual workup gave 41 mg (90%) of a yellow gum which was analyzed by VPC (Table I).

Repeating the reaction under identical conditions with $HClO_4$ gave 91% of a yellow gum (Table I). When this reaction was continued for 24 h at room temperature, 90% of a yellow gum was obtained (Table I).

Acid-Catalyzed Cyclization Reactions of the Diazomethyl Ketone 1b under Various Conditions. General Conditions. (a) With HBF_4 in Benzene. An ice-cold (ca. 5 °C) magnetically stirred solution of the diazo ketone **1b**[1] (200 mg, 0.67 mmol) in dry benzene (70 mL) was treated with HBF_4 (0.5 mL, 3.85 mmol). It was allowed to stir in the cold for 1 h followed by an additional 30 min at room temperature. After the usual workup the resultant semisolid residue was chromatographed on neutral alumina (10 g). Petroleum ether (bp 60–80 °C) elution afforded the unsaturated cyclobutanone **3b** as a colorless solid: 165 mg (92%); mp 101–103 °C, alone or in admixture with the authentic sample[1] (Table II).

The result of the cyclization of **1b** with HBF_4 in dry $CHCl_3$ under identical conditions is summarized in Table II.

(b) With $BF_3 \cdot OEt_2$ in Dry Chloroform. A solution of the diazo ketone **1b** (100 mg, 0.336 mmol) in dry $CHCl_3$ (10 mL) was treated with a 10% (v/v) solution of $BF_3 \cdot OEt_2$ in $CHCl_3$ (0.36 mmol) at room temperature for 5 min. The usual workup followed by chromatography on neutral alumina (10 g) afforded the unsaturated cyclobutanone **3b** (70 mg, 75%) in petroleum ether (bp 60–80 °C) eluents; mp 101–103 °C, alone or in admixture with an authentic sample[1] (Table II).

(c) With H_2SO_4 in Nitromethane. Preparation of (±)-4aβ-Hydroxy-7-methoxy-4α-methyl-1,2,3,4,4a,9,10,10a-octahydro-4β,10aβ-ethanophenanthren-12-one (7b). To a well-stirred solution of 200 mg (0.675 mmol) of the diazo ketone **1b** in 5 mL of nitromethane at room temperature (25–30 °C) was

(20) For only a few compounds having the parent tricyclo[7.3.0.0^{1,6}]-dodecane ring system reported see: (a) Peet, N. P.; Cargill, R. L. *J. Org. Chem.* **1973**, *38*, 4281. (b) Chandrasekhar, S.; Rajagopalan, K.; Swaminathan, S. *Tetrahedron* **1978**, *44*, 2483. (c) Woolsey, N. F.; Radonovich, L. J.; Saad, F. M.; Koch, F. J. *J. Org. Chem.* **1979**, *44*, 2483. (d) Reference 13e.

(21) Brown, B. R.; White, A. M. S. *J. Chem. Soc.* **1957**, 3755.

(22) For a review see: Martin, S. *Tetrahedron* **1980**, *36*, 419.

added 0.20 mL (3.66 mmol) of H_2SO_4 during 15–20 s. The deep-red solution was immediately quenched with 15 mL of ice-cold water. The organic layer was separated, washed with water, 5% aqueous Na_2CO_3, and water, and dried (Na_2SO_4). Removal of the solvent under reduced pressure and chromatographic purification of the resultant light red gummy solid over neutral alumina (8 g) with benzene as eluent afforded the hydroxy ketone **7b** (150 mg, 79%; Table II) which was crystallized from Et_2O: mp 119–120 °C; IR (KBr) 3460, 2920, 1725, 1605, 1500, 1400, 1310, 1250, 1235, 1105, 1030, 915, 840, 810, 600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (3 H, s, CH_3), 1.80 (1 H, s, OH, exchangeable with D_2O), 1.55–2.00 (7 H, complex m, methylenes), 2.12 (δ_A) and 2.42 (δ_B) (AB_q, 2 H, J = 18 Hz, $COCH_2$, overlaps with a signal for 1 H), 2.84–3.10 (2 H, m, Ar CH_2), 3.78 (3 H, s, Ar OCH_3), 6.66–6.75 (2 H, m, Ar C_6 H and Ar C_8 H), 7.36 (1 H, d, $J_{5,6}$ = 9 Hz, Ar C_5 H); MS, m/e (relative intensity) 286 (M^+, 76), 227 (64), 226 (58), 189 (100), 171 (12), 161 (13), 149 (10). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.48; H, 7.78.

