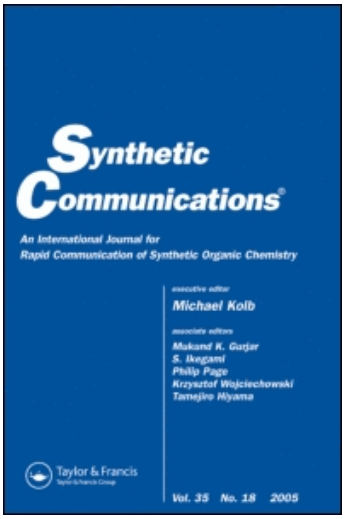

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Synthesis of Some Angularly Cyclopentanone Fused Hydrophenanthrene and Hydrofluorene Derivatives by Acid-Catalyzed Intramolecular C-Alkylation of γ,δ - Unsaturated α'-Diazomethyl Ketones

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SYNTHESIS OF SOME ANGULARLY CYCLOPENTANONE FUSED HYDROPHENANTHRENE AND HYDROFLUORENE DERIVATIVES BY ACID-CATALYZED INTRAMOLECULAR C-ALKYLATION OF γ,δ-UNSATURATED α'-DIAZOMETHYL KETONES

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Abstract : A facile synthesis of a few new angularly cyclopentanone fused hydrophenanthrene and hydrofluorene derivatives is described based on intramolecular C-alkylation of γ,δ-unsaturated α'-diazomethyl ketones.

Earlier we reported[1] the synthesis of racemic angularly cyclopentanone fused hydrophenanthrene derivatives **Ia** and **Ib**, representing highly degenerated estrone skeleton, through a novel cyclopentenone annulation reaction involving a formylation-cyclization process[2]. In line with our continuing interest in the synthesis of condensed cyclic and bridged-ring systems[3] and in the intramolecular C-alkylation reactions of unsaturated diazomethyl ketones[4,5], we wish to describe in this paper the synthesis of a few new angularly cyclopentanone fused hydrophenanthrene and hydrofluorene derivatives **1a,b**, **2a,b**, **3a,b**, **4a**, **5a**, **6b** and **7a,b** starting from the easily accessible unsaturated diazomethyl ketones **8a,b**[6] and **9a,b**[6].

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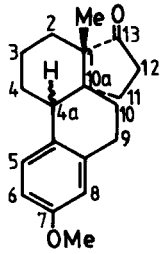
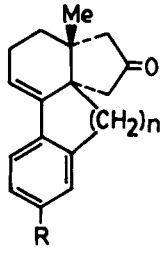
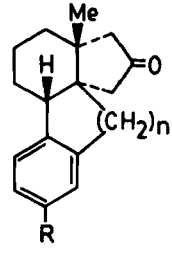


