Acid-catalysed Intramolecular *C*-Alkylation in βγ-Unsaturated Diazomethyl Ketones. A New Synthetic Route to Angularly Fused Cyclobutanones, Bridged Cyclopentanones, and γ-Lactones

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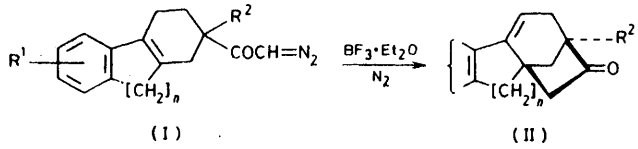
Acid-induced decomposition of rigid polycyclic βγ-unsaturated diazomethyl ketones (2a and b) and (4a and b) is shown to give, in excellent yields, the respective angularly fused unsaturated cyclobutanones (5a and b) and (6a and b) and/or the rearranged bridged hydroxycyclopentanones (7a) and (9a) depending upon the reagents, reaction conditions, and the nature of the substrates. Under certain conditions (5a) and (7a) undergo rearrangement to 3a-methyl-1,2,3,3a,6,7-hexahydropentaleno[1,6a-*a*]naphthalen-4-one (12a). The unsaturated cyclobutanones undergo stereoselective catalytic hydrogenation to the respective *trans*-angularly substituted hydrophenanthrene and hydrofluorene cyclobutanones (13a and b) and (14a and b) which on facile Bayer–Villiger oxidation produce the γ-lactones (18a and b) and (19a and b). The unsaturated cyclobutanones (5a and b) also afford the respective γ-lactones (20a and b) on oxidation with alkaline hydrogen peroxide.

DIAZO-KETONES may lead to a variety of products [1] arising either through the reactions of nucleophiles with the protonated diazocarbonyl function (diazonium or oxo-carbonium ion intermediates) or by the loss of nitrogen resulting in an oxo-carbenoid species. Intramolecular carbon–carbon bond formation of the oxocarbenoids with an appropriately situated olefinic group has been thoroughly investigated and is of great synthetic utility.[2] However, until very recently, there



R^1 = H or OMe; R^2 = H or CH_3, n = 1, 2, 3

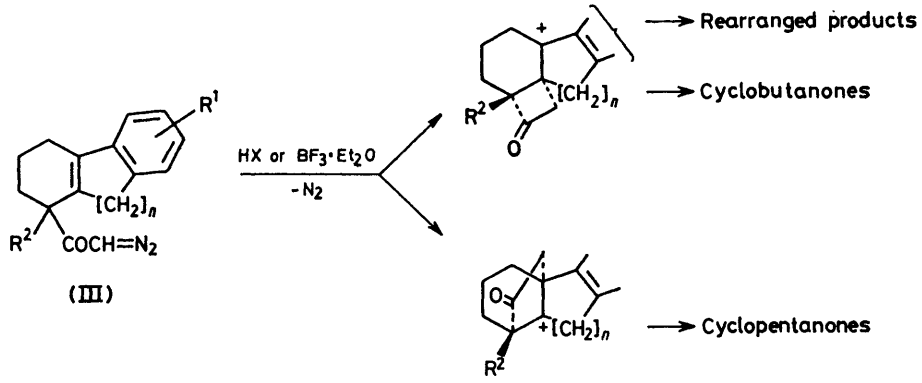
SCHEME 1

were only two recorded examples of six-membered aromatic cycloalkylations [3] involving protonated diazoketones. In the early nineteen-seventies, a new cyclopentanone-annulation reaction of synthetic potential was developed [4] for the introduction of a bicyclo[3.2.1]-octanone or a bicyclo[2.2.1]heptanone moiety into a variety of systems by the acid-catalysed intramolecular electrophilic cyclisation of γδ-unsaturated α'-diazomethyl ketones. For example, we [4b,5] and others [4c] demonstrated the usefulness of this reaction in the facile synthesis of a series of tetracyclic ketones (II) from the respective γδ-unsaturated diazo-ketones (I) by intramolecular *C*-alkylation (Scheme 1).

The elegant studies of Mander [6] have further elaborated the aryl participations in protonated diazomethylcarbonyl alkylation as a viable method for bridged- and spiro-ring annulations.

In connection with our studies on stereocontrolled angular alkylation in polycyclic systems,[7] it was of special interest to test the scope of this type of approach particularly for the rigidly held βγ-double bond proximate to the protonated diazocarbonyl function in the substrates (III) in which π-bond participation in the displacement of nitrogen may result in either four or five-membered ring formation (Scheme 2).

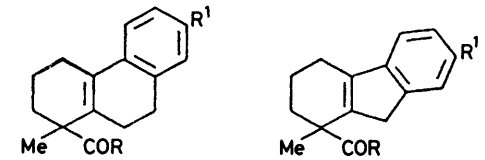
We reported in a preliminary communication [8] some results of our studies on the intramolecular alkylation of the βγ-unsaturated diazo-ketone substrates (2a and b) and (4a and b) leading in excellent yields to the respective angularly fused unsaturated cyclobutanones (5a and b)



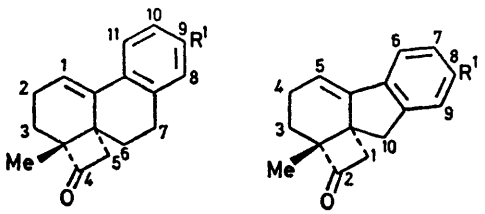
R^1 = H or OMe; R^2 = H or Me; n = 1, 2

SCHEME 2

and (6a and b). The usefulness of this simple new cyclobutanone annulation * reaction for stereospecific angular alkylation [10] has also been demonstrated. Subsequent to our report, Smith [11] studied acid-catalysed cyclisations in a few relatively flexible βγ-unsaturated diazomethyl ketones using boron trifluoride–ether in nitromethane and found the respective cyclopentenones to be the only annulation products. After considerable experimentation we have now discovered that it is not the structure of the substrate alone [11a] which controls the nature of the products in such cyclisations but that the choice of the acid-catalyst and solvent is also critical. The present paper constitutes a detailed account of our



(1) R = OH (3) R = OH
(2) R = CHN_2 (4) R = CHN_2



(5) (6)

a, R^1 = H; b, R^1 = OMe

studies with the βγ-unsaturated diazomethyl ketones (2a and b) and (4a and b), along with the development of a new synthetic route to angularly fused cyclobutanones, γ-lactones, a few bridged cyclopentanones, and substituted tricyclo[7.3.0.$0^{1,6}$]dodecane systems.

RESULTS AND DISCUSSION

Preparation and Cyclisations of the Diazo-ketones.—The diazo-ketone substrates (2a), (2b), (4a), and (4b) were prepared [5a] through the usual sequence of reactions (see Experimental section) from the respective known acids (1a),[12] (1b),[13] (3a),[14] and (3b).[15] Our initial cyclisation studies were conducted with the easily accessible diazo-ketone (2a).

Treatment of an ice-cold dilute solution of (2a) in chloroform (containing ethanol stabiliser) with an excess of 70% perchloric acid ($HClO_4$) or 48% tetrafluoroboric acid (HBF_4) gave brisk evolution of nitrogen and afforded the crystalline unsaturated cyclobutanone (5a) in virtually quantitative yield. Repetition of the reaction with $HClO_4$ in benzene or 98% H_2SO_4 in $CHCl_3$ gave (5a) as the only isolable product in 92 and 82% yields respectively. The spectral and analytical data of (5a) are consistent with the assigned structure. The i.r. spectrum displayed the expected cyclobutanone C=O peak at 1 765 cm^{-1} and a styrenoid chromophore in the u.v. spectrum. In the ^1H n.m.r. spectrum the methyl singlet appeared at δ 1.20 and the vinyl proton as a broad triplet at δ 6.37 (J 4 Hz).

In contrast, when the diazo-ketone (2a) was subjected to cyclisation with HBF_4 or $BF_3{\cdot}Et_2O$ in dry nitromethane [11] a mixture of the cyclobutanone (5a) and a bridged hydroxycyclopentanone was obtained [ratio 1 : 9 (g.l.c.)] in over 90% yield. Chromatography of the mixture gave a crystalline hydroxy-ketone. The i.r. spectrum of this exhibited strong absorptions at 3 485 and 1 725 cm^{-1} consistent with the presence of a hydroxy and a cyclopentanone chromophore, and its ^1H n.m.r. spectrum showed a methyl singlet at δ 1.46 and a tertiary OH proton singlet at δ 1.76 (slowly exchangeable with D_2O). The complete structure and stereochemistry of this ketone has been determined as (7a) by X-ray crystal structure analysis carried out at the X-ray Laboratory of the Presidency College, Calcutta, by Basak and Kundu Das.† A perspective drawing of the final X-ray model of (7a) is shown in Figure 1. Hydrogen atoms are omitted for clarity and the crystal is racemic so the *enantiomer* shown is an arbitrary choice.