(d) With HBF_4 in Nitromethane. A solution of **1b** (100 mg, 0.336 mmol) in 10 mL of nitromethane was treated at room temperature with HBF_4 (0.1 mL, 0.77 mmol) during 15–20 s. The usual workup afforded a light yellow gum: IR ($CHCl_3$) 1760, 1730 cm^{-1}. This on chromatography on a neutral alumina (10 g) column afforded the cyclobutanone **3b** (41 mg, 45%)[23] in petroleum ether (bp 60–80 °C) elutes; mp 101–103 °C, alone or in admixture with an authentic sample.[1] Elution of the column with benzene–ethyl acetate (1:1) gave a light yellow gum which solidified on standing. Crystallization from ether afforded the pure hydroxy ketone **7b**: 30 mg (32%); mp 118–120 °C, alone or in admixture with the sample described above (Table II).

Acid-Catalyzed Cyclization Reactions of the Diazomethyl Ketone 1c under Different Conditions. (a) With HBF_4 in Nitromethane. Preparation of (±)-4aβ-Hydroxy-6-methoxy-4α-methyl-1,2,3,4,4a,9,10,10a-octahydro-4β,10aβ-ethanophenanthren-12-one (7c). A solution of 1 g (3.40 mmol) of **1c**[6b] in 100 mL of nitromethane was stirred for 15–20 s with 0.5 mL of 48% aqueous HBF_4 at room temperature. The light yellow solution was quenched with water and worked up as described for **1b**. Removal of the solvent and purification by chromatography on neutral alumina (10 g) with benzene–petroleum ether (bp 60–80 °C) (2:1) as eluent afforded pure **7c** (800 mg, 82%), which was crystallized from ether: mp 154–155 °C; IR (KBr) 3510, 2960, 2890, 1740, 1600, 1570, 1490, 1425, 1070, 1030, 1010, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (3 H, s, CH_3), 1.85 (1 H, s, OH, exchangeable with D_2O), 1.47–2.00 (7 H, complex m, methylenes), 2.17 (δ_A) and 2.49 (δ_B) (ABq, 2 H, J = 18 Hz, $COCH_2$, overlaps with a signal for 1 H), 2.66–3.07 (2 H, m, Ar CH_2), 3.73 (3 H, s, Ar OCH_3), 6.60–7.23 (3 H, m, Ar H); MS, m/e (relative intensity) 286 (M^+, 34), 268 (27), 227 (73), 226 (63), 211 (39), 189 (100), 171 (52). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.53; H, 7.60.

(b) With BF_3·OEt_2 in Nitromethane. Treatment of **1c** (100 mg, 0.34 mmol) in 10 mL of nitromethane with a 10% (v/v) solution of BF_3·OEt_2 (0.5 mL, 0.35 mmol) in nitromethane at room temperature for 5 min followed by the usual workup afforded a yellow gum (92 mg) which was analyzed by VPC (Table II).

(c) Under identical conditions 100 mg of **1c** in 10 mL of nitromethane with 0.22 mL (0.4 mmol) of H_2SO_4 afforded 90 mg of a yellow gum which was analyzed by VPC (Table II).

Alkylation–Rearrangement of the Diazo Ketone 1a with *p*-TsOH in Benzene to 3a and 8a. A solution of *p*-TsOH·H_2O (100 mg) in 50 mL of benzene was refluxed for 30 min under N_2 with a water trap. It was cooled to 25–30 °C and a solution of the diazo-ketone **1a** (50 mg, 0.19 mmol) in 5 mL of benzene was added. The temperature of the mixture was gradually raised and finally refluxed for 5 min. Usual work-up and removal of the solvent afforded a light yellow gum (98 mg) which was found to be a mixture of **3a** and **8a** in a ratio of 45:55 in VPC analysis.

Rearrangement of 7a–c to 8a–c. A mixture of the hydroxy ketone **7a** (100 mg, 0.39 mmol) and iodine (100 mg, 0.79 mmol) in 40 mL of anhydrous benzene was refluxed for 4 h under N_2. It was cooled, washed successively with water, 5% aqueous $Na_2S_2O_3$, and water, and dried (Na_2SO_4). Removal of the solvent and filtration of the resultant material through a short column of alumina afforded **8a** (75 mg, 81%) in petroleum ether (bp 60–80 °C) eluents; mp 95 °C, alone or in admixture with the authentic sample.[1]

