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CONDENSED CYCLIC AND BRIDGED-RING SYSTEMS-14[1]. SYNTHESIS OF SOME BRIDGED PROPANO-HYDROPHENANTHRENE, -HYDROFLUORENE AND POLYCYCLIC BENZO-PROPELLANE DERIVATIVES THROUGH INTRAMOLECULAR C-ALKYLATIONS OF γ,δ-UNSATURATED α'-DIAZOMETHYL KETONES

Chhanda Ray, Bijali Saha (in part) and Usha Ranjan Ghatak*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, INDIA.

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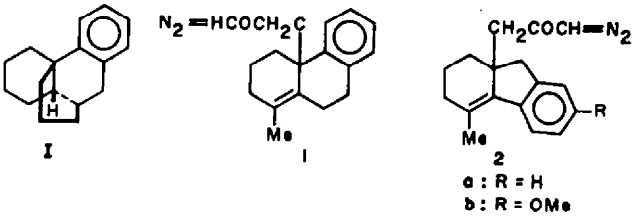
Abstract : Stereocontrolled synthesis of the bridged hydroaromatic ketones **7** and **8** through regiospecific reductive cleavages of the cyclopropyl ketone **5**, obtained by intramolecular keto-carbenoid addition of (±)-1-diazo-3-(1'-methyl-2',3',4',4a',9',10'-hexahydrophenanthren-4a'-yl)propan-2-one **(1)**, are described. An alternate stereocontrolled synthesis of **8** has been achieved by a regioselective α-oxocarbenoid insertion across the benzylic C-H (at C-4a) bond in the copper-catalyzed carbenoid decomposition of the α-diazomethyl ketone**(12)**. The cyclopropyl ketone **15a**, derived from the diazoketone (±)-1-diazo-3-(4'-methyl-2',3',9',9a'-tetrahydro-1'H-fluoren-9a'-yl)propan-2-one **(2a)** or the hydroxy ketone **17** produced by acid-catalyzed cleavage of **15a**, on catalytic hydrogenation with palladium-on-charcoal and reduction with lithium in liquid ammonia produced exclusively the epimeric bridged ketones **19a** and **20a** respectively. Unlike the cyclopropyl ketone **15a**, the corresponding 7-methoxy analogue **15b**, on acid-catalyzed cleavage, produced a benzo propellenone **18** through an interesting rearrangement.

The discovery of a remarkably powerful insect attractant bridged-hydrocarbon, (±)-9a-carbomorphinan **(I)**, reported in the preceding paper[1] in this series, prompted us to undertake exploratory synthetic investigations on related compounds for structure-activity evaluations. In this paper we describe synthesis of a few new bridged-propano-

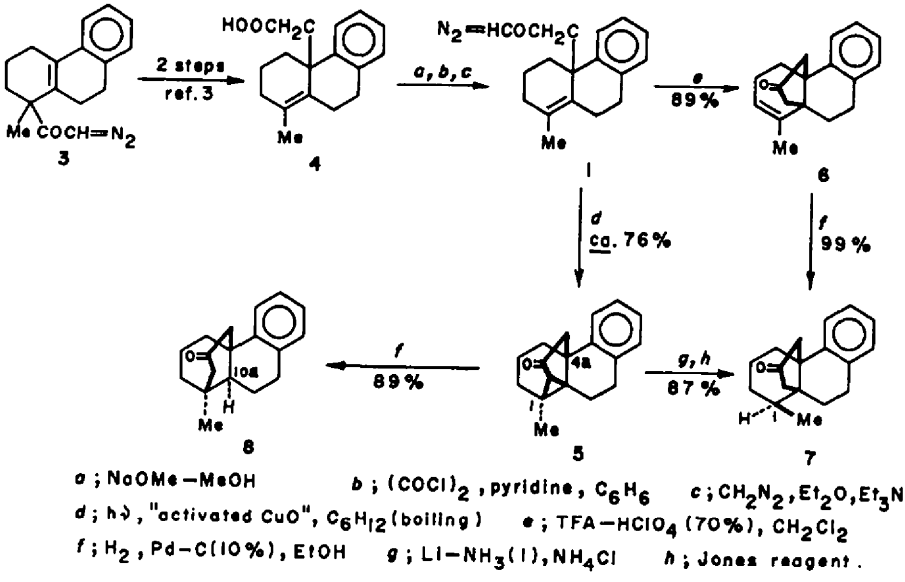


hydroaromatic and benzo-propellane derivatives by using intramolecular C-alkylations[2] of γ,δ-unsaturated α'-diazomethyl ketones **1**, **2a** and **2b** followed by some interesting fragmentations of the resulting products.