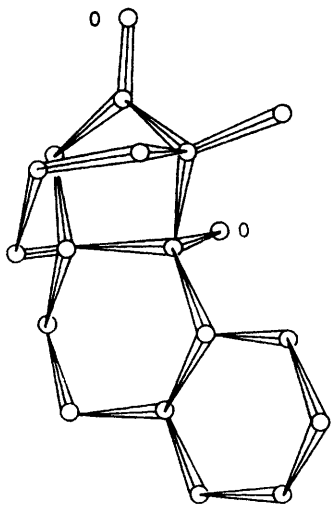


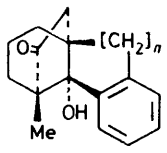
FIGURE 1 Perspective view of the bridged hydroxycyclopentanone (7a)

The methoxy-analogue (2b) on cyclisation with $HClO_4$ or HBF_4 in $CHCl_3$ afforded the unsaturated cyclobutanone (5b) in excellent yield. Reaction of (2b) with HBF_4 or $BF_3{\cdot}Et_2O$ in nitromethane gave a mixture of products consisting of 68—80% of (5b) along with at least two other components (g.l.c.) which were not characterised.

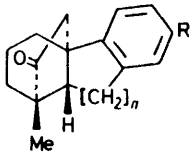
* For application of this reaction for the preparation of a D-norsteroidal skeleton see ref. 9.

† B. S. Basak and S. C. Kundu Das, in preparation. We thank Professor Basak for forwarding us the perspective drawing of the final X-ray model of (7a).

Unlike the hydrophenanthrene analogues, cyclisation of the hydrofluorene diazo-ketone (4a) with $HClO_4$ in $CHCl_3$ gave the respective unsaturated cyclobutanone (6a) only in 56% yield along with other uncharacterised products. The lower yield of (6a) was due to its apparent instability in the strongly acidic medium. However, by



(7a) $n = 2$
(9a) $n = 1$



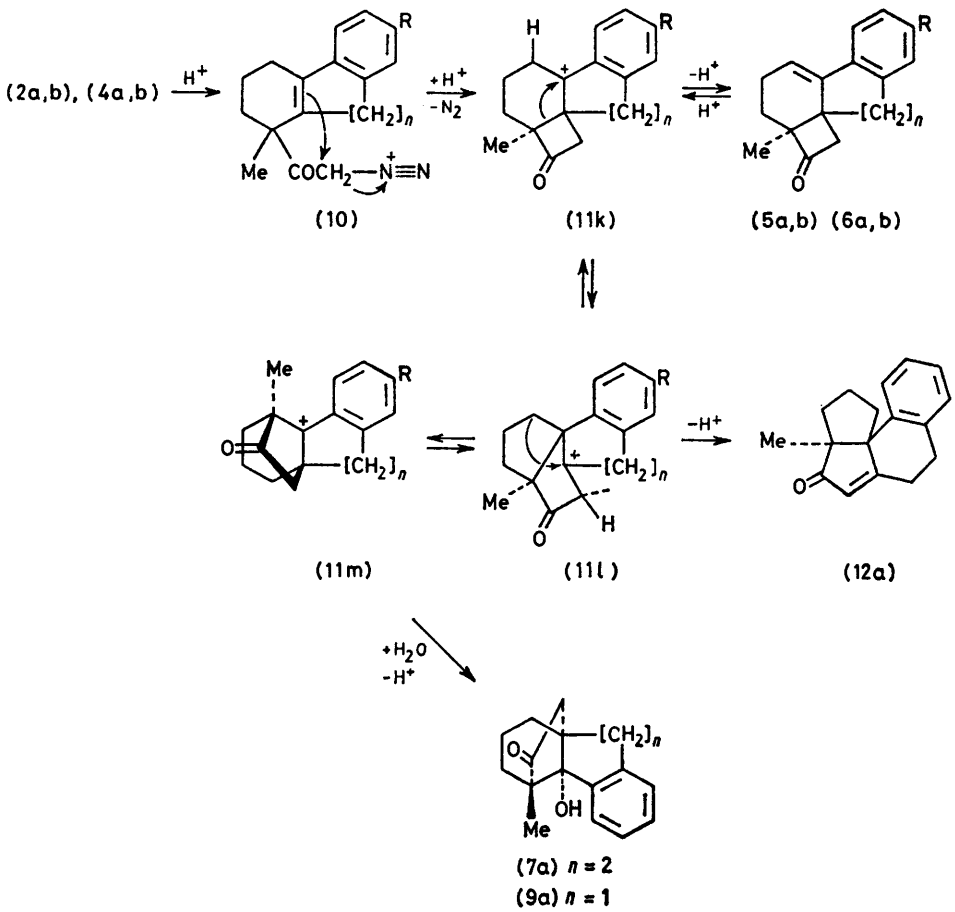
(8a) R = H, $n = 2$
(8b) R = OMe, $n = 2$
(17a) R = H, $n = 1$
(17b) R = OMe, $n = 1$

using less than one molar equivalent of $HClO_4$ in trifluoroacetic acid as the catalyst in dry $CHCl_3$ solution in a homogeneous condition, the diazo-ketone (4a) afforded the desired cyclobutanone (6a) in 84% yield. The dramatic effect of the reagent in the cyclisation of (4a) was again revealed in the formation of the respective hydroxycyclopentanone (9a) in excellent yield, with HBF_4 or $BF_3{\cdot}Et_2O$ in nitromethane. Its i.r. spectrum showed strong bands at 3 420 and 1 740 cm^{-1} consistent with the presence of OH and a cyclopentanone moiety. The ^1H n.m.r. spectrum exhibited a methyl singlet at δ 1.33 and a tertiary OH singlet at δ 1.68 (exchangeable with D_2O). The benzylic C-9 methylene protons appeared as an AB quartet at δ_A 2.73, δ_B 2.90 (J 16 Hz). The structure and stereochemistry of (9a) has been tentatively assigned from its mode of formation by analogy with the respective hydrophenanthrene compound (7a).

Finally, the methoxyhydrofluorene diazo-ketone (4b) gave the best yield of the respective unsaturated cyclobutanone (6b) with HBF_4 in $CHCl_3$. In this case both $HClO_4$ and $HClO_4$–trifluoroacetic acid in $CHCl_3$ gave (6b) in considerably lower yields.

Interestingly, reaction of the diazo-ketones (2a and b) and (4a and b) in $CHCl_3$ with 57% HI under Wolfrom-reduction conditions,[16] a reaction which has been widely used for the conversion of diazomethyl ketones into the respective methyl ketones, again produced in each case a mixture of products from which the respective cyclobutanones (5a and b) and (6a and b) could be isolated in 40—60% yields by chromatography.

The optimum experimental conditions for the formation of the cyclic ketones from the unsaturated diazomethyl ketones we feel have to be determined individu-



SCHEME 3

ally for each case. From a large number of experiments, it can so far be generalised that $HClO_4$ or HBF_4 in $CHCl_3$ are the best catalyst and solvent system for the cyclobutanone formation, whereas a highly polar solvent such as nitromethane with HBF_4 or $BF_3{\cdot}Et_2O$ as catalyst is suitable for the cyclopentanone [11] annulation.

The mechanistic pathways for the cyclisation of (2a and b) and (4a and b) with protic acids possibly involve, in the first step, a rate-determining protonation [17] of the sterically hindered diazocarbonyl group to form the charged species (10) (Scheme 3) followed by its intramolecular π-bond participation in the displacement of nitrogen resulting in the tertiary carbo-cations (11k).

In the case of less polar solvents such as $CHCl_3$ or benzene, the cyclisation proceeds through the benzyl cation (11k) which on deprotonation leads to the respective strained unsaturated cyclobutanones. In the polar ambident solvent nitromethane, the strained cyclobutanone cation (11k) undergoes bond rearrangement through the cyclopentanone cation (11l) leading ultimately to the most stable tertiary benzylic cation (11m) by complexation with the solvent. This on subsequent attack of water * results in the respective hydroxy-cyclopentanones (7a) and (9a). Since no significant differences in results were obtained in the cyclisations of (2a) and (4a) by substitution of aqueous HBF_4 with $BF_3{\cdot}Et_2O$ in nitromethane, we favour, in agreement with Mander,[6a] a similar mechanism for the latter case.