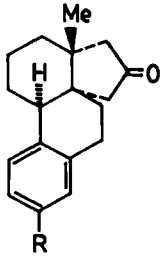
1a; 4aβ
1b; 4aα



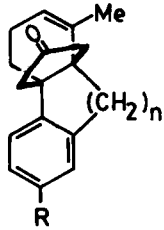
1; n=2
4; n=1



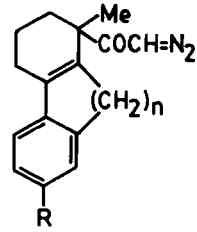
2; n=2
5; n=1



3



6; n=2
7; n=1

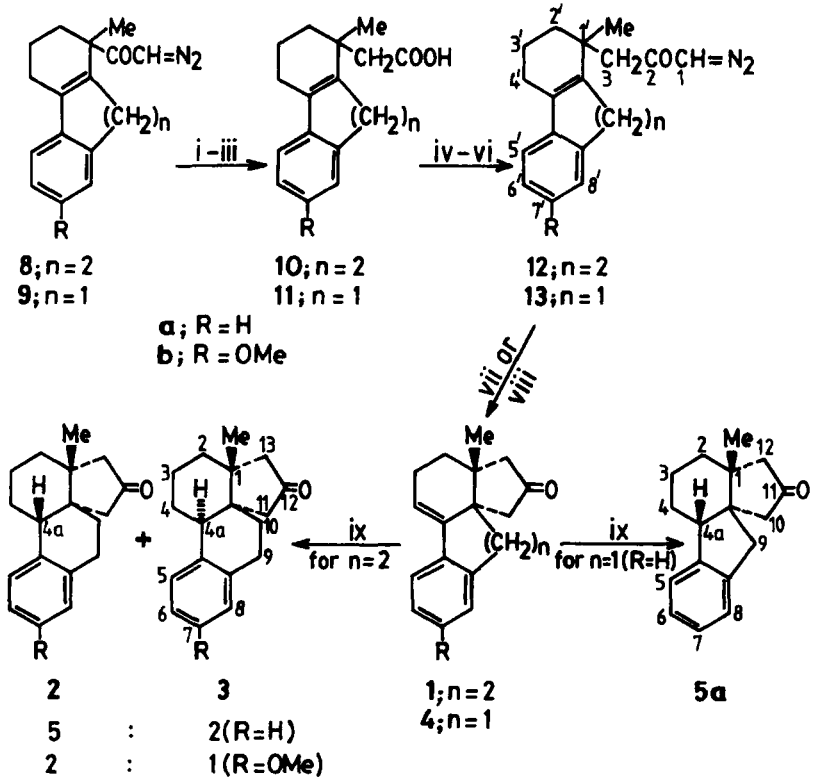


8; n=2
9; n=1

1-9: **a**; R=H
b; R=OMe

The known[7] key γ,δ-unsaturated acids **10a**, **10b** and **11a**, prepared in excellent yields by photoinduced Wolff-Rearrangement[7] of the β,γ-unsaturated diazoketones **8a**, **8b** and **9a**, were converted into the diazoketones **12a**, **12b** and **13a** respectively, via sodium salts and corresponding acyl chlorides by a standard method[8] (Scheme-1). Treatment of the ice-cold dilute solutions of the diazoketones **12a**, **12b** and **13a** in CH_2Cl_2 with $HClO_4$ (70%) and trifluoroacetic acid mixture or dilute nitromethane solution with HBF_4 (48%) yielded the corresponding styrenoid cyclopentanones **1a**, **1b** and **4a** in excellent yields (Scheme-1).

Scheme-1



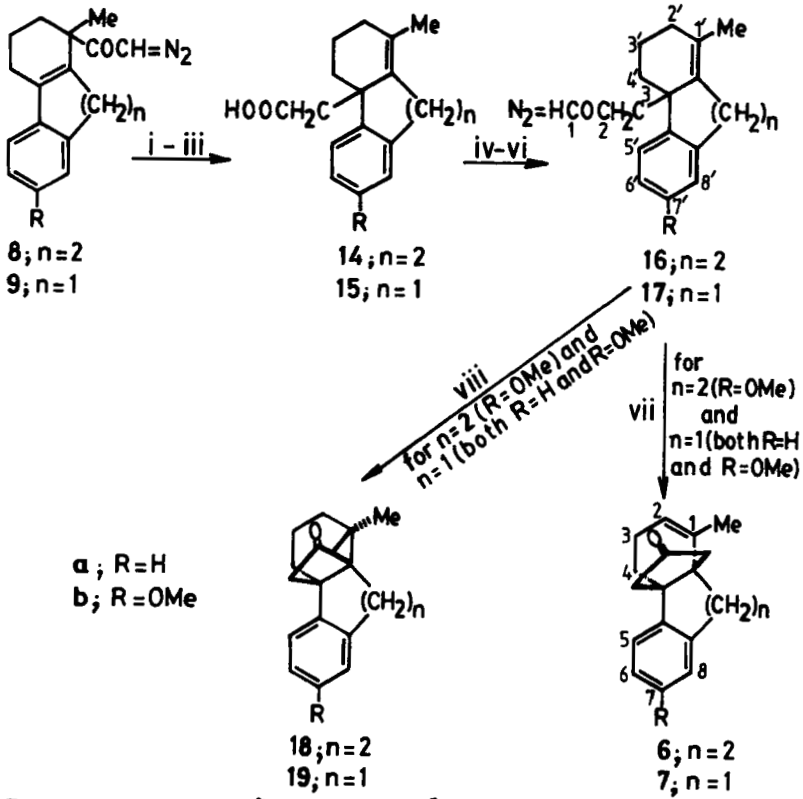
Reagents: i, hν, MeOH; ii, KOH, H_2O, MeOH, heat;
iii, dil.HCl; iv, NaOMe - MeOH;
v, $(COCl)_2$, pyridine, C_6H_6;
vi, CH_2N_2, Et_2O, Et_3N;
vii, TFA-$HClO_4$(70%), CH_2Cl_2;
viii, HBF_4(48%), CH_3NO_2;
ix, H_2, Pd-C(10%), EtOH.

Catalytic hydrogenation of the styrenoid bond in the ketone **1a** in the presence of palladium-charcoal (10%) in ethanol gave a mixture of 4aβ and 4aα-epimers **2a** and **3a** in a ratio of ca. 5:2 (from GC and ^{1}H NMR) in 89% yield, which

was separated by careful fractional crystallization. While the major epimer **2a** exhibits its C-1 methyl singlet at δ 1.18, the minor epimer **3a** shows it at δ 1.04. The observed upfield shift of the methyl singlet for **3a** can be rationalized as resulting from the ring-current shielding effect[9] similar to that noted[1] for the isomeric ketone **Ib**. The methoxy enone **1b** on catalytic hydrogenation gave an inseparable mixture of the epimeric ketones **2b** and **3b** in a ratio of ca. 2:1 (from GC and ^1H NMR). In contrast, the styrenoid ketone **4a**, incorporating the hydrofluorene system, on hydrogenation in ethanol in the presence of palladium-charcoal (10%) gave a single saturated cyclopentanone isomer, assigned as **5a** (Scheme-1) by analogy[10].