RESULTS AND DISCUSSIONS

Intramolecular C-Alkylation of the Diazoketone 1 and Transformations of the Resulting Products to the Benzopropellanone (7) and the Bridged Oxopropanohydrophenanthrene (8). The known acid 4 prepared in excellent yield through 'Vinylogous Wolff Rearrangement'[3] of the easily accessible diazoketone 3[4], was converted into the desired diazoketone 1 via sodium salt and corresponding acyl chloride by a standard method[5], which in turn was treated with an excess of ethereal diazomethane solution (Scheme-1). Intramolecular keto-carbenoid addition of the diazoketone 1 in the presence of 'activated CuO' catalyst[6] in boiling cyclohexane under irradiation with tungsten lamps produced the cyclopropyl ketone 5 (ca 76% by GC) along with other unidentified products. The trifluoroaceticacid-$HClO_4$ catalyzed cyclization[4] of the diazoketone 1 gave the unsaturated cyclopentanone 6 exclusively.

SCHEME-I



In general, the catalytic hydrogenation cleaves the least hindered bond of the three-membered ring[7], whereas in cyclopropyl ketones, lithium-ammonia induced reduction proceeds by cleavage of the cyclopropane bond most closely paralleling the neighbouring keto-carbonyl π-orbital[7,8].

Hydrogenolysis of the cyclopropyl ketone 5 in the presence of Pd-C (10%) in ethanol[9] at room temperature and pressure gave a six-membered ketone 8 in 89% yield, as the only isolable product. The stereochemistry of 8, initially assigned from analogies involving inversion at C-10a as was observed by us[5,6,9] in aromatic ring conjugated cyclopropane σ-bond cleavage under similar condition, has been confirmed by an alternate

stereocontrolled synthesis (Scheme-2). The examination of Drieding model of the cyclopropyl ketone 5 clearly indicates that the stereochemistry at C-10a in the hydrogenolyzed product 8 should be predominantly governed by the hindrance exerted by the C-1 and C-4a bridge in this compound. In contrast, lithium-liquid ammonia induced reduction[8] of the cyclopropyl ketone 5 followed by oxidation of the crude product with Jones reagent afforded the isomeric saturated cyclopentanone 7 in 87% yield. Catalytic hydrogenation of the hindered double bond in the unsaturated cyclopentanone 6 [Pd-C(10%) in ethanol], although proceeded quite slowly, gave the same ketone 7 exclusively. This observation lends strong support to the assigned stereochemistry of the C-1 methyl group in 7 involving the incoming hydrogen from the opposite side of the five-membered propellanone bridge in 6. Although the ^{1}H NMR spectrum of 7 displayed a complex pattern (see the Experimental Section) from which the stereochemistry of the C-1 methyl could not be ascertained, the relatively high field doublet at δ 0.88 indicated the β-configuration in analogy to related propellane systems[10]. The structure and stereochemistry of 7 has been confirmed by an X-ray crystal structure analysis† as shown in Figure-1.

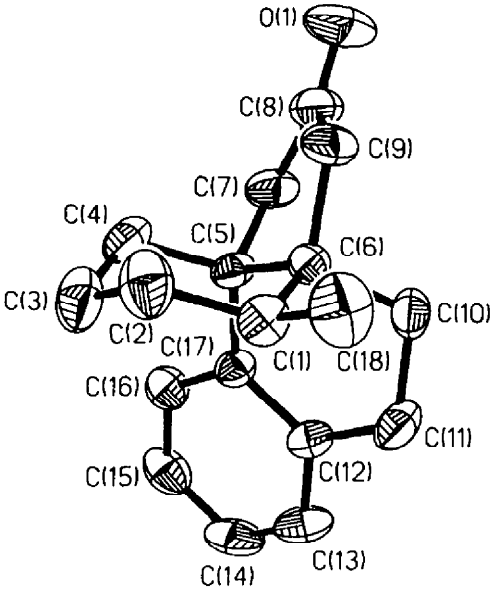
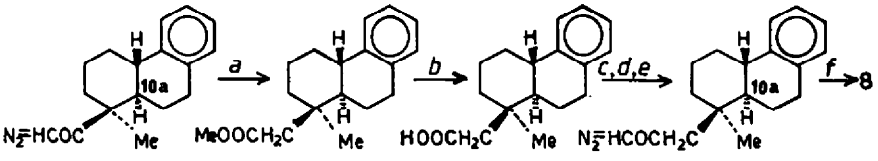


Figure-1. ORTEP plot of the X-ray model of 7 showing the crystallographic numbering.