The possibility of reversibility in the carbo-cations (11k), (11l), and (11m) cannot be ruled out. The presence of carbo-cations such as (11l) in the equilibrium has been confirmed by isolation of the tetracyclic unsaturated ketone (12a) [18] in excellent yield by rearrangement of the hydroxy-cyclopentanone (7a) with toluene-*p*-sulphonic acid in boiling benzene. Under similar conditions the cyclobutanone (5a) afforded a mixture of (5a) and (12a) in a ratio of *ca.* 1 : 1 along with an equal amount of uncharacterised material. Interestingly, direct cyclisation of the diazo-ketone (2a) in dry chloroform with 48% aqueous HBF_4 gave a mixture of (5a), (7a), and (12a) in a ratio of *ca.* 38 : 50 : 12. The structure of (12a) initially assigned from the spectral data (see Experimental section) has been confirmed by an *X*-ray crystal structure analysis carried out by Das *et al.* † at the *X*-ray Laboratory of the Presidency College, Calcutta. A perspective drawing of the final *X*-ray model of (12a) is shown in Figure 2.

Specifically, the difference in the nature of the cyclisation products between the demethoxy-ketones (2a) and (4a) and the respective methoxy-analogues (2b) and (4b), giving rise to the corresponding cyclopentanones (7a) and (9a), and the cyclobutanones (5b) and (6b) as the major products in HBF_4–nitromethane,

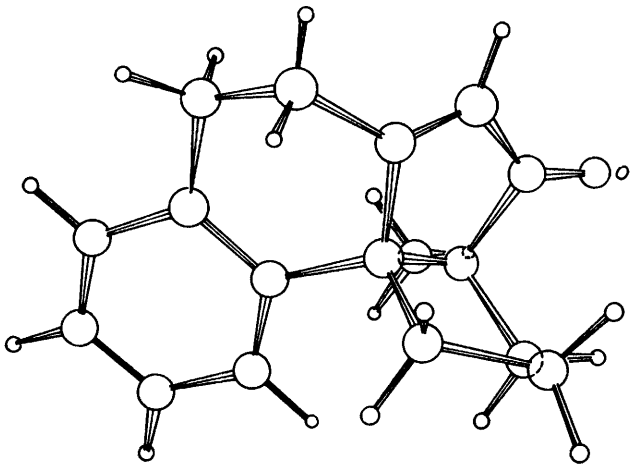


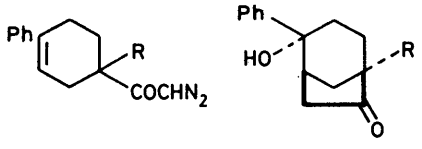
FIGURE 2 Perspective view of the tetracyclic unsaturated ketone (12a)

reflects the importance of the relative stabilities of the intermediate benzylic cation (11k; R = H) and *p*-methoxyphenyl cation (11k; R = OMe) with respect to the corresponding cyclopentanone cations (11l) in determining the course of cyclisation.

Synthesis of the Saturated Cyclobutanones (13a *and* b) *and* (14a *and* b), *and of the γ-Lactones* (18a *and* b) *and* (19a *and* b).—Catalytic hydrogenation of the styrenoid bond in the unsaturated cyclobutanones (5b) and (6b) in the presence of 10% Pd–C catalyst in ethanol proceeded with high stereoselectivity affording the respective crystalline saturated cyclobutanones (13b) and (14b) in excellent yield. ^1H N.m.r. and t.l.c. properties of these ketones indicated their stereo-homogeneity. Under the same conditions, hydrogenation of the demethoxy-analogues (5a) and (6a), however, produced a mixture of the respective diastereoisomers (13a) and (15a) (*ca.* 9 : 1) and (14a) and (16a) (*ca.* 4 : 1) as revealed from the ^1H n.m.r. spectra of the crude reduction products. The major isomers (13a) and (14a) could be separated from each of these mixtures by crystallisation. The assigned stereochemistry at the chiral centres at C-11b in (13a and b) and at C-5a in (14a and b) followed from their subsequent transformations into the respective bridged cyclopentanones (8a and b) and (17a and b) through a novel rearrangement [10a] using triethyloxonium tetrafluoroborate.

With the availability of the angularly fused cyclobutanones [19] in a simple and high-yield route from the readily accessible starting acids, their synthetic applications for the introduction of functionalised angular

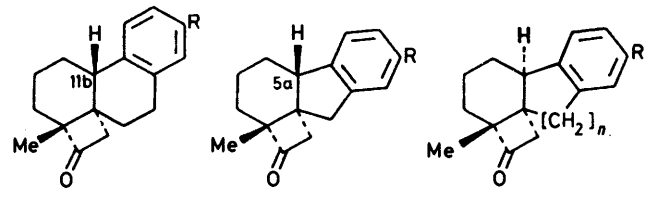
* Cyclisations of the γδ-unsaturated diazomethyl ketones (i; R = H or Me) with aqueous HBF_4 (48%) in nitromethane also



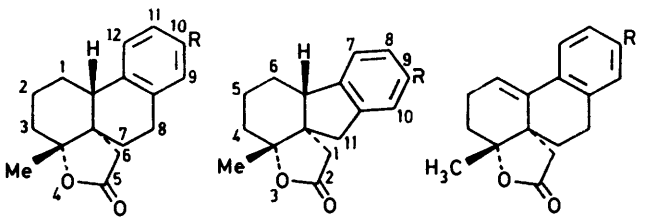
produce the respective hydroxy-ketones (ii) in moderate yields (ref. 5*b*).

† S. Roychowdhury, S. Chaudhury, D. N. Lahiri, and B. N. Das, in preparation. We thank Dr. Das for forwarding us the perspective drawing of the final *X*-ray model of (12a).

substituents in the hydrophenanthrene and hydrofluorene systems were next investigated. It has been well established that the high strain energy [20] in cyclobutanones provides a driving force for many transformations: particularly, Baeyer–Villiger oxidation occurs extremely readily in the cyclobutanones. Accordingly, oxidation of the saturated cyclobutanones (13a and b) and (14a and b) in methylene chloride with *m*-chloroperbenzoic acid [21] in the presence of a catalytic amount of toluene-*p*-sulphonic acid or with 30% alkaline hydrogen peroxide [20a,22] afforded in each case the respective γ-lactones (18a and b) and (19a and b) in excellent yields.



(13) (14) (15) $n=2$ (16) $n=1$



(18) (19) (20)

a, R = H; b, R = OMe

Since the use of basic hydrogen peroxide as the Baeyer–Villiger oxidation reagent allows the presence of a double bond, which normally interferes with the standard peracid methods, we also studied this reaction for the unsaturated cyclobutanones (5a and b) and (6a and b). Oxidation of (5a) and (5b) with alkaline hydrogen peroxide gave the respective styrenoid γ-lactones (20a) and (20b) (88 and 65% yield respectively), which on catalytic hydrogenation afforded the γ-lactones (18a) and (18b) as the sole products. Attempted alkaline hydrogen peroxide oxidation of the relatively strained unsaturated cyclobutanones (6a) and (6b), however, produced intractable mixtures consisting of considerable amounts of acidic products. In all the oxidative reactions of the cyclobutanones, the rearrangements by alkaline hydrogen peroxide proceeded completely analogously to the *m*-chloroperbenzoic-acid-induced reactions. These data indicate the same order of migratory preference, namely tertiary > secondary, as found for the peracid oxidations in other cases.[20,23]

The regioselectivity in intramolecular acid-catalysed *C*-alkylation reactions in the rigid βγ-unsaturated diazomethyl ketones, reported in this paper, depends mainly upon the reaction conditions and the nature of the substrates. This route provides a simple and efficient method for annulation of cyclobutanones and cyclopentanones. The importance of the angularly fused cyclobutanones relating to the stereocontrolled synthesis of certain diterpene alkaloids and C_{20}-gibberellins has already been described.[24] The facile oxidative rearrangement of the cyclobutanones also constitutes a simple route for the stereocontrolled introduction of an angularly fused γ-lactone moiety in polycyclic systems, some of which are suitable intermediates for the synthesis of clerodane diterpenoids.[25] Work in these directions is being pursued in these laboratories. In essence, the most significant outcome of the present studies is the development of a new simple stereocontrolled angular alkylation for polycyclic systems,[26] which has attracted endless areas of research in synthetic organic chemistry.