Finally, as a follow up to our recently reported[3] studies, the γ,δ-unsaturated acids[7] **14b**, **15a** and **15b**, prepared in excellent yields by "Vinylogous Wolff Rearrangement[7]" of the β,γ-unsaturated diazoketones **8b**, **9a** and **9b**, were converted to the desired diazoketones **16b**, **17a** and **17b** respectively, via sodium salts and the corresponding acyl chlorides (Scheme-2). Cyclization of the diazoketones **16b**, **17a** and **17b** in CH_2Cl_2 by treatment with $HClO_4$ (70%) and trifluoroacetic acid mixture produced the unsaturated cyclopentanones **6b**, **7a** and **7b** in 22%, 14% and 15% yields respectively. Intramolecular keto-carbenoid addition of the diazoketones **16b**, **17a** and **17b** in the presence of "activated CuO" catalyst[11] in boiling cyclohexane, under irradiation with two 250 watt tungsten lamps, gave the respective cyclopropyl ketones **18b**, **19a** and **19b** only in poor isolable yields.

Scheme-2



Reagents: i, hν, C_6H_{12}, "activated CuO" catalyst, MeOH(1%), heat; ii, KOH, H_2O, MeOH, heat; iii, dil.HCl; iv, NaOMe-MeOH; v, $(COCl)_2$, pyridine, C_6H_6; vi, CH_2N_2, Et_2O, Et_3N; vii, TFA-$HClO_4$(70%), CH_2Cl_2; viii, hν, "activated CuO" catalyst, C_6H_{12}(boiling).

In conclusion, the present work provides efficient synthetic entry to some angularly cyclopentanone fused hydrophenanthrene and hydrofluorene derivatives by intramolecular C-alkylation reactions of γ,δ-unsaturated α'-diazomethyl ketones.

EXPERIMENTAL

The compounds described are all racements. IR spectra were recorded on a Perkin-Elmer model PE 298 spectrometer. ^1H NMR spectra were recorded on a Jeol FX-100, a Varian EM-360L or a Varian XL-200 instrument. Chemical shifts are referred to TMS on the "δ" scale. Analytical GC was performed on a Shimadzu GC-9A model with a flame ionization detector employing 1.5% OV-17 (6.5 ft x 0.25 in) column with N_2 as the carrier gas. UV spectra were recorded on a Beckmann DU spectrometer for solutions in ethanol (95%). Elemental analyses were performed by P.P. Bhattacharya and S. Sarkar of this laboratory. Column chromatography was performed on neutral alumina (Brockman Grade 1). Petroleum refers to fractions of bp 60-80°C.

Synthesis of the Diazomethyl Ketones 12a, 12b and 13a.

(±)-1-Diazo-3-(1'-methyl-1',2',3',4',9',10'-hexahydrophenanthren-1'-yl)propan-2-one (12a). The sodium salt of the acid **10a**[7] (500 mg, 1.95 mmol) was prepared adopting the usual procedure[8]. To a stirred ice-cold suspension of this sodium salt in dry benzene (20 ml) containing pyridine (0.1 ml, 1.24 mmol) was added dropwise oxalyl chloride (1.10 ml, 12.60 mmol). The mixture was kept at 0°C for 30 min with occasional shaking, at room temperature for 30 min and finally warmed at 55-56°C for 1 h. The precipitated salt was filtered off and the filtrate concentrated under reduced pressure. The

crude acid chloride was dissolved in anhydrous Et_2O (20 ml) and added dropwise over 15 min to ice-cold and magnetically stirred solution of ethereal diazomethane [from N-methyl N-nitrosourea (2.0 g, 19.42 mmol)] containing dry triethylamine (0.3 ml, 2.16 mmol) and left overnight. The precipitated material was filtered off. Evaporation of ether from the filtrate gave a yellow residue which was filtered through a column of neutral alumina (20 g). Elution with Et_2O-petroleum (1:4) furnished 505 mg (92%) of the diazoketone **12a** as a light yellow liquid; IR (neat) 2100 and 1630 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) 1.18 (s, 3H, $\geq C-CH_3$), 1.33-2.03 (m, 8H, methylenes), 2.31 (s, 2H, $-CH_2CO-$), 2.73 (br t, 2H, $ArCH_2-$), 5.13 (br s, 1H, $-COCHN_2$), 6.76-7.36 (m, 4H, ArH).