Preparation of (3a*SR*,11b*SR*)-9-Methoxy-3a-methyl-1,2,3,3a,6,7-hexahydropentaleno[6a,1-*a*]naphthalen-4-one (8b). (a) A solution of 100 mg (0.35 mmol) of the hydroxy ketone **7b** and 100 mg (0.40 mmol) of iodine in 20 mL of benzene was refluxed under N_2 atmosphere for 15 h. The usual workup followed by filtration of the crude product through a wide, short column of alumina (5 g) and elution with petroleum ether (bp 60–80 °C) afforded 70 mg (75%) of **8b** as a colorless solid which was crystallized from ether–petroleum ether (bp 40–60 °C): mp 101 °C; IR (KBr) 2965, 2950, 1690, 1630, 1605, 1565, 1490, 1470, 1450, 1370, 1350, 1330, 1265, 1240, 1155, 1120, 1040, 870, 810 cm^{-1}; UV λ_{max} 230 nm (log ϵ 4.49), 278 (3.36), 313 (2.23); ^1H NMR ($CDCl_3$) δ 0.87 (3 H, s, CH_3), 1.00–2.33 (6 H, m, methylenes), 2.50–3.00 (4 H, m, Ar CH_2 and COCH=C—CH_2), 3.75 (3 H, s, Ar OCH_3), 5.95 (1 H, br s, COCH=C), 6.52–7.22 (3 H, m, Ar H); MS, m/e (relative intensity) 268 (M^+, 62), 241 (17), 240 (100), 225 (32), 212 (25), 165 (25), 153 (22), 115 (24). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.33; H, 7.65.

(b) Treatment of the hydroxy ketone **7b** (200 mg, 0.70 mmol) with *p*-TsOH·H_2O (50 mg) under the aforementioned conditions followed by chromatographic purification of the resultant crude product over alumina (5 g) afforded **8b** (130 mg, 69%) in petroleum eluents.

Preparation of (3a*SR*,11b*SR*)-10-Methoxy-3a-methyl-1,2,3,3a,6,7-hexahydropentaleno[6a,1-*a*]naphthalen-4-one (8c). The hydroxy ketone **7c** (500 mg, 1.75 mmol) and 80 mg (0.465 mmol) of *p*-TsOH·H_2O in 100 mL of benzene was refluxed under nitrogen for 4 h. The usual workup gave 375 mg (80%) of **8c** as yellowish gummy solid which was purified by chromatography on alumina (8 g) with ether–petroleum ether (bp 60–80 °C) (1:9) as the eluent. Recrystallization from ether–petroleum ether (bp 60–80 °C) (1:9) afforded the colorless crystals: mp 131–132 °C; IR (KBr) 2960, 2860, 1680, 1620, 1600, 1570, 1490, 1450, 1280, 1040, 890, 820 cm^{-1}; UV λ_{max} 224 nm (log ϵ 4.49), 283 (3.54); ^1H NMR ($CDCl_3$) δ 0.90 (3 H, s, CH_3), 1.13–2.50 (6 H, m, methylenes), 2.50–3.07 (4 H, m, Ar CH_2 and C=C—CH_2), 3.76 (3 H, s, Ar OCH_3), 5.91 (1 H, s, COCH=C), 6.53–7.03 (3 H, m, Ar H). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.67; H, 7.69.

Rearrangements of the Cyclobutanones 3b and 3c with *p*-TsOH in Benzene to 8b and 8c. A mixture of 100 mg (0.37 mmol) of the unsaturated cyclobutanone **3b** and 100 mg of *p*-TsOH·H_2O in 50 mL of dry benzene was refluxed for 9 h under N_2 in a flask fitted with a Dean–Stark water separator. The cooled reaction mixture was washed with 2% aqueous $NaHCO_3$ and water and dried (Na_2SO_4). Removal of the solvent and chromatographic purification on 3 g of alumina afforded **8b** as a light yellow solid (60 mg, 60%) which was recrystallized from petroleum ether (bp 60–80 °C); mp 100–101 °C, alone or in admixture with the sample described above.

With an identical procedure, rearrangement of **3c**[6b] (1 g, 3.73 mmol) in 200 mL of benzene afforded a greenish mass which on chromatographic purification over silica gel (15 g) with petroleum ether (bp 60–80 °C)–ether (9:1) yielded 920 mg (92%) of **8c**, mp 131–132 °C, alone or in admixture with the sample described above.