EXPERIMENTAL

Melting points were taken in open capillary tubes in a sulphuric-acid bath. I.r. spectra were recorded on Perkin-Elmer model 21 and Beckman Acculab models 4 and 20a spectrometers for solutions in chloroform. U.v. spectra were recorded on a Beckman DU spectrophotometer for solutions in 95% ethanol. ^{1}H N.m.r. spectra were recorded at 60 MHz on Varian Associates models T-60A or A-60 spectrometers for solutions in $CDCl_3$ with tetramethylsilane as internal standard. Analytical g.l.c. was performed on a Hewlett Packard model 5730A chromatograph equipped with a flame-ionisation detector (20 × 1/8 in, 10% UCW-982 at 185 °C). Elemental analyses were performed by Mrs. C. Dutta of this laboratory and by Mr. B. Bhattacharyya of Jadavpur University, Calcutta.

Unless otherwise mentioned, chloroform used in all reactions was Proanalysis (E. Merck) containing ethanol as stabiliser. Dry chloroform was prepared immediately before use, by distillation over phosphorus pentaoxide. Nitromethane was distilled just before use. Aqueous perchloric acid ($HClO_4$), tetrafluoroboric acid (HBF_4), and hydriodic acid (HI) used were 70, 48, and 57% solutions respectively. Column chromatography was performed on neutral alumina using aluminium oxide ' Standardised for chromatographic analysis acc. to Brockmann ' (M/s. Sarabhai M. Chemicals) (30 g of Al_2O_3 per g of compound). Petroleum and light petroleum refer to the fractions of b.p. 60—80 and 40—60 °C, respectively.

Preparation of Diazo-ketones.—*1-Diazoacetyl-1-methyl-1,2,3,4,9,10-hexahydrophenanthrene* (2a). To a solution of the acid (1a) [14] (5 g, 20.63 mmol) in dry methanol (75 ml) was added dropwise a 10% solution of sodium methoxide in methanol until the solution became alkaline (phenolphthalein). Methanol was distilled out from the alkaline solution. The last trace of methanol was removed by azeotropic distillation (twice) with dry benzene under reduced pressure. The solid residue was finally dried in vacuum (100 °C at 10 mmHg) for 1 h. To a stirred ice-cold suspension of this sodium salt in dry benzene (100 ml) containing pyridine (0.5 ml, 5.81 mmol) was added dropwise oxalyl chloride (5.5 ml, 64.13 mmol). The mixture was kept at room temperature for 30 min and finally warmed to 60 °C for 1 h. The precipitated salt was filtered off and the filtrate was concentrated under reduced pressure. The brown semi-solid residue thus obtained was dissolved in anhydrous ether (100 ml) and added over 1 h to ice-cold and magnetically stirred ethereal diazomethane [from *N*-methylnitrosourea (10.3 g, 100 mmol)] containing triethyl-

amine (2.93 ml, 21 mmol) and left overnight. The precipitated material was filtered off. Evaporation of ether from the filtrate afforded a yellow gummy solid which was dissolved in dry ether (100 ml). The solution was filtered through a short wide column of neutral alumina (20 g) to afford the diazo-ketone (2a) as a light yellow solid (5.2 g, 95%). Recrystallisation of a portion of this material from ether–light petroleum afforded an analytically pure specimen as pale yellow *rosettes*, m.p. 104 °C (decomp.) (Found: C, 76.55; H, 6.85. $C_{17}H_{18}N_2O$ requires C, 76.66; H, 6.81%); $\nu_{max.}$ 2 130, 1 610, and 1 595 cm^{-1}.

1-*Diazoacetyl*-7-*methoxy*-1-*methyl*-1,2,3,4,9,10-*hexahydrophenanthrene* (2b). Following the general procedure, the acid (1b) [13] (800 mg, 2.93 mmol) was converted into the *diazo-ketone* (2b) (850 mg, 98%), a pale yellow solid, m.p. 96—97 °C (decomp.) (Found: C, 73.0; H, 6.8. $C_{18}H_{20}N_2O_2$ requires C, 72.95; H, 6.80%); $\nu_{max.}$ 2 115 and 1 630 cm^{-1}.

1-*Diazoacetyl*-1-*methyl*-1,2,3,4-*tetrahydrofluorene* (4a). The acid (3a) [14] (2 g, 8.76 mmol) was converted by the general procedure into the *diazo-ketone* (4a) (2.0 g, 90%), a light yellow solid, m.p. 103 °C (decomp.) (from ether–light petroleum) (Found: C, 76.3; H, 6.45. $C_{16}H_{16}N_2O$ requires C, 76.16; H, 6.39%); $\nu_{max.}$ 2 125 and 1 610 cm^{-1}.

1-*Diazoacetyl*-7-*methoxy*-1-*methyl*-1,2,3,4-*tetrahydrofluorene* (4b). Following the general procedure, the acid (3b) [15] (1.0 g, 3.87 mmol) was converted into the diazo-ketone (4b) (1.0 g, 92%) which was obtained as a light yellow low-melting solid; $\nu_{max.}$ 2 125 and 1 630 cm^{-1}.

Acid-catalysed Cyclisation Studies of the Diazo-ketones (2a *and* b) *and* (4a *and* b) *with Various Catalysts and Solvents*.—(a) *General procedure for* (2a) *with* $HClO_4$ *in* $CHCl_3$. *Preparation of the unsaturated cyclobutanone* (5a). To a cold (*ca.* 5 °C) magnetically stirred solution of the diazo-ketone (2a) (200 mg, 0.75 mmol) in $CHCl_3$ (100 ml) was added dropwise 70% aqueous $HClO_4$ (0.4 ml, 4.67 mmol), when immediate evolution of nitrogen was observed. The mixture was stirred in the cold for 1 h followed by an additional 30 min at 20—25 °C. The light brown 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 a light brown solid which, on filtration through a short wide column of neutral alumina (petroleum as eluant), afforded 3a-*methyl*-3,3a,6,7-*tetrahydro*-2H-*cyclobuta*[d]*phenanthren*-4(5H)-*one* (5a) (177 mg, 99%). A sample, crystallised from petroleum, had m.p. 91—92 °C (Found: C, 85.6; H, 7.65. $C_{17}H_{18}O$ requires C, 85.67; H, 7.61%); $\nu_{max.}$ 1 765 and 1 600 cm^{-1}; $\lambda_{max.}$ 255 nm (log ε 4.07); δ 1.20 (s, 3 H, CCH_3), 1.28—2.0 (m, 4 H, methylenes), 2.30 (m, 2 H, CH_2–CH=C<), 2.85—3.06 (m, 4 H, $COCH_2$ and $ArCH_2$), 6.40br (t, *J* 4 Hz, 1 H, CH_2CH=C<), 7.10—7.15 (m, 3 H, ArH), and 7.45—7.65 (m, 1 H, ArH); *m/e* 238 (M^+, 100%), 223 (45), 210 (89), 196 (50), 195 (50), and 181 (36).

(b) Repeating the reaction of the diazo-ketone (2a) (200 mg, 0.75 mmol) in benzene (100 ml) with $HClO_4$ (0.4 ml, 4.67 mmol) under the above conditions gave 92% of the cyclobutanone (5a), m.p. and mixed m.p. 91—92 °C.

(c) *General procedure for diazo-ketone* (2a) *with* HBF_4 *in* $CHCl_3$. To an ice-cold stirred solution of the diazo-ketone (2a) (200 mg, 0.75 mmol) in $CHCl_3$ (70 ml) was added dropwise aqueous HBF_4 (1.0 ml, 7.70 mmol). The mixture was stirred in the cold for 1 h and then for 30 min at room temperature. The usual work-up and chromatography afforded 170 mg (95%) of the cyclobutanone (5a), m.p. and mixed m.p. 90—92 °C with the sample described above.

(d) *Diazo-ketone* (2a) *with* H_2SO_4 *in* $CHCl_3$. To an ice-cold stirred solution of (2a) (200 mg, 0.75 mmol) in $CHCl_3$ (20 ml) was added dropwise a solution of H_2SO_4 (98%; 0.2 ml, 3.66 mmol) in $CHCl_3$ (20 ml). The mixture was stirred in the cold for 30 min and then for an additional 30 min at room temperature. Usual work-up followed by column chromatography of the crude product on neutral alumina afforded the cyclobutanone (5a) (146 mg, 82%), m.p. 90—92 °C, alone or mixed with an authentic sample.

(e) *Diazo-ketone* (2a) *with* HI *in* $CHCl_3$. To an ice-cold stirred solution of (2a) (200 mg, 0.75 mmol) in $CHCl_3$ (20 ml) was added dropwise freshly distilled HI (57%; 0.4 ml, 3.03 mmol). The mixture was stirred in the cold for 30 min followed by an additional 30 min at room temperature. The dark brown product obtained by usual work-up showed $\nu_{max.}$ 1 765 and 1 695 cm^{-1}. Chromatography on neutral alumina afforded the cyclobutanone (5a) (108 mg, 60%), m.p. and mixed m.p. 90—92 °C.