(±)-1-Diazo-3-(7'-methoxy-1'-methyl-1',2',3',4',9',10'-hexahydrophenanthren-1'-yl)propan-2-one (12b). The acid **10b**[7] (500 mg, 1.75 mmol) was converted to the diazoketone **12b** (502 mg, 93%) as a light yellow liquid [purified by passing through a column of neutral alumina (15 g) with Et_2O-petroleum (1:3) as eluant] following an identical procedure as described earlier for the preparation of **12a**; IR (neat) 2100 and 1630 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) 1.16 (s, 3H, $\geq C-CH_3$), 1.30-2.26 (m, 8H, methylenes), 2.48 (s, 2H, $-CH_2CO-$), 3.04 (br t, 2H, $ArCH_2-$), 3.76 (s, 3H, $ArOCH_3$), 5.10 (br s, 1H, $-COCHN_2$), 6.35-7.34 (m, 2H, ArH), 7.40 (d, J = 8 Hz, 1H, C_5,-ArH).

(±)-1-Diazo-3-(1'-methyl-1',2',3',4'-tetrahydro-9'H-fluoren-1'-yl)propan-2-one (13a). The crude diazoketone, prepared from

500 mg (2.07 mmol) of the acid **11a**[7] following the aforementioned procedure, was filtered through neutral alumina (15 g) with Et_2O-petroleum (1:4) as eluant to furnish 510 mg (93%) of pure **13a**; IR (neat) 2100 and 1635 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) 1.30 (s, 3H, $\gtrless C-CH_3$), 1.35-2.66 (m, 6H, methylenes), 2.46 (s, 2H, $-CH_2CO-$), 2.74 (δ_A) and 3.42 (δ_B) (AB_q, J = 16 Hz, 2H, $ArCH_2-$), 5.06 (s, 1H, $-COCHN_2$), 6.83-7.43 (m, 4H, ArH).

Acid-Catalyzed Cyclization Studies of the Diazoketones 12a, 12b and 13a.

Cyclization of 12a : (±)-1β-Methyl-1,2,3,9,10,10a-hexahydro-1α,10aα-propanophenanthren-12-one (1a).

Method (A) : With TFA-$HClO_4$ in methylene chloride . To an ice-cold stirred solution of the diazoketone **12a** (250 mg, 0.89 mmol) in dry CH_2Cl_2 (50 ml) was added dropwise a mixture of TFA (0.4 ml, 5.19 mmol) and 70% aqueous $HClO_4$ (0.1 ml, 1.16 mmol) in CH_2Cl_2 (10 ml) over 5 min. The mixture was kept at 0°C for an additional 10 min. The deep red solution was diluted with water. The organic phase was separated, washed successively with water, $NaHCO_3$ aq. (5%), water and dried (Na_2SO_4). Removal of the solvent and chromatography of the resulting semi-solid mass on neutral alumina (8 g) and elution with petroleum afforded the unsaturated cyclopentanone **1a** (200 mg, 89%), mp 99-100°C (petroleum), homogeneous in GC (R_t 4.32 min at 230°C); UV (EtOH) λ_{max} 250 nm (log ε 4.14); IR (KBr) 1735 and 1635 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.10 (s, 3H,

$\rangle C-CH_3$), 1.20-2.66 (m, 10H, two sets of $-CH_2CO-$ and methylenes), 2.88 (br t, J = 6 Hz, 2H, $ArCH_2-$), 6.10 (t, J = 4 Hz, 1H, $-C=CH-$), 6.83-7.46 (m, 4H, ArH). Anal. calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found : C, 85.36; H, 8.01%.

Method (B) : With HBF_4 (48%) in dry nitromethane. To a stirred solution of the diazoketone **12a** (250 mg, 0.89 mmol) in nitromethane (25 ml) at room temperature (25-30°C) was added dropwise 48% aqueous HBF_4 (0.25 ml, 1.92 mmol) over 2 min. Immediately, rapid evolution of nitrogen with development of brown colour was observed. After stirring for 1 min, the reaction mixture was decomposed with 10% $NaHCO_3$, washed repeatedly with water and dried (Na_2SO_4). Evaporation of the solvent furnished a brown gummy mass which on chromatography over neutral alumina (7 g) and elution with petroleum afforded the unsaturated cyclopentanone **1a** (195 mg, 87%), mp and mixed mp 99-100°C, identical with the sample described above in all respect (^1H NMR, IR, UV and GC).

Cyclization of 12b : (±)-7-Methoxy-1β -methyl-1,2,3,9,10,10a-hexahydro-1α,10aα-propanophenanthren-12-one (1b).