Hydrogenolysis of 7a–c. Preparation of (±)-4α-Methyl-1,2,3,4,4aα,9,10,10a-octahydro-4β,10aβ-ethanophenanthren-12-one (12a). A solution of 100 mg (0.39 mmol) of the hydroxy ketone **7a** in 20 mL of ethanol containing 0.1 mL (1.17 mmol) of 70% $HClO_4$ was hydrogenated in the presence of 100 mg of 10% Pd/C for 1 h. The catalyst was filtered off, and the filtrate was neutralized with powdered $NaHCO_3$. The insoluble materials were filtered off, and the solvent was removed to afford a homogenous (VPC) white solid (90 mg, 93%) which was recrystallized from petroleum ether (bp 40–60 °C): mp 126 °C; IR (KBr) 2880, 2865, 1725, 1495, 1410, 1380, 1345, 1270, 1200, 1180, 1120, 810, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (3 H, s, CH_3), 1.72 (8 H, br s, methylenes), 2.03–2.25 (2 H, m, $COCH_2$), 2.66–3.03 (3 H, m, Ar CH_2 and ArCH), 7.08 (4 H, br s, Ar H); MS, m/e (relative

(23) In our earlier work[1] we were unable to separate **7b** from this reaction mixture. VPC analyses indicated the presence of **3b** along with three other components which we have now confirmed as the decomposition products arising from **7b**.

intensity) 240 (M^+, 98.7), 212 (15), 198 (38), 197 (40), 196 (37), 156 (66), 149 (65), 141 (100), 129 (60), 128 (89), 115 (65). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 85.19; H, 8.57.

Preparation of (±)-4α-Methyl-7-methoxy-1,2,3,4,4aα,9,10,10a-octahydro-4β,10aβ-ethanophenanthren-12-one (12b). A solution of 120 mg (0.42 mmol) of **7b** in 25 mL of ethanol was hydrogenated in the presence of 100 mg of 10% Pd/C and 0.1 mL (1.17 mmol) of 70% $HClO_4$ for 1 h. The usual workup afforded **12b** (100 mg, 89%) as a homogenous (VPC) white solid, which was recrystallized from petroleum ether (bp 40–60 °C): mp 91 °C; IR (KBr) 2930, 2850, 1735, 1600, 1495, 1470, 1445, 1370, 1310, 1300, 1270, 1235, 1160, 1100, 1035, 840, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (3 H, s, CH_3), 1.72 (8 H, br s, methylenes), 2.05–2.28 (2 H, m, $COCH_2$), 2.65–2.88 (3 H, m, Ar CH_2 and ArCH), 3.73 (3 H, s, Ar OCH_3), 6.55 (1 H, br s, Ar C_8 H), 6.66–6.71 (1 H, m, Ar C_6 H), 7.00–7.08 (1 H, m, Ar C_5H). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.91; H, 8.38.

Preparation of (±)-4α-Methyl-6-methoxy-1,2,3,4,4aα,9,10,10a-octahydro-4β,10aβ-ethanophenanthren-12-one (12c). A solution of 100 mg (0.35 mmol) of **7c** in 20 mL of ethanol was hydrogenated in presence of 50 mg of 10% Pd/C and 0.15 mL (1.75 mmol) of 70% $HClO_4$ for 1 h to afford 12c as a homogeneous (VPC) semisolid mass (80 mg, 85%) which solidified on cooling. It was recrystallized from petroleum ether (bp 40–60 °C): mp 101–102 °C; IR (KBr) 2960, 2940, 1730, 1600, 1580, 1420, 1410, 1310, 1235, 1035, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (3 H, s, CH_3), 1.30–2.40 (10 H, complex m, methylenes), 2.37–3.00 (3 H, m, Ar CH_2 and ArCH) 3.66 (3 H, s, Ar OCH_3), 6.40–7.00 (3 H, m, Ar H). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.93; H, 8.10.

Catalytic Hydrogenation of 8a–c. (3a*SR*,5a*RS*,11b*SR*)-3a-Methyl-1,2,3,3a,5,5a,6,7-octahydropentaleno[6a,1-*a*]naphthalen-4-one (13a). A solution of 100 mg (0.42 mmol) of the unsaturated ketone **8a** in 15 mL of ethanol was hydrogenated at room temperature and atmospheric pressure in presence of 100 mg of 10% Pd/C for 15 h. The catalyst was filtered off, and the solvent was removed under reduced pressure to afford 100 mg (100%) of a homogeneous (VPC) white solid (**13a**) which was recrystallized from petroleum ether (bp 60–80 °C): mp 92 °C; IR (KBr) 2920, 1720, 1480, 1440, 1400, 1360, 1225, 1125, 1090, 735, 730 cm^{-1}; ^1H NMR (CCl_4) δ 0.71 (3 H, s, CH_3), 1.33–2.50 (10 H, complex m, methylenes and methine), 2.55–2.86 (3 H, m), 6.93–7.10 (4 H, m, Ar H); MS, *m/e* (relative intensity) 240 (M^+, 97), 212 (57), 198 (69), 197 (100), 183 (51), 169 (60), 156 (60), 155 (60), 143 (64), 142 (57), 141 (68), 128 (63), 115 (43); ^{13}C NMR ($CDCl_3$) δ 225.8, 143.1, 138.0, 135.4, 129.9, 127.7, 126.8, 62.3, 56.8, 48.3, 45.5, 43.4, 43.2, 30.0, 29.5, 27.2, 23.1. Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.75; H, 8.38.