(f) *Diazo-ketone* (2a) *with* HBF_4 *in nitromethane*. *Preparation of the bridged hydroxy-ketone* (7a). To a stirred solution of the diazo-ketone (2a) (500 mg, 1.87 mmol) in nitromethane (50 ml) at room temperature (25—30 °C) was added dropwise 48% of aqueous HBF_4 (0.5 ml, 3.85 mmol) during 1—2 min. Immediately, rapid evolution of nitrogen with development of a green fluorescence was observed. After stirring for 2 min the reaction mixture was diluted with water. The organic phase was separated and dried (Na_2SO_4). Nitromethane was recovered by distillation under reduced pressure and the residual light yellow solid (450 mg, 89%) was found to be a mixture of (5a) and (7a) in the ratio 1 : 9 (g.l.c.). Careful chromatography of this mixture on neutral alumina afforded, with petroleum as eluant, the cyclobutanone (5a) (40 mg, 9%), m.p. and mixed m.p. 90—92 °C, and, with petroleum–diethyl ether (1 : 1 v/v) to pure ether as eluant, the cyclopentanone (7a) (310 mg, 64%), m.p. 130 °C. Crystallisation from ether afforded pure 4aα-*hydroxy*-4β-*methyl*, 1,2,3,4,4a,9,10,10a-*octahydro*-4,10a-*ethanophenanthren*-12-*one* (7a), m.p. 131 °C (Found: C, 79.6; H, 7.65. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%); $\nu_{max.}$ (KBr) 3 485, 2 930, 1 725, 1 435, 1 370, and 1 020 cm^{-1}; δ 1.46 (s, 3 H, CCH_3), 1.76 (s, 1 H, OH, exchangeable with D_2O), 1.55—2.0 (complex m, 7 H), 2.1 (δ_A) and 2.44 (δ_B) (ABq, 2 H, *J* 18 Hz, $COCH_2$, overlaps with signal for 1 H), 2.9—3.1 (m, 2 H, $ArCH_2$), and 7.1—7.5 (m, 4 H, Ar*H*); *m/e* 256 (M^+, 29%), 238 (5), 197 (83), 196 (99), 159 (100), 141 (58), 117 (41), and 115 (45); δ_C ($CDCl_3$) 219.9, 137.0, 136.9, 129.9, 127.3, 125.5, 125.3, 79.6, 55.8, 45.6, 41.2, 34.3, 32.1, 26.7, 25.2, 19.0, and 16.4.

(g) *Diazo-ketone* (2a) *with* $BF_3{\cdot}Et_2O$ *in Nitromethane*. A solution of the diazo-ketone (2a) (200 mg, 0.75 mmol) in nitromethane (20 ml) was treated with a 10% solution of $BF_3{\cdot}Et_2O$ (1.1 ml, 0.80 mmol) in nitromethane under the conditions described in (f). The reaction mixture was decomposed by addition of saturated aqueous NH_4Cl and worked up in the usual way. The light yellow solid (180 mg, 90%) obtained was a mixture of (5a) and (7a) in the ratio of 1 : 9 (g.l.c.).

Rearrangement of the cyclopentanone (7a) *to* (±)-3a-*methyl*-1,2,3,3a,6,7-*hexahydropentaleno*[6a,1-a]*naphthalen*-4-*one* (12a). A solution of the hydroxy-ketone (7a) (200 mg, 0.78 mmol) in benzene (100 ml) was refluxed with a catalytic amount of $TsOH{\cdot}H_2O$ (50 mg) for 4 h under nitrogen.

After washing the organic layer successively with water, 5% aqueous Na_2CO_3, and water, the solvent was removed under reduced pressure to afford the *ketone* (12a) as a light yellow solid (170 mg, 94%), m.p. 88—92 °C. An analytical sample was prepared by filtration over a short wide column of neutral alumina using petroleum as solvent and subsequent recrystallisation from petroleum, m.p. 96 °C (Found: C, 85.55; H, 7.7. $C_{17}H_{18}O$ requires C, 85.67; H, 7.61%); $\nu_{max.}$ (KBr) 1 690, 1 625, 1 370, 860, and 760 cm^{-1}; $\lambda_{max.}$ 230 nm (log ε 4.2); δ (270 MHz) 0.89 (s, 3, CCH_3), 1.24—2.29 (complex m, 6 H, methylenes), 2.67—3.14 (complex m, 4 H, $ArCH_2$ and $COCH{=}C{-}CH_2$), 6.01 (d, 1 H, *J* 1.41 Hz, $COCH{=}C{-}CH_2$), and 7.08—7.27 (4 H, m, ArH); *m/e* 238 (M^+, 100%), 223 (50), 210 (86.8), 196 (39.5), 195 (40), 182 (25), 181 (31.5) 167 (28), and 165 (26); δ_C ($CDCl_3$) 213.6, 183.2, 140.8, 136.0, 129.4, 128.3, 126.2, 125.8, 125.3, 61.0, 60.1, 44.9, 38.6, 32.2, 27.1, 23.2, and 21.0.

Rearrangement of the cyclobutanone (5a) *with* TsOH *in benzene*. To a solution of the unsaturated cyclobutanone (5a) (100 mg, 0.42 mmol) in dry benzene (50 ml) was added a catalytic amount of $TsOH{\cdot}H_2O$ (100 mg) and the mixture was refluxed under nitrogen for 9 h. Usual work-up followed by removal of the solvent afforded a light yellow gum (100 mg), which was found to be a mixture of (5a), (12a), and an uncharacterised compound in the ratio 1 : 1 : 1 (g.l.c.).

Cyclisation of the diazo-ketone (2a) *in ethanol-free* $CHCl_3$ *with* HBF_4. To a cold (5 °C) stirred solution of the diazo-ketone (2a) (200 mg, 0.75 mmol) in dry $CHCl_3$ was added 48% aqueous HBF_4 (0.5 ml, 3.85 mmol). The mixture was stirred in the cold for 1 h and then for 30 min at 20—25 °C. The light brown solution was washed successively with water, 5% aqueous Na_2CO_3, and water and dried (Na_2SO_4). Evaporation under reduced pressure afforded as a light brown gum (185 mg) a mixture of (5a), (7a), and (12a), in the ratio 38 : 50 : 12 (g.l.c.).

Cyclisation of the diazo-ketone (2b). (a) *With* $HClO_4$ *in* $CHCl_3$. *Preparation of the unsaturated cyclobutanone* (5b). To an ice-cold stirred solution of the diazo-ketone (2b) (300 mg, 1.01 mmol) in $CHCl_3$ (100 ml), 70% aqueous $HClO_4$ (0.6 ml, 7.0 mmol) was added. It was stirred in the cold for 1 h and worked up in the usual way to afford a light yellow gummy solid (280 mg). Chromatography on neutral alumina using petroleum as eluant afforded 9-*methoxy*-3a-*methyl*-3,3a,6,7-*tetrahydro*-2H-*cyclobuta*[d]-*phenanthren*-4(5H)-*one* (5b) (240 mg, 88%) which crystallised from light petroleum as white rosettes, m.p. 102—103 °C (Found: C, 80.6; H, 7.65. $C_{18}H_{20}O_2$ requires C, 80.56; H, 7.51%); $\nu_{max.}$ 1 765 and 1 600 cm^{-1}; $\lambda_{max.}$ 262 nm (log ε 4.24); δ 1.20 (s, 3, CCH_3), 1.21—2.0 (m, 4 H, methylenes), 2.1—2.55 (m, 2 H, $CH_2CH{=}C\langle$), 2.90br [(s, $COCH_2$) overlapped with 2.61—3.20 (m, $ArCH_2$) (total 4 H)], 3.78 (s, 3 H, OCH_3), 6.2br (t, *J* 4 Hz, 1 H, $CH_2CH{=}C\langle$), 6.61br (s, partly overlapped with dd, 8-H), 6.77 (d, $J_{8,10}$ 3 Hz, 10-H), and 7.45br (d, $J_{6,11}$ 9 Hz, 1 H, 11-H).

(b) *With* HBF_4 *in* $CHCl_3$. A solution of the diazo-ketone (2b) (100 mg, 0.336 mmol) in $CHCl_3$ (35 ml) was treated with aqueous HBF_4 (0.5 ml, 3.85 mmol) to afford a light yellow solid (90 mg) consisting only (g.l.c.) of the cyclobutanone (5b). Column chromatography afforded (5b) (80 mg, 88%), m.p. and mixed m.p. 101—103 °C.