Method (A) : With TFA-$HClO_4$ in methylene chloride. The diazoketone **12b** (300 mg, 0.97 mmol) in dry CH_2Cl_2 (50 ml) was cyclized with TFA (0.4 ml, 5.19 mmol) and 70% aqueous $HClO_4$ (0.1 ml, 1.16 mmol) in CH_2Cl_2 (10 ml) under the same conditions as described for the preparation of **1a**. The crude product on column chromatography over neutral alumina (10 g)

and elution with petroleum furnished the pure unsaturated cyclopentanone **1b** (240 mg, 88%) as a colourless liquid, bp 210-212°C (0.3 mm Hg), homogeneous in GC (R_t 5.19 min at 230°C); UV (EtOH) λ_{max} 258 nm (log ε 4.42); IR (neat) 1735, 1640 and 1600 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.10 (s, 3H, $\geq C-CH_3$), 1.18-2.74 (m, 10H, two sets of $-CH_2CO-$ and methylenes), 2.86 (br t, J = 6 Hz, 2H, $ArCH_2-$), 3.72 (s, 3H, $ArOCH_3$), 5.93 (t, J = 4 Hz, 1H, $-C=CH-$), 6.21-7.40 (m, 2H, ArH), 7.44 (d, J = 8 Hz, 1H, C_5-ArH). Anal. calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found : C, 80.67; H, 7.90%.

Method (B) : With HBF_4 (48%) in dry nitromethane. The diazoketone **12b** (100 mg, 0.32 mmol) in dry nitromethane (10 ml) was cyclized with 48% aqueous HBF_4 (0.10 ml, 0.77 mmol) under identical conditions as described earlier for the preparation of **1a**. Usual work-up followed by chromatography of the crude product over neutral alumina (2 g) and elution with petroleum produced the unsaturated cyclopentanone **1b** (80 mg, 88%) as a colourless liquid, bp 210-212°C (0.3 mm Hg), identical with the sample described above in all respect (^1H NMR, IR, UV, GC).

Cyclization of 13a : (±)-1β-Methyl-2,3,9,9a-tetrahydro-1α,9aα-propano-1H-fluoren-11-one (4a).

Method (A) : With TFA-$HClO_4$ in methylene chloride. The diazoketone **13a** (400 mg, 1.50 mmol) in dry CH_2Cl_2 (75 ml) was cyclized with TFA (0.8 ml, 10.38 mmol) and 70% aqueous

$HClO_4$ (0.2 ml, 2.32 mmol) in CH_2Cl_2 (10 ml) under the same conditions as described before for the preparation of **1a.** The crude product on column chromatography over neutral alumina (15 g) and elution with petroleum afforded the pure unsaturated cyclopentanone **4a** (340 mg, 95%) as a colourless liquid, bp 200-205°C (0.2 mm Hg), homogeneous in GC (R_t 3.82 min at 230°C); UV (EtOH) λ_{max} 250 nm (log ε 4.14); IR (neat) 1735 and 1635 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.15 (s, 3H, $\geq C-CH_3$), 1.16-2.56 (m, 8H, methylenes), 2.55 (δ_A) and 3.09 (δ_B) (AB_q, J = 16 Hz, 2H, $ArCH_2-$), 5.88 (t, J = 4 Hz, 1H, $-\underset{|}{C}=CH-$), 6.83-7.40 (m, 4H, ArH). Anal. calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.49; H, 7.77%.

Method (B) : With HBF_4 (48%) in dry nitromethane. Cyclization of 100 mg (0.38 mmol) of the diazoketone **13a** in dry nitromethane (10 ml) was carried out with 48% aqueous HBF_4 (0.10 ml, 0.77 mmol), under the same conditions as described earlier for the preparation of **1a.** Work up as usual followed by column chromatography of the crude product over neutral alumina (2 g) and elution with petroleum afforded the unsaturated cyclopentanone **4a** (75 mg, 84%) as a colourless liquid, bp 200-205°C (0.2 mm Hg), identical in all respect (^1H NMR, IR, UV, GC) with the sample prepared above.

Catalytic Hydrogenation of the Unsaturated Cyclopentanones 1a, 1b and 4a.

Hydrogenation of 1a : (±)-1β-Methyl-1,2,3,4,4aβ,9,10,10a-octahydro-1α,10aα-propanophenanthren-12-one (2a) and (±)-1β-

Methyl-1,2,3,4,4aα,9,10,10a-octahydro-1α,10aα-propanophenanthren-12-one (3a). A solution of the unsaturated cyclopentanone **1a** (200 mg, 0.79 mmol) in EtOH (15 ml) was hydrogenated at room temperature and atmospheric pressure over Pd-C (10%) (100 mg) for 2 h. The catalyst was filtered off and the filtrate concentrated to afford a semi-solid mass (180 mg, 89%) which showed the presence of the two epimeric ketones **2a** and **3a** in the ratio of ca. 5:2 (by GC and ^{1}H NMR). The IR spectrum showed a single carbonyl band at 1735 cm^{-1}. The ^{1}H NMR spectrum of the crude product showed signals for the tertiary methyl at δ 1.18 and δ 1.04, the former value corresponding to the major epimer. The GC analysis also showed a mixture of two products with R_t values at 7.20 and 9.10 min respectively at 200°C, the former value corresponding to the minor epimer. Repeated fractional crystallization of the isomeric cyclopentanone mixture from petroleum afforded a pure sample of the minor epimer **3a** (38 mg, 19%), mp 135-136°C (petroleum), homogeneous in GC (R_t 7.20 min at 200°C); IR (KBr) 1735 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.04 (s, 3H, >C-CH_3), 2.13-3.04 (m, 15H, methylenes and methine), 6.87-7.40 (m, 4H, ArH). Anal. calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found : C, 84.64 ; H, 8.80%.