†We thank Professor S. Ray and Dr. D. Ray for forwarding us the ORTEP plot of the final X-ray model of 7 (details to be published) carried out at 'The National Single Crystal Diffractometer facility' (Department of Science and Technology, Government of India) installed in the Department of Inorganic Chemistry of this Institute.

Stereocontrolled Synthesis of the Bridged Ketone 8 by Intramolecular α-oxocarbenoid Insertion of the Diazoketone 12. Although intramolecular carbon-hydrogen insertion through copper-catalyzed thermolysis of appropriately substituted cyclohexyl or polycarbocyclic diazomethyl ketones constitutes an attractive method for the synthesis of bridged bicyclo-[3.2.1]octanones[2,11], to our knowledge there is no report of the formation of bridged bicyclo[3.3.1]nonanone system by this method.

SCHEME— 2



9 10 11 12

a; hν, MeOH *b*; KOH, H_2O, MeOH *c*; NaOMe, MeOH
d; $(COCl)_2$, pyridine, C_6H_6 *e*; CH_2N_2, Et_2O, Et_3N
f; hν, "activated CuO", C_6H_{12}–THF (9:1) (boiling)

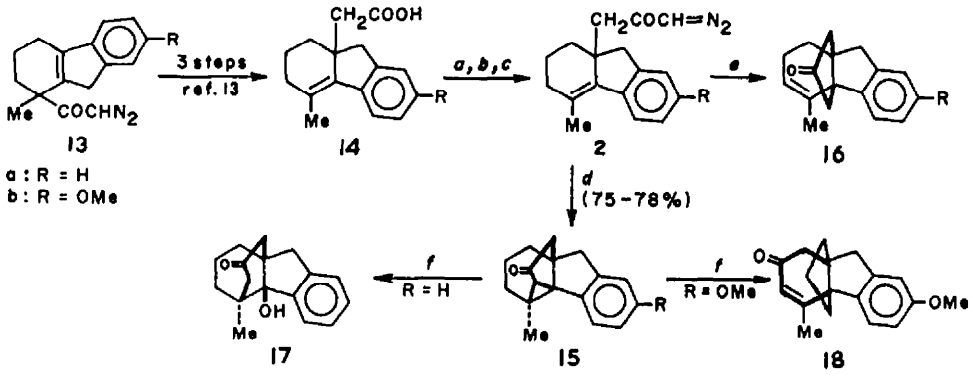
The known diazoketone 9[12] on photolysis in methanol[3] gave the homologated ester **10** in excellent yield. This on saponification gave the corresponding acid **11** which was converted to the diazoketone **12** by the usual procedure. Decomposition of **12** in dilute cyclohexane-THF mixture in the presence of 'activated CuO catalyst' under irradiation with tungsten lamps and chromatographic purification of the crude product gave the tetracyclic ketone **8** in 56% yield as the only isolable product (Scheme-2).

Intramolecular C-Alkylations of the Diazoketones 2a and 2b and Transformations of the Resulting Products to the Benzopropellenones (16) and (18) and the Bridged Oxopropano-hydrofluorenes (19a), (20a) and (20b). The starting γ,δ-unsaturated hydrofluorene acids **14a** and **14b**, prepared from the respective β,γ-unsaturated diazoketones **13a**[4] and **13b**[4] by alkylation rearrangement reactions[13], were converted to the respective diazoketones **2a** and **2b** by the standard procedure (Scheme-3). Intramolecular ketocarbenoid additions of **2a** and **2b** in the presence of 'activated CuO' catalyst in boiling cyclohexane under irradiation afforded the respective cyclopropyl ketones **15a** and **15b** in excellent yields. The acid-catalyzed cyclisation of the diazoketone **2a** with trifluoroacetic acid-$HClO_4$ (70%) in CH_2Cl_2 gave the propellenone **16a** (68% by GC) along with two other unidentified products; the methoxy analogue **2b** however, gave a complex mixture of products from which the propellenone **16b** could not be isolated in pure form (see Experimental).