(3a*SR*,5a*RS*,11b*SR*)-9-Methoxy-3a-methyl-1,2,3,3a,5,5a,6,7-octahydropentaleno[6a,1-*a*]naphthalen-4-one (13b). A solution of 100 mg (0.37 mmol) of **8b** in 15 mL of ethanol was hydrogenated in presence of 100 mg of 10% Pd/C as described in the previous experiment to afford 100 mg (100%) of saturated ketone **13b** as a homogeneous (VPC) colorless thick liquid: bp 150 °C (0.1 mmHg); IR ($CHCl_3$) 2960, 2940, 1730, 1610, 1575, 1375, 1320, 1130, 1100, 1040 cm^{-1}; ^1H NMR (CCl_4) δ 0.71 (3 H, s, CH_3), 1.33–2.50 (10 H, complex m, methylenes), 2.63–2.88 (3 H, m), 3.71 (3 H, s, Ar OCH_3), 6.47 (1 H, dd, $J_{8,10}$ = 3 Hz, $J_{10,11}$ = 8 Hz, Ar C_{10} H), 6.68 (1 H, d, $J_{8,10}$ = 3 Hz, Ar C_8 H), 7.00 (1 H, d, $J_{10,11}$ = 8 Hz, Ar C_{11} H). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.87; H, 8.24.

(3a*SR*,5a*RS*,11b*SR*)-10-Methoxy-3a-methyl-1,2,3,3a,5,5a,6,7-octahydropentaleno[6a,1-*a*]naphthalen-4-one (13c). A solution of 100 mg (0.37 mmol) of **8c** in 15 mL of ethanol was hydrogenated in presence of 50 mg of 10% Pd/C to afford 95 mg (95%) of **13c** as a colorless liquid [homogeneous (VPC)]. This on filtration through a column of alumina (10 g) and elution with ether–petroleum ether (bp 60–80 °C) (1:4) gave the analytically pure sample: IR ($CHCl_3$) 2940, 2860, 1725, 1600, 1570, 1490, 1450, 1380, 1180, 1095, 1040, 1030 cm^{-1}; ^1H NMR (CCl_4) δ 0.75 (3 H, s, CH_3), 0.83–2.87 (13 H, complex m, methylenes and methine), 3.71 (3 H, s, Ar OCH_3), 6.40–7.06 (3 H, m, Ar H). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.95; H, 8.27.

Lithium–Ammonia Reduction of 8a–c. (3a*SR*,5a*SR*,11b*SR*)-3a-Methyl-1,2,3,3a,5,5a,6,7-octahydropentaleno[6a,1-*a*]naphthalen-4-one (14a and 13a). To a stirred solution of 475 mg (2 mmol) of the unsaturated ketone **8a** in 40 mL of dry Et_2O and 200 mL of anhydrous liquid ammonia (distilled over sodium) was added 200 mg (28 mmol) of small pieces of lithium wire during 1–2 min. Stirring was continued for a further 5–7 min, and the blue color was discharged by the addition of solid NH_4Cl. The ammonia was allowed to evaporate at room temperature. The residue was dissolved in water, acidified with cold 6 N HCl, and extracted with Et_2O. The ethereal extract was washed and dried (Na_2SO_4). Removal of the solvent afforded a colorless viscous liquid, which was directly subjected to Jones oxidation[24] as described below.