Crystallization of the combined mother liquors from petroleum furnished the major epimer **2a** (100 mg, 50%), mp 100-101°C (petroleum), homogeneous in GC (R_t 9.10 min at 200°C); IR (KBr) 1735 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$), 1.18

(s, 3H, $\geq C-CH_3$), 2.10-3.24 (m, 15H, methylenes and methine), 6.84-7.42 (m, 4H, ArH). Anal. calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found : C, 84.87; H, 8.90%.

Hydrogenation of 1b : (±)-7-Methoxy-1β-methyl-1,2,3,4,4aβ,9,10,10a-octahydro-1α,10aα-propanophenanthren-12-one (2b) and its 4aα -epimer (3b). A solution of the unsaturated cyclopentanone **1b** (200 mg, 0.71 mmol) in EtOH (15 ml) was hydrogenated at room temperature and atmospheric pressure over Pd-C (10%) (100 mg) for 2 h. Usual work up afforded a light brown liquid (170 mg, 84%) which indicated the presence of the two epimeric ketones **2b** and **3b** in a ratio of ca. 2:1(from ^1H NMR and GC analyses). The IR spectrum showed a single carbonyl band at 1735 cm^{-1}. The ^1H NMR spectrum of the crude product showed signals for the tertiary methyl at δ 1.60 and δ 1.17, the former value corresponding to the major epimer. The GC analysis also showed a mixture of two products with R_t values at 8.14 and 10.52 min respectively at the column temperature 200°C, the former value corresponding to the minor epimer. Attempted separation of the reduction products by chromatography or preparative TLC was not successful. Anal. calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.27; H, 8.85%.

Hydrogenation of 4a : (±)-1β-Methyl-2,3,4,4aβ,9,9a-hexahydro-1α,9aα-propano-1H-fluoren-11-one (5a). A solution of the unsaturated cyclopentanone **4a** (250 mg, 1.05 mmol) in EtOH (20 ml) was hydrogenated over Pd-C (10%) (100 mg) under the same conditions as described. Usual work up furnished a single

ketonic product evident from the ^1H NMR and GC analyses. Column chromatography of the crude product over neutral alumina (5 g) followed by elution with petroleum afforded the pure saturated ketone **5a** (220 mg, 87%) as a colourless liquid, bp 200°C (0.2 mm Hg), homogeneous in GC (R_t 3.07 min at 200°C); IR (neat) 1735 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.12 (s, 3H, $\geq C-CH_3$), 1.20-3.40 (m, 13H, methylenes and methine), 6.76-7.23 (m, 4H, ArH). Anal. calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found : C, 84.97; H, 8.54%.

Synthesis of the Diazomethyl Ketones 16b, 17a and 17b.

(±)-1-Diazo-3-(7'-methoxy-1'-methyl-2',3',4',4a',9',10'-hexahydrophenanthren-4a'-yl)propan-2-one (16b). The acid **14b** (295 mg, 1.03 mmol) was converted to the diazoketone **16b** (301 mg, 94%) as a light yellow liquid, [purified by passing through a column of neutral alumina (7 g) with Et_2O-petroleum (2:5) as eluant] following an identical procedure as described earlier for the preparation of **12a**. IR (neat) 2100 and 1630 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 1.10-3.03 (m, 10H, $-CH_2CO-$ and methylenes), 1.63 (s, 3H, $-C_i=C_i-CH_3$), 2.45 (m, 2H, $ArCH_2-$), 3.66 (s, 3H, $ArOCH_3$), 4.39 (s, 1H, $-CHN_2$), 6.33-6.72 (m, 2H, ArH), 7.03 (d, J = 8 Hz, 1H, C_5,-ArH).

(±)-1-Diazo-3-(1'-methyl-2',3',4',4a'-tetrahydro-9'H-fluoren-4a'-yl)propan-2-one (17a). The crude diazoketone, prepared from 514 mg (2.12 mmol) of the acid **15a**, following the aforementioned procedure, was filtered through neutral alumina

(10 g) with Et_2O-petroleum (1:4) as eluant to furnish 500 mg (89%) of pure **17a** as a light yellow liquid. IR (neat) 2100 and 1635 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) 1.12-2.39 (m, 6H, methylenes), 1.66 (s, 3H, $-\underset{|}{C}=\underset{|}{C}-CH_3$), 2.48 (br s, 2H, $-CH_2CO-$), 3.48 (br s, 2H, $ArCH_2-$), 4.60 (s, 1H, $-CHN_2$), 6.94-7.42 (m, 4H, ArH).