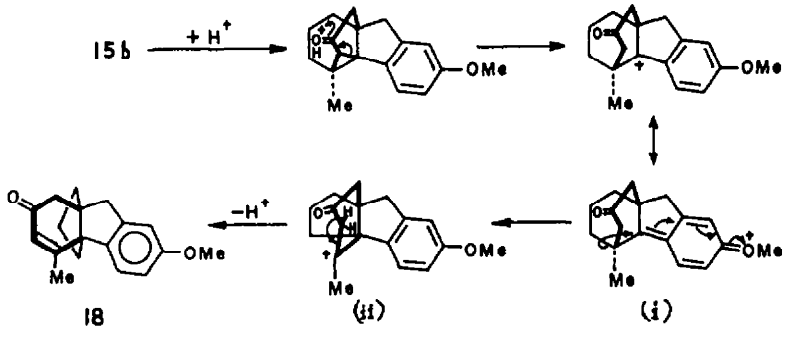
While fragmentation of the cyclopropyl ketone **15a** with dry HCl gas in $CHCl_3$[5] produced a stereochemically homogeneous bridged hydroxycyclohexanone **17** in 73% yield, the corresponding methoxy analogue **15b** gave a rearranged cyclohexenone **18** (73% by GC) along

with another minor component. The structures of **17** and **18** were identified by spectral and analytical data (see Experimental Section). The stereochemical assignment of the hydroxy ketone **17** has been established by correlation of the resulting hydrogenolysis products

SCHEME-3



with those of the cyclopropyl ketone **15a** (Scheme-4). The formation of **18** in the acid-catalyzed fragmentation of the cyclopropyl ketone **15b** can be easily rationalized through the intermediate cations (i) and (ii) as shown below :

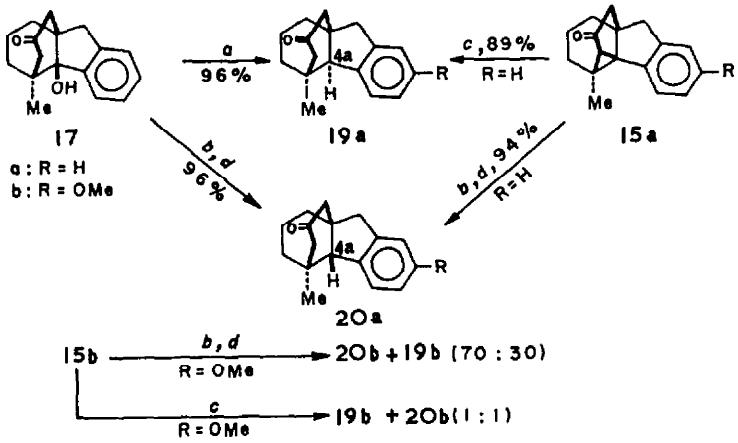


The difference in the fragmentation reactions of the cyclopropyl ketones **15a** and **15b** is possibly due to the stabilization of the benzylic cation (i) in the latter by the p-methoxy group[14] leading to the rearranged product **18**.

While catalytic hydrogenation of the hydroxy-ketone **17** over Pd-C (10%) in ethanol containing catalytic amount of $HClO_4$, produced exclusively **19a**, the reductive cleavage of **17** with lithium in liquid ammonia followed by oxidation with Jones reagent gave the epimeric ketone **20a** in excellent yield (Scheme-4). The stereochemistry at C-4a in the

epimeric ketones **19a** and **20a** have been assigned by analogies with the results of hydrogenolyses of similar bridged-hydroxycyclopentanones by catalytic[13,15] and chemical[13,16] reductions. These stereochemical assignments have been further confirmed by reductive cleavages of the cyclopropyl ketone **15a** by catalytic (Pd-C, H_2) and chemical [Li-NH_3(l)] methods, leading exclusively to the epimeric ketones **19a** and **20a** respectively (Scheme-4). It has been well established in our laboratory that in aryl conjugated cyclopropyl ketones

SCHEME-4



a; H_2, Pd-C (10%), EtOH, $HClO_4$ (70%, catalytic amount)
b; Li-NH_3(l), NH_4Cl *d*; Jones reagent
c; H_2, Pd-C (10%), EtOH.