The crude product (470 mg) was dissolved in 5 mL of acetone and was treated with Jones reagent[24] at 10–15 °C until the color of the reagent persisted for 10 min. It was stirred for further 10 min. Excess reagent was decomposed with 2-propanol, diluted with water, and extracted with ether. The ether extract was washed and dried (Na_2SO_4). The solvent was removed, and the resultant crude product was filtered through a short, wide column of neutral alumina (10 g) with petroleum ether (bp 60–80 °C) as the eluent to give a mixture (430 mg, 89%) of **14a** and **13a** in a ratio of 85:15 (from the integration of the ^1H NMR of the quaternary methyl singlets) which solidified on standing. Two recrystallizations from petroleum ether (bp 60–80 °C) afforded analytically pure **14a**: 200 mg (42%); mp 80–82 °C; IR (KBr) 2950, 2870, 1735, 1485, 1450, 1375, 1310, 1090, 1040, 760, 730 cm^{-1}; ^1H NMR (CCl_4) δ 1.01 (s, 3 H, CCH_3), 1.33–2.33 (complex m, 11 H, methylenes and methine), 2.83–3.10 (m, 2 H, Ar CH_2), 7.00 (m, 4 H, Ar H). Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.85; H, 8.53.

(3a*SR*,5a*SR*,11b*SR*)-9-Methoxy-3a-methyl-1,2,3,3a,5,5a,6,7-octahydropentaleno[6a,1-*a*]naphthalen-4-one (14b and 13b). Reduction of **8b** (200 mg, 0.74 mmol) with lithium (100 mg, 14 mmol) in Et_2O (20 mL) and anhydrous liquid ammonia (100 mL) as described for the demethoxy analogue **8a** followed by oxidation with Jones reagent afforded a light yellow viscous material: 190 mg (93%); IR (neat) 2930, 2880, 1735, 1605, 1500, 1450, 1255, 1090, 1040, 790, 760 cm^{-1}; ^1H NMR (CCl_4) of the crude mixture showed two quaternary CH_3 signals at δ 0.71 and 0.98. From the NMR integrations as well as by direct comparison with **13b**, the ratio of **14b** and **13b** was estimated as 2:1. The methoxy signal for both **14b** and **13b** resonates at δ 3.70.

So far we have failed to separate this mixture by PLC or by column chromatography.

(3a*SR*,5a*SR*,11b*SR*)-10-Methoxy-3a-methyl-1,2,3,3a,5,5a,6,7-octahydropentaleno[6a,1-*a*]naphthalen-4-one (14c and 13c). Reduction of **8c** (300 mg, 1.11 mmol) with 200 mg (28 mmol) of lithium in 10 mL of Et_2O and 200 mL of anhydrous liquid ammonia as described for **8a** followed by oxidation with Jones reagent in 15 mL of acetone afforded a gummy viscous liquid which was found to be a mixture of **14c** and **13c** in a ratio of 87:13 (VPC and ^1H NMR). Chromatographic separation through silica gel (50 g) by elution with petroleum ether yielded 200 mg (66%) of pure **14c** as a colorless solid, which was recrystallized from petroleum ether (bp 40–60 °C): mp 112–113 °C; IR (KBr) 2960, 2870, 2830, 1730, 1610, 1590, 1490, 1290, 1230, 1190, 1075, 1045, 880, 800 cm^{-1}; ^1H NMR (CCl_4) δ 1.01 (3 H, s, CH_3), 1.33–2.35 (11 H, complex m, methylenes and methine), 2.70–3.07 (2 H, m, Ar CH_2), 3.70 (3 H, s, Ar OCH_3), 6.37–7.07 (3 H, m, Ar H). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.87; H, 8.35.

Oxidation of the Hydroxycyclopentanone 7a. (±)-4aβ-Hydroxy-4α-methyl-1,2,3,4,4a,10a-hexahydro-4β,10aβ-ethanophenanthrene-9,12(10*H*)-dione (15a). A solution of 100 mg (0.39 mmol) of the hydroxy ketone **7a** in 3 mL of AcOH was oxidized[19] with 150 mg (1.5 mmol) of CrO_3 in 0.5 mL of water for 72 h. It was diluted, saturated with NaCl, and extracted with ether. The ether layer was washed with 5% aqueous Na_2CO_3, water and brine and dried (Na_2SO_4). Removal of the solvent gave a pale yellow solid which was purified by chromatography on alumina (5 g) with ether as the eluent to furnish 90 mg (84%) of **15a** as white solid. This was crystallized from ether: mp 155 °C; IR (KBr) 3605, 2945, 2880, 2860, 1745, 1685, 1600, 1470, 1455, 1380, 1285, 1100, 1050, 955, 915 cm^{-1}; UV λ_{max} 252 nm (log ε 4.07),

(24) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2555.

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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Received March 27, 1982

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

0022-3263/82/1947-5361$01.25/0