(±)-1-Diazo-3-(7'-methoxy-1'-methyl-2',3',4',4a'-tetrahydro-9'H-fluoren-4a'-yl)propan-2-one (17b). The diazoketone **17b** was prepared from 520 mg (1.91 mmol) of the acid **15b** following an identical procedure as described before for the preparation of **12a**, with the only alteration that the dried sodio salt was suspended in dry methylene chloride (10 ml) instead of dry benzene and the acid chloride was prepared in ice-cold condition for 2 h. The crude product was filtered through a column of neutral alumina (10 g) with Et_2O-petroleum (2:5) as eluant to furnish 500 mg (88%) of the pure diazoketone **17b** as a light yellow liquid. IR (neat) 2100, 1635 and 1610 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 1.37-2.74 (m, 8H, $-CH_2CO-$ and methylenes), 1.63 (br s, 3H, $-\underset{|}{C}=\underset{|}{C}-CH_3$), 3.40 (br s, 2H, $ArCH_2-$), 3.67 (s, 3H, $ArOCH_3$), 4.46 (s, 1H, $-CHN_2$), 6.40-6.83 (m, 2H, ArH), 6.83-7.17 (m, 1H, C_5,-ArH).

Acid-Catalyzed Intramolecular Alkylation Reactions of the Diazoketones 16b, 17a and 17b.

Alkylation of 16b : (±)-7-Methoxy-1-methyl-3,4,4a,9,10,10a-hexahydro-4aβ,10aβ-propanophenanthren-12-one (6b). The diazoketone **16b** (100 mg, 0.32 mmol) was cyclized with TFA (0.2 ml,

2.60 mmol) and 70% aqueous $HClO_4$ (0.05 ml, 0.58 mmol) under the same conditions as described earlier for the preparation of **1a**. The resultant product showed the presence of **6b** (IR : 1740 cm^{-1}, 74% by GC) which on column chromatography over neutral alumina (5 g) and elution with Et_2O-petroleum (2:3) afforded pure **6b** (20 mg, 22%), bp 180°C (0.1 mm Hg), homogeneous in GC (R_t 7.53 min at 230°C); IR (neat) 1740 and 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.48-2.40 (m, 6H, methylenes), 1.70 (br s, 3H, -HC=C(-CH_3)-), 2.40-2.82 (m, 2H, $ArCH_2$-), 2.51 (δ_A) and 2.69 (δ_B) (AB_q, J = 16 Hz, 4H, two sets of -CH_2CO-), 3.78 (s, 3H, $ArOCH_3$), 5.54 (br t, 1H, -C(-)=CH-), 6.60-6.88 (m, 2H, ArH), 7.20 (d, J = 8 Hz, 1H, C_5-ArH). Anal. calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found : C, 80.91; H, 7.79%.

Alkylation of 17a : (±)-1-Methyl-4,4a,9,9a-tetrahydro-4aβ,9aβ-propano-3H-fluoren-11-one (7a). The diazoketone **17a** (200 mg, 0.75 mmol) in dry CH_2Cl_2 (20 ml) was cyclized with TFA (0.4 ml, 5.19 mmol) and 70% aqueous $HClO_4$ (0.1 ml, 1.16 mmol) in CH_2Cl_2 (10 ml) under the same conditions as described for the preparation of **1a**. The crude product containing **7a** (IR : 1740 cm^{-1}, 68% by GC) on column chromatography over neutral alumina (10 g) and elution with Et_2O-petroleum (1:1) furnished pure **7a** (25 mg, 14%), bp 140°C (0.1 mm Hg), homogeneous in GC (R_t 2.98 min at 230°C); IR (neat) 1740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.64-2.20 (m, 4H, methylenes), 1.78 (br s, 3H, -HC=C(-CH_3)-), 2.30 (δ_A) and 2.56 (δ_B) (AB_q, J = 20 Hz, 2H, -CH_2CO-), 2.58 (s, 2H, -CH_2CO-), 3.08 (s, 2H, $ArCH_2$-), 5.54

(br t, 1H, -C=CH-), 7.16-7.40 (m, 4H, ArH). Anal. calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.53; H, 7.80%.

Alkylation of 17b : (±)-7-Methoxy-1-methyl-4,4a,9,9a-tetrahydro-4aβ,9aβ-propano-3H-fluoren-11-one (7b). The diazoketone **17b** (200 mg, 0.68 mmol) was cyclized under the same conditions as described for **1a** to yield the unsaturated benzopropellanone **7b** (28 mg, 15%) as a faint yellow liquid, after column chromatography of the crude product over neutral alumina (10 g) with Et_2O-petroleum (1:1) as eluant. Analytical sample was prepared by evaporative distillation, bp 163°C (0.1 mm Hg); IR (neat) 1740 and 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.16-2.16 (m, 4H, methylenes), 1.76 (m, 3H, -HC=C-CH_3), 2.28 (δ_A) and 2.56 (δ_B) (AB_q, J = 20 Hz, 2H, -CH_2CO-), 2.54 (s, 2H, -CH_2CO-), 3.04 (s, 2H, ArCH_2-), 3.78 (s, 3H, ArOCH_3), 5.53 (br t, 1H, -C=CH-), 6.76-6.94 (m, 2H, ArH), 7.10 (d, J = 8 Hz, 1H, C_5-ArH). Anal. calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found : C, 80.43; H, 7.50%.