similar to **15a**, Pd-C (10%), EtOH induced hydrogenolysis proceed through inversion of configuration at the benzylic asymmetric centre[5,6,9]. The present result of lithium-ammonia induced cyclopropyl bond cleavage in **15a** clearly shows that the stereochemical outcome in the product **20a**, with retention of configuration at the benzylic C-4a centre, is similar to that observed in the respective hydroxy cyclohexanone **17** or similar systems[13,16]. In contrast to the cyclopropyl ketone **15a**, the corresponding methoxy analogue **15b** on reductive cleavage with Li-NH_3(l) gave a mixture of two epimeric ketones **20b** and **19b** in a ratio of ca 70:30, from which the major epimer **20b** was separated (Scheme-4). Catalytic hydrogenolysis of **15b** with Pd-C (10%) in ethanol gave an inseparable mixture of **19b** and **20b** in a ratio of ca 1:1. As before, the stereochemical assignments at C-4a in the epimeric ketones **20b** and **19b** were made by analogies with the results of hydrogenolyses of related bridged hydroxycyclopentanones by catalytic[13,15] and chemical[13,16] methods. The difference in the stereochemical outcome in the hydrogenolyses of the des-methoxy and the p-methoxy cyclopropyl ketones **15a** and **15b** again reveal that the reactivities at the benzylic centre is strongly influenced by the p-methoxy group.

In conclusion, the present work provides efficient synthetic routes to some new bridged oxopropano-hydrophenanthrene, -hydrofluorene and benzopropellane[17] derivatives involving few mechanistically and stereochemically interesting fragmentation reactions of easily accessible intermediates derived by intramolecular C-alkylation reactions in γ,δ-unsaturated α'-diazomethyl ketones.

EXPERIMENTAL

The compounds described are all racemates. IR spectra were recorded on a Perkin-Elmer model PE 298 spectrometer. ^{1}H 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 ionisation 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%). The mass spectra were recorded on a VG Micromass 7070H instrument with 70 ev electric energy and 200A emission current by the courtesy of Indian Institute of Chemical Technology, Hyderabad. Elemental analyses were performed by P.P. Bhattacharya and S. Sarkar of this laboratory. Column chromatography was performed on neutral alumina (Brockman Grade I) or silica gel [Glaxo Laboratories (India) Ltd.]. Petroleum refers to fractions of bp 60-80°C.

(±)-1-Diazo-3-(1'-methyl-2',3',4',4a',9',10'-hexahydrophenanthren-4a'-yl)propan-2-one (1). The sodium salt of the acid **4**[3] (1.0 g, 3.91 mmol) was prepared adopting the usual procedure[5]. To a stirred ice-cold suspension of this sodium salt in dry benzene (25 ml) containing pyridine (0.1 ml, 1.16 mmol) was added dropwise oxalyl chloride (2.0 ml, 23.32 mmol). The mixture was kept at 0°C for 30 min, at room temperature for 30 min and finally warmed to 60°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 over 15 min to ice-cold and magnetically stirred ethereal diazomethane [from N-methyl N-nitrosourea (4.0 g, 38.83 mmol)] containing dry triethylamine (0.6 ml, 4.3 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 (30 g). Elution with Et_2O-petroleum (1:4) furnished 950 mg (87%) of the diazoketone **1** as a yellowish thick liquid; IR (neat) 2100 (CHN_2), 1630 (CO) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.58-3.04 (total 10H, m, $COCH_2$ and 4 x CH_2), 1.70 (3H, s, C=C-Me), 2.73 (2H, br t, $ArCH_2$), 4.62 (1H, br s, CHN_2), 7.12-7.30 (3H, m, ArH), 7.34 (1H, dd, J = 12 and 2 Hz, $C_{5'}$-ArH).

Carbenoid Decomposition of the Diazoketone 1 : (±)-4,5-Benzo-10α-methyltetracyclo[5,4,3,$0^{1,10}$,$0^{1,11}$]tridec-4-en-12-one (5). The diazoketone **1** (250 mg, 0.89 mmol) in anhydrous cyclohexane (100 ml) was stirred and refluxed with 'activated copper oxide' catalyst[6] (1g, 12.5 mmol) under irradiation by two 250W tungsten lamps under N_2atmosphere. The time required for complete decomposition of the diazoketone was 10 h. The cooled mixture