(c) *With* HBF_4 *in nitromethane*. A solution of the diazo-ketone (2b) (100 mg, 0.336 mmol) in nitromethane (10 ml) was treated at room temperature with 48% aqueous HBF_4 (0.1 ml, 0.77 mmol) for 1—2 min. Usual work-up afforded a light yellow gum; $\nu_{max.}$ 1 760 and 1 730 cm^{-1}. G.l.c. showed the presence of (5b) (60%) with three other unidentified components Chromatography afforded the pure cyclobutanone (5b) (41 mg, 45%).

(d) *With* $BF_3{\cdot}Et_2O$ *in nitromethane*. A solution of the diazo-ketone (2b) (100 mg, 0.336 mmol) in nitromethane (10 ml) was treated with a 10% solution of $BF_3{\cdot}Et_2O$ (0.5 ml, 0.365 mmol) in nitromethane under the conditions described in (g) for (2a). Decomposition of the reaction mixture by saturated aqueous NH_4Cl followed by usual work-up afforded a light yellow gum (90 mg, 91%); $\nu_{max.}$ 1 760 and 1 730 cm^{-1}. G.l.c. showed the presence of (5b) (80%) with three other unidentified components. The pure cyclobutanone (5b) (64 mg, 70%) was obtained by column chromatography on neutral alumina.

(e) *With* HI *in* $CHCl_3$. A solution of the diazo-ketone (2b) (500 mg, 1.69 mmol) in $CHCl_3$ (20 ml) was treated with 57% HI (1.5 ml, 11.4 mmol) to afford a brown gum; $\nu_{max.}$ 1 765 and 1 695 cm^{-1}. Chromatography afforded the cyclobutanone (5b) (231 mg, 51%), m.p. and mixed m.p. 101—103 °C.

Cyclisation of the diazo-ketone (4a). (a) *With* $HClO_4$ *in* $CHCl_3$. *Preparation of the unsaturated cyclobutanone* (6a). To an ice-cold stirred solution of the diazo-ketone (4a) (200 mg, 0.793 mmol) in $CHCl_3$ (100 ml) was added dropwise 70% aqueous $HClO_4$ (0.4 ml, 4.67 mmol) and the mixture was stirred in the cold for 1 h. Usual work-up afforded a yellow oil, $\nu_{max.}$ (film) 1 765, 1 730, and 1 600 cm^{-1}. The crude product was carefully chromatographed on neutral alumina. Elution with petroleum afforded a colourless oil which solidified on keeping in an ice-box (99 mg, 56%), $\nu_{max.}$ 1 768 and 1 600 cm^{-1}. A sample was recrystallised from light petroleum to afford 2a-*methyl*-2a,3,4,10-*tetrahydrocyclobuta*[j]*fluoren*-2(1H)-*one* (6a) as rectangular plates, m.p. 77—78 °C (Found: C, 85.5; H, 7.3. $C_{16}H_{16}O$ requires C, 85.68; H, 7.19%); $\lambda_{max.}$ 255 and 290 nm (log ε 4.12 and 3.66); δ 1.30 (s, 3 H, CCH_3), 1.38—2.75 (m, 4 H, CH_2 and $CH_2CH{=}C\langle$), 2.8—3.3 (complex, m, 4 H, $COCH_2$ and $ArCH_2$), 6.26br (t, *J* 5 Hz, 1 H, $CH{=}C\langle$), and 7.26 (m, 4 H, ArH); *m/e* 224 (M^+, 13%), 182 (86), 167 (100), 165 (61), 152 (43), 128 (40), and 115 (66). The remaining material could not be purified.

(b) *With trifluoroacetic acid*–$HClO_4$ *in dry* $CHCl_3$. To an ice-cold stirred solution of the diazo-ketone (4a) (940 mg, 3.7 mmol) in dry $CHCl_3$ (130 ml) was added dropwise a mixture of trifluoroacetic acid (2 ml, 2.6 mmol) and $HClO_4$ (0.2 ml, 2.34 mmol) in $CHCl_3$ (30 ml) over 5 min. The mixture was kept at 0 °C for an additional 10 min and then washed repeatedly with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to afford a light brown oil. Chromatography of this material afforded the cyclobutanone (6a) (700 mg, 84%) as a colourless oil which solidified on keeping in an ice-box. Crystallisation from light petroleum afforded a pure sample, m.p. and mixed m.p. 77—78 °C with the sample obtained in (a).

(c) *With* HBF_4 *in nitromethane*. *Preparation of the bridged hydroxycyclopentanone* (9a). To a stirred solution of the diazo-ketone (4a) (500 mg, 1.98 mmol) in nitromethane (50 ml) at room temperature (25—30 °C) was added dropwise 48% aqueous HBF_4 (0.5 ml, 3.85 mmol) over 2 min. After stirring for a further 2 min the reaction mixture was worked up following the method described in (f) for (2a) to afford a light yellow solid (450 mg, 94%), $\nu_{max.}$ 1 735 cm^{-1}, shown (g.l.c.) to be a single component. Chromatography on neutral alumina with petroleum–

benzene (9 : 1 v/v) as eluant gave a white solid (395 mg, 82%). Crystallisation from ether–petroleum afforded 4aα-*hydroxy*-4β-*methyl*-2,3,4,4a,9,9a-*hexahydro*-4aα,9aα-*ethano*-1H-*fluoren*-11-*one* (9a), m.p. 126 °C (Found: C, 79.15; H, 7.7. $C_{16}H_{18}O_2$ requires C, 79.31; H, 7.49%); $\nu_{max.}$ (KBr) 3 420, 3 350, 2 940, 1 740, 1 715, 1 450, 1 390, 1 110, 1 050, and 768 cm^{-1}; δ 1.33 (s, 3 H, CCH_3), 1.68 (s, 1 H, OH, exchangeable) overlapped with 1.51—1.76 (m, 4 H, methylenes), 1.88—2.5 (m, 4 H, CH_2 and $COCH_2$), and 2.73 (δ_A) and 2.90 (δ_B) (ABq, 2 H, *J* 16 Hz, $ArCH_2$); *m/e* 242 (M^+, 54%), 224 (6), 214 (9), 146 (39), 145 (100), and 98 (31).

(d) *With* BF_3·Et_2O *in nitromethane*. A solution of the diazo-ketone (4a) (100 mg, 0.396 mmol) in nitromethane (10 ml) was treated with a 10% solution of BF_3·Et_2O in nitromethane (0.6 ml, 0.438 mmol). After the usual work-up, a light yellow solid, identical with (9a) (g.l.c.), was obtained. Chromatography of this material afforded the pure bridged cyclopentanone (9a) (80 mg, 83%), m.p. and mixed m.p. 126 °C.

(e) *With* HI *in* $CHCl_3$. A solution of the diazo-ketone (4a) (500 mg) in $CHCl_3$ (50 ml) was treated with 57% HI (1.5 ml, 11.4 mmol), under the conditions described in (e) for (2a) to afford a yellow gum. Chromatography afforded the cyclobutanone (6a) (225 mg, 50%), m.p. and mixed m.p. 75—77 °C. The rest of the material could not be purified.

Cyclisation of the diazo-ketone (4b). (a) *With* HBF_4 *in dry* $CHCl_3$. *Preparation of the unsaturated cyclobutanone* (6b). An ice-cold solution of the diazo-ketone (4b) (380 mg, 1.34 mmol) in dry chloroform (100 ml) was treated with 48% aqueous HBF_4 (0.6 ml, 4.62 mmol) for 1 h with stirring. After usual work-up a light yellow gummy solid was obtained. Chromatography on neutral alumina using petroleum as eluant gave a solid (250 mg, 73%) which was crystallised from light petroleum to afford 8-*methoxy*-2a-*methyl*-2a,3,4,10-*tetrahydrocyclobuta*[j]*fluoren*-2(1H)-*one* (6b) as needles, m.p. 93—94 °C (Found: C, 80.55; H, 7.25. $C_{17}H_{18}O_2$ requires C, 80.28; H, 7.13%); $\nu_{max.}$ 1 765 and 1 620 cm^{-1}; $\lambda_{max.}$ 262 and 300 nm (log ε 4.26 and 3.75); δ 1.28 (s, 3 H, CCH_3), 1.38—2.45 (complex, m, 4 H, $CH_2CH{=}C\langle$ and CH_2), 2.70—3.41 (overlapping dd, 4 H, $COCH_2$ and $ArCH_2$), 3.78 (s, 3 H, OCH_3), 6.11br (t, *J* 5 Hz, 1 H, $CH{=}C\langle$), and 6.60—7.41 (m, 3 H, ArH).