Carbenoid Decomposition of the Diazoketones 16b, 17a and 17b.

Carbenoid Decomposition of 16b : (±)-4,5-(3'-Methoxybenzo)-10α-methyltetracyclo[5,4,3,$0^{1,10}$,$0^{1,11}$]tridec-4-en-12-one (18b). The diazoketone **16b** (200 mg, 0.65 mmol) in anhydrous cyclohexane (90 ml) was stirred and refluxed with 'activated CuO' catalyst[11] (1 g, 12.58 mmol) under irradiation by two 250 watt tungsten lamps under N_2 atmosphere. The time required for complete decomposition of the diazoketone was 11-12 h. The cooled

mixture was filtered and the solvent was distilled off in vacuo. The resultant product showed the presence of the cyclopropyl-ketone **18b** (IR : 1710 cm^{-1}, 40% by GC) which on column chromatography over neutral alumina (12 g) and elution with Et_2O-petroleum (1:3) afforded pure **18b** (30 mg, 16%), mp 180°C (Et_2O-petroleum), homogeneous in GC (R_t 3.01 min at 280°C); IR (KBr) 1710 and 1610 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), 1.26 (s, 3H, $\rangle C-CH_3$), 1.28-2.50 (m, 8H, methylenes), 1.56 (s, 1H, -COCH-), 2.50-2.72 (m, 2H, $-CH_2CO-$), 2.80 (t, J = 6 Hz, 2H, $ArCH_2-$), 3.80 (s, 3H, $ArOCH_3$), 6.70-6.90 (m, 2H, ArH), 7.14 (d, J = 8 Hz, 1H, C_5,-ArH). Anal. calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found : C, 80.59; H, 7.90%.

Carbenoid Decomposition of 17a : (±)-3,4-Benzo-9α-methyltetracyclo[5,3,3,$0^{1,9}$,$0^{1,10}$]dodec-3-en-11-one (19a). The diazoketone **17a** (250 mg, 0.94 mmol) was decomposed with 'activated CuO' catalyst (1 g, 12.58 mmol) for 10-11 h under the same conditions as described before for the preparation of **18b**, to yield the cyclopropyl ketone **19a** (34 mg, 15%) as a solid, mp 108-109°C (Et_2O-petroleum), homogeneous in GC (R_t 3.26 min at 230°C); IR (KBr) 1710 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.21 (s, 3H, $\rangle C-CH_3$), 1.28-2.26 (m, 6H, methylenes), 1.67 (s, 1H, -COCH-), 2.56 (δ_A) and 2.70 (δ_B) (AB_q, J = 16 Hz, 2H, $-CH_2CO-$), 3.17 (δ_A) and 3.43 (δ_B) (AB_q, J = 16 Hz, 2H, $ArCH_2-$), 7.18-7.44 (m, 4H, ArH). Anal. calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.37; H, 7.79%.

Carbenoid Decomposition of 17b : (±)-3,4-(3'-Methoxybenzo)-9α-methyltetracyclo[5,3,3,$0^{1,9}$,$0^{1,10}$]dodec-3-en-11-one (19b). A solution of the diazoketone **17b** (250 mg, 0.84 mmol) in anhydrous cyclohexane (100 ml) was decomposed with 'activated CuO' catalyst (1. g, 12.58 mmol) for 12 h under the same conditions as described for the preparation of **18b**. The crude product showed the presence of the cyclopropyl ketone **19b** (IR : 1740 cm^{-1}, 42% by GC) which on column chromatography over neutral alumina (15 g) and elution with Et_2O-petroleum (1:3) afforded pure **19b** (35 mg, 15%), mp 176-177°C (Et_2O-petroleum), homogeneous in GC (R_t 3.29 min at 270°C); IR (KBr) 1710 and 1600 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.18 (s, 3H, $\geq C-CH_3$), 1.20-2.62 (m, 6H, methylenes), 1.62 (s, 1H, $-COCH-$), 2.66 (s, 2H, $-CH_2CO-$), 3.10 (δ_A) and 3.42 (δ_B) (AB_q, J = 16 Hz, 2H, $ArCH_2$), 3.78 (s, 3H, $ArOCH_3$), 6.68 -7.14 (m, 2H, ArH), 7.20 (d, J = 8 Hz, 1H, C_5,-ArH). Anal. calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found : C, 80.51; H, 7.62%.

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