was filtered and the solvent was distilled off in vacuo. The resultant semisolid product showed the presence of the cyclopropyl ketone **5** (76% by GC) which on column chromatography over neutral alumina (15 g) and elution with Et_2O-petroleum (2:3) afforded pure **5** (60 mg, 27%); mp 105-106°C (Et_2O-petroleum), homogeneous in GC (R_t 5.42 min at 230°C); IR (KBr) 1710 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.24 (3H, s, Me), 1.32-2.18 (8H, m, 4 x CH_2), 2.59 (1H, s, COCH), 2.65 (δ_A) and 2.77 (δ_B) (2H, ABq, J = 16 Hz, $COCH_2$), 2.84 (2H, t, J = 8 Hz, $ArCH_2$), 7.16-7.36 (4H, m, ArH); MS, m/e (relative intensity) 252 (M^+, 44), 224 (29), 210 (100), 195 (31), 181 (35), 165 (23), 141 (21), 128 (18). Anal. calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found : C, 85.60; H, 8.22%.

Acid-catalyzed Intramolecular Alkylation Reaction of the Diazoketone 1 : (±)-1-Methyl-3,4,4a,9,10,10a-hexahydro-4aβ,10aβ-propanophenanthren-12-one (6). To an ice-cold stirred solution of the diazoketone **1** (200 mg, 0.71 mmol) in dry CH_2Cl_2 (20 ml) was added dropwise a mixture of TFA (0.4 ml, 0.52 mmol) and 70% aqueous $HClO_4$ (0.1 ml, 1.17 mmol) in CH_2Cl_2 (10 ml) over 5 min. The mixture was kept at 0°C for an additional 5 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 (10 g) and elution with Et_2O-petroleum (1:9) afforded the unsaturated cyclopentanone **6** (160 mg, 89%), mp 108-109°C (Et_2O-petroleum), homogeneous in GC (R_t 4.54 min at 230°C); IR (KBr) 1735 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.42-2.28 (6H, m, 3 x CH_2), 1.72 (3H, br s, C=C-Me), 2.46 (δ_A) and 2.74 (δ_B) (2H, ABq, J = 20 Hz, $COCH_2$), 2.60 (2H, s, $COCH_2$), 2.72 (2H, t, J = 6 Hz, $ArCH_2$), 5.58 (1H, br t, C=CH), 7.08-7.44 (4H, m, ArH); MS (m/e) (relative intensity) 252 (M^+, 100), 195 (93), 179 (20), 165 (23), 156 (22), 141 (28), 135 (21), 115 (20). Anal. calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found : C, 85.88; H, 7.89%.

Catalytic Hydrogenolysis of the Cyclopropyl Ketone 5 : (±)-1α-Methyl-1,2,3,4,4a,9,10,10aα-octahydro-1β,4aβ-propanophenanthren-12-one (8). A solution of the cyclopropyl ketone **5** (50 mg, 0.19 mmol) in ethanol (10 ml) was hydrogenolyzed over Pd-C (10%, 35 mg). The uptake of hydrogen was complete within 15-20 min. The catalyst was filtered off and the filtrate concentrated to afford **8** (45 mg, 89%), mp 107-108°C (Et_2O-petroleum), homogeneous in GC (R_t 6.12 min at 230°C); IR (KBr) 1710 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.26 (3H, s, Me), 1.34-2.74 (total 13 H, m, 2 x $COCH_2$, CH and 4 x CH_2), 2.84 (2H, t, J = 8 Hz, $ArCH_2$), 6.98-7.38 (4H, m, ArH). Anal. calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found : C, 84.69; H, 8.62%.

(±)-1β-Methyl-1,2,3,4,4a,9,10,10a-octahydro-4aβ,10aβ-propanophenanthren-12-one (7).

(A) Hydrogenolysis of the Cyclopropyl Ketone 5 with Li-NH_3(l) : To a magnetically stirred solution of the cyclopropyl ketone **5** (25 mg, 0.099 mmol) in dry Et_2O (10 ml) and anhydrous liquid NH_3 (50 ml) distilled over Na, was added freshly scrapped Li-wire (20 mg, 2.85 mg-atom) in small portions over 3 min. Stirring was continued for a further