(b) *With* $HClO_4$ *in* $CHCl_3$. A solution of the diazo-ketone (4b) (380 mg) in $CHCl_3$ (100 ml) was treated identically with aqueous $HClO_4$ (0.4 ml, 4.67 mmol) for 1 h. The yellow gum ($\nu_{max.}$ 1 765, 1 720, 1 690, and 1 620 cm^{-1}) isolated was chromatographed to afford the cyclobutanone (6b) (120 mg, 35%), m.p. and mixed m.p. with the sample obtained in (a) 92—94 °C.

(c) *With* HI *in* $CHCl_3$. An ice-cold solution of the diazo-ketone (4b) (300 mg, 1.05 mmol) in chloroform (100 ml) was treated with hydriodic acid (1.5 ml, 11.4 mmol) for 30 min with stirring at room temperature. The usual work-up afforded a yellow gum; $\nu_{max.}$ 1 765, 1 700, and 1 620 cm^{-1}. Chromatography gave the cyclobutanone (6b) (106 mg, 40%), m.p. and mixed m.p. 92—94 °C.

Catalytic Hydrogenation of the Unsaturated Cyclobutanones (5a), (5b), (6a), *and* (6b).—The unsaturated cyclobutanone (5a) (90 mg, 0.377 mmol) in ethanol (20 ml) was hydrogenated at room temperature and pressure in the presence of 10% palladium–charcoal (100 mg). Uptake of hydrogen was very fast and was complete within 30 min. The catalyst was removed by filtration and ethanol was removed under reduced pressure to afford a white solid shown (^1H n.m.r.) to be a mixture of (13a) and (15a) in the ratio *ca.* 9 : 1. Two recrystallisations from light petroleum afforded 3aβ-*methyl*-1,3,3a,6,7,11bβ-*hexahydro*-2H-*cyclobuta*[d]-*phenanthren*-4(5H)-*one* (13a) (75 mg, 83%), m.p. 102 °C (Found: C, 84.85; H, 8.5. $C_{17}H_{20}O$ requires C, 84.95; H, 8.39%); $\nu_{max.}$ 1 765 and 1 600 cm^{-1}; $\lambda_{max.}$ 264 and 271 nm (log ε 2.73 and 2.65); δ 1.10 (s, 3 H, CCH_3), 1.20—2.40 (m, 8 H, methylenes), 2.50—3.25 (complex m, 5 H, $COCH_2$, $ArCH_2$, and ArC*H*), and 7.10 (m, 4 H, ArH).

The unsaturated cyclobutanone (5b) (200 mg, 0.75 mmol) in ethanol (45 ml) was hydrogenated in presence of 10% palladium–charcoal (100 mg) for 30 min under identical conditions. The usual work-up gave a solid consisting (n.m.r. and t.l.c.) of a single component. Crystallisation from light petroleum afforded 9-*methoxy*-3aβ-*methyl*-1,3,3a,-6,7,11bβ-*hexahydro*-2H-*cyclobuta*[d]*phenanthren*-4(5H)-*one* (13b) (182 mg, 92%) as rosettes, m.p. 100—101 °C (Found: C, 79.8; H, 8.3. $C_{18}H_{22}O_2$ requires C, 79.96; H, 8.20%); $\nu_{max.}$ 1 765 and 1 600 cm^{-1}; $\lambda_{max.}$ 278 nm (log ε 3.45); δ 1.08 (s, 3 H, CCH_3), 1.56—1.94 (complex m, 6 H, methylenes), 2.36 (δ_A) and 3.03 (δ_B) (ABq, *J* 19 Hz, $COCH_2$) partly overlapped with a multiplet at 2.68—3.23 (total 7 H), 3.71 (s, 3 H, OCH_3), 6.58br (s, 8-H), 6.63 (partly resolved dd, $J_{10,11}$ 9, $J_{8,10}$ 3 Hz, 10-H), and 7.1br (d, $J_{10,11}$ 9 Hz, 11-H).

The unsaturated cyclobutanone (6a) (450 mg, 2.01 mmol) in ethanol (50 ml) was hydrogenated in the presence of 10% palladium–charcoal (100 mg) for 30 min. Usual work-up afforded a solid (450 mg) which was shown (n.m.r.) to be a mixture (*ca.* 4 : 1) of (14a) and (16a). Repeated crystallisation from light petroleum afforded 2aβ-*methyl*-2a,3,4,5,5aβ,10-*hexahydrocyclobuta*[j]*fluoren*-2(1H)-*one* (14a) (*ca.* 60%), m.p. 79—80 °C (Found: C, 85.05; H, 8.0. $C_{16}H_{18}O$ requires C, 84.91; H, 8.02%); $\nu_{max.}$ 1 765 and 1 600 cm^{-1}; $\lambda_{max.}$ 260, 266, and 273 nm (log ε 2.99, 3.18, and 3.25); δ 1.25 (s, 3 H, CCH_3), 1.36—3.53 (complex m, 11 H), and 7.15 (m, 4 H, Ar*H*). The minor epimer (16a) could not be separated from the mixture.

The unsaturated cyclobutanone (6b) (200 mg, 0.786 mmol) in ethanol (30 ml) was hydrogenated in presence of 10% palladium–charcoal (50 mg) for 20 min. The crude saturated ketone was shown to be a single isomer (n.m.r. and t.l.c.). Crystallisation from light petroleum afforded 8-*methoxy*-2aβ-*methyl*-2a,3,4,5,5aβ,10-*hexahydrocyclobuta*[j]-*fluoren*-2(1H)-*one* (14b) (185 mg, 92%), m.p. 75 °C (Found: C, 79.65; H, 7.8. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.86%); $\nu_{max.}$ 1 765 and 1 630 cm^{-1}; $\lambda_{max.}$ 227 and 282 nm (log ε 3.84 and 3.50); δ 1.25 (s, 3 H, CCH_3), 1.36—3.50 (complex m, 11 H), 3.75 (s, 3 H, OCH_3), and 6.40—7.06 (m, 3 H, ArH).

Bayer–Villiger Oxidation of the Saturated Cyclobutanones (13a), (13b), (14a), *and* (14b).—*Oxidation of* (13a) *to the* γ-*lactone* (18a). (a) *With* m-*chloroperbenzoic acid*. A saturated solution of the cyclobutanone (13a) (100 mg, 0.416 mmol) in anhydrous methylene chloride (30 ml) containing a crystal of TsOH·H_2O was thoroughly mixed with *m*-chloroperbenzoic acid (76 mg, 0.44 mmol) and was left in the lower chamber of a deep-freeze for 4 days when *m*-chlorobenzoic acid crystallised out. The reaction mixture was kept at room temperature in the dark for another 3 days and then washed with water, 10% aqueous sodium carbonate, and water, and dried ($CaCl_2$). Removal of solvent under reduced pressure furnished a light yellow solid (76 mg, 71%) which was crystallised from ethyl acetate to afford 3aβ-*methyl*-1,3,3a,7,8,12bβ-*hexahydro*-2H-*phenanthro*[1,10a-b]*furan*-5(6H)-*one* (18a) as prisms, m.p. 173—174 °C (Found: C, 79.7; H, 7.9. $C_{17}H_{20}O_2$ requires

C, 79.65; H, 7.86%); $\nu_{max.}$ 1 750 and 1 600 cm^{-1}; $\lambda_{max.}$ 265 and 273 nm (log ε 2.67 and 2.66); δ 1.42 (s, 3 H, CCH_3), 1.50—3.10 (complex m, 13 H), and 7.08 (m, 4 H, ArH).

(b) *With alkaline hydrogen peroxide.* To a magnetically stirred solution of the ketone (13a) (100 mg, 0.416 mmol) in ethanol (10 ml) was added 10%aqueous sodium hydroxide (30 ml) followed by dropwise addition of 30% aqueous hydrogen peroxide (20 ml) in two equal lots at an interval of 1 h. The mixture was left at room temperature for 20 h, and was then diluted with water and extracted with ethyl acetate. The extract was washed with brine and dried ($CaCl_2$). Removal of solvent under reduced pressure afforded a white solid (80 mg, 75%) which on recrystallisation from ethyl acetate afforded the lactone (18a) as prisms, m.p. and mixed m.p. with the above sample 173—174 °C.

Oxidation of (13b) *to the γ-lactone* (18b). (a) *With m-chloroperbenzoic acid.* A solution of the ketone (13b) (180 mg, 0.66 mmol) in anhydrous methylene chloride (30 ml) was oxidised with *m*-chloroperbenzoic acid (150 mg, 0.879 mmol) and a crystal of $TsOH \cdot H_2O$ according to the general procedure to afford 10-*methoxy*-3aβ-*methyl*-1,3,3a,-7,8,12bβ-*hexahydro*-2H-*phenanthro*[1,10a-b]*furan*-5(6H)-*one* (18b) as a yellow solid (120 mg, 63%), m.p. 177—178 °C (from ethyl acetate) (Found: C, 75.2; H, 7.8. $C_{18}H_{22}O_3$ requires C, 75.49; H, 7.74%); $\nu_{max.}$ 1 750 and 1 600 cm^{-1}; $\lambda_{max.}$ 280 nm (log ε 3.46); δ 1.43 (s, 3 H, CCH_3), 1.47—3.10 (complex m, 13 H), 3.77 (s, 3 H, OCH_3), 6.60br (s, 9-H), 6.66 (partly resolved dd, $J_{11.12}$ 9, $J_{9.11}$ 13 Hz, 11-H), and 7.11br (d, $J_{11,12}$ 9 Hz, 12-H).

(b) *With alkaline hydrogen peroxide.* A solution of the ketone (13b) (120 mg, 0.444 mmol) in ethanol (10 ml) and 10% aqueous sodium hydroxide (30 ml) was oxidised with 30% hydrogen peroxide (20 ml) following the general procedure to give a light yellow solid (90 mg, 71%) which was recrystallised from ethyl acetate to afford the γ-lactone (18b), m.p. and mixed m.p. 176—178 °C with the sample prepared by method (a).

Oxidation of (14a) *to the γ-lactone* (19a). (a) *With m-chloroperbenzoic acid.* A solution of the ketone (14a) (200 mg, 0.88 mmol) in dry methylene chloride (40 ml) containing a crystal of $TsOH \cdot H_2O$ was oxidised with *m*-chloroperbenzoic acid (160 mg, 0.93 mmol) under the usual conditions to give a light yellow solid (169 mg, 79%). Recrystallisation from ethyl acetate afforded 3aβ-*methyl*-3a,4,5,6,6aβ,11-*hexahydrofluoreno*[1,9a-b]*furan*-2(1H)-*one* (19a) as prisms, m.p. 122 °C (Found: C, 79.15; H, 7.7. $C_{16}H_{18}O_2$ requires C, 79.31; H, 7.49%); $\nu_{max.}$ 1 755 and 1 600 cm^{-1}; δ 1.42 (s, 3 H, CCH_3), 1.50—2.35 (m, 6 H), 2.37 (δ_A) and 2.62 (δ_B) (ABq, *J* 16 Hz, $OCOCH_2$), 2.60—3.28 (m, 3 H, $ArCH_2$- and ArCH) and 7.23 (m, 4 H, ArH).

(b) *With alkaline hydrogen peroxide.* A solution of the ketone (14a) (200 mg) in ethanol (10 ml) and 10% aqueous sodium hydroxide (30 ml) was oxidised with 30% hydrogen peroxide (20 ml) by the general procedure to afford the lactone (19a) (180 mg, 84%), m.p. 122 °C alone or mixed with the sample described above.

Oxidation of (14b) *to the γ-lactone* (19b). (a) *With m-chloroperbenzoic acid.* A solution of the ketone (14b) (200 mg, 0.781 mmol) in methylene chloride (40 ml) containing a crystal of $TsOH \cdot H_2O$ was oxidised with *m*-chloroperbenzoic acid (150 mg, 0.869 mmol) according to the usual procedure to afford a yellow solid (143 mg, 66%) which was recrystallised from ethyl acetate to give 9-*methoxy*-3aβ-*methyl*-3a,4,5,6,6aβ,11-*hexahydrofluoreno*[1,9a-b]*furan*-2(1H)-*one*, m.p. 156—157 °C (Found: C, 74.85; H, 7.5. $C_{17}H_{20}O_3$ requires C, 74.97; H, 7.40%); $\nu_{max.}$ 1 755 and 1 620 cm^{-1}; δ 1.40 (s, 3, CCH_3), 1.43—3.26 (complex m, 9 H), 7.76 (s, 3 H, OCH_3), and 6.63—7.15 (m, 3 H, ArH).

(b) *With alkaline hydrogen peroxide.* A solution of the ketone (14b) (200 mg) in ethanol (15 ml) and 10% aqueous sodium hydroxide (40 ml) was oxidised with 30% hydrogen peroxide (20 ml) according to the general procedure to give the γ-lactone (19b) (158 mg, 75%), m.p. 156—157 °C alone or in admixture with the sample obtained in method (a).

Preparation of the Unsaturated γ-Lactone (20a). *Oxidation of the Unsaturated Cyclobutanone* (5a) *with Alkaline Hydrogen Peroxide.*—To a cooled (*ca.* 5 °C) and stirred solution of the unsaturated cyclobutanone (5a) (150 mg, 0.63 mmol) in ethanol (10 ml) was added 10% aqueous sodium hydroxide (40 ml) followed by dropwise addition of 30% hydrogen peroxide (10 ml). Stirring was continued for 1 h. A second portion of 30% hydrogen peroxide solution (10 ml) was then added and the reaction mixture was left for 20 h at room temperature. The reaction mixture was diluted with water and the white solid was extracted repeatedly with ethyl acetate. The organic extract was washed with brine and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave 3a-*methyl*-3,3a,7,8-*tetrahydro*-2H-*phenanthro*[1,10a-b]*furan*-5(6H)-*one* (20a) (140 mg, 87%), m.p. 149 °C (from ethyl acetate) (Found: C, 80.35; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.28; H, 7.13); $\nu_{max.}$ 1 755 and 1 600 cm^{-1}; $\lambda_{max.}$ 250 and 283 nm (log ε 4.18 and 3.16); δ 1.42 (s, 3 H, CH_3), 1.50—2.0 (m, 4 H, methylenes), 2.25 (m, 2 H, $CH_2CH{=}C\langle$), 2.40 (δ_A) and 2.65 (δ_B) (ABq, *J* 15 Hz, $OCOCH_2$), 3.10 (m, 2 H, $ArCH_2$), 6.20br (t, 1 H, *J* 5 Hz, $CH{=}C\langle$), 7.07 (m, 3 H, ArH), and 7.40 (m, 1 H, ArH).

Oxidation of the Unsaturated Cyclobutanone (5b) *to the γ-Lactone* (20b).—Following the above procedure, the unsaturated cyclobutanone (5b) (100 mg, 0.373 mmol) in ethanol (10 ml) and 10% aqueous sodium hydroxide (30 ml) was oxidised with 30% hydrogen peroxide (20 ml) to the lactone 10-*methoxy*-3a-*methyl*-3,3a,7,8-*tetrahydro*-2H-*phenanthro*[1,10a-b]*furan*-5(6H)-*one* (20b) (71 mg, 67%), m.p. 166—167 °C (from ethyl acetate) (Found: C, 75.8; H, 7.3. $C_{18}H_{20}O_3$ requires C, 76.03; H, 7.09%); $\nu_{max.}$ 1 755 and 1 600 cm^{-1}; $\lambda_{max.}$ 260 and 292 nm (log ε 4.3 and 3.61); δ 1.30 (s, 3 H, CCH_3), 1.38—2.0 (m, 4 H, methylenes), 2.40 (δ_A) and 2.65 (δ_B) (ABq, J_{AB} 15 Hz, $OCOCH_2$), 3.0 (m, 2 H, $ArCH_2$), 6.13br (t, *J* 5 Hz, 1 H, $CH{=}C\langle$), 6.55—6.80 (complex m, 2 H, 2-H), and 7.38 (d, $J_{1.2}$ 9 Hz, 1 H, 1-H).

Catalytic Hydrogenation of the Unsaturated Lactones (20a) *and* (20b).—*Hydrogenation of* (20a) *to* (18a). The unsaturated lactone (20a) (100 mg) in ethanol (20 ml) was hydrogenated in the presence of 10% palladium–charcoal (100 mg). The uptake of hydrogen was very fast and was complete within 30 min, when the catalyst was filtered off. Removal of solvent from the filtrate afforded the saturated lactone (18a) (99 mg, 99%), m.p. 172—174 °C alone or mixed with the sample prepared by oxidation of (13a).

Hydrogenation of (20b) *to* (18b). The unsaturated lactone (20b) (200 mg) in ethanol (20 ml) was hydrogenated in the presence of 10% palladium–charcoal (100 mg) for 30 min. Work-up in the usual way afforded the saturated lactone (18b) (198 mg, 99%), m.p. 176—178 °C alone or mixed with the sample prepared by oxidation of (13b).

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