5 min after which an excess of powdered NH_4Cl was added and the NH_3 was allowed to evaporate. The residue was diluted with water and extracted with Et_2O. The extract was dried (Na_2SO_4) and evaporated and the resulting crude viscous gum (24 mg) was dissolved in acetone (5 ml) and oxidised with Jones reagent[18] at 10-15°C until the colour of the reagent persisted for 10 min; the mixture was then worked up. The crude product was chromatographed on neutral alumina (2.5 g) and elution with Et_2O-petroleum (3:17) afforded the cyclopentanone **7** (22 mg, 87%), mp 129-130°C (Et_2O-petroleum), homogeneous in GC (R_t 5.43 min at 230°C); IR (KBr) 1730 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 0.88 (3H, d, J = 8 Hz, Me), 0.94-3.10 (total 11H, m, $COCH_2$, CH and 4 x CH_2), 2.26 (δ_A) and 2.60 (δ_B) (2H, ABq, J = 20 Hz, $COCH_2$), 2.70 (2H, t, J = 10 Hz, $ArCH_2$), 7.14-7.26 (4H, m, ArH). Anal. calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found : C, 85.31; H, 8.66%.

(B) Catalytic Hydrogenation of the Unsaturated Ketone 6 : The unsaturated cyclopentanone **6** (100 mg, 0.39 mmol) in ethanol (15 ml) was hydrogenated as usual. The uptake of hydrogen was very slow and required ca 24 h for completion. This on work-up gave **7** (100 mg, 99%), mp and mixed mp 129-130°C, identical with the sample described above in all respect (^1H NMR, IR, GC).

(±)-Methyl 1α-methyl-1,2,3,4,4aβ,9,10,10aα-octahydrophenanthren-1β-ylacetate (10). Photo-Wolff Rearrangement of the Diazoketone (9) : A solution of the diazoketone **9** (250 mg, 0.93 mmol) in dry methanol (120 ml) was irradiated with a 450-W Hanovia medium pressure mercury vapour lamp using a pyrex filter for 3 h 40 min. Evaporation of the solvent and chromatography of the resulting semi-solid mass on neutral alumina (10 g) and elution with Et_2O-petroleum (1:4) afforded the homologated ester **10** (240 mg, 94%), mp 48°C (Et_2O-petroleum), homogeneous in GC (R_t 4.37 min at 230°C); IR (KBr) 1735 (CO) cm^{-1}; ^1H NMR (60 MHz, CCl_4) 1.07 (3H, s, Me), 1.10-2.93 (total 14H, m, $COCH_2$, 2 x CH, 5 x CH_2), 3.57 (3H, s, OMe), 6.83-7.37 (4H, m, ArH). Anal. calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found : C, 79.44; H, 9.07%.

(±)-1α-Methyl-1,2,3,4,4aβ,9,10,10aα-octahydrophenanthren-1β-ylacetic acid (11). Saponification of **10** (200 mg, 0.74 mmol) with 10% methanolic KOH (2.5 ml) afforded **11** which on chromatography over silica gel (7 g) and elution with Et_2O-petroleum (1:3) afforded pure **11** (170 mg, 90%), mp 175°C (EtOAc-petroleum); IR (KBr) 1695 (CO) cm^{-1}. Anal. calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found : C, 79.30; H, 8.95%.

(±)-1-Diazo-3-(1'α-methyl-1',2',3',4',4a'β,9',10',10a'α-octahydrophenanthren-1'β-yl)propan-2-one (12). The acid **11** (100 mg, 0.38 mmol) was converted to the diazoketone **12** (100 mg, 92%) as a light yellow liquid [purified by passing through a column of neutral alumina (2.5 g) with Et_2O-petroleum (1:3) as eluant] following the identical procedure as described earlier the preparation of **1**. IR (neat) 2105 (CHN_2), 1630 (CO) cm^{-1}; ^1H NMR (60 MHz, CCl_4) 1.10 (3H, s, Me), 1.17-2.93 (total 14H, m, $COCH_2$, 2 x CH and 5 x CH_2), 5.13 (1H, br s, CHN_2), 6.83-7.33 (4H, m, ArH).

Intramolecular Insertion Reaction of the Diazoketone 12. A solution of the diazoketone **12** (40 mg, 0.14 mmol) in a mixture of anhydrous C_6H_{12} and THF (9:1) was added during 1 h to a magnetically stirred and refluxing solution of 'activated CuO catalyst' (200 mg, 2.5 mmol) in dry cyclohexane (50 ml) under irradiation by two 100-W tungsten lamps; the refluxing was continued for further 9 h when the diazoketone i.r. band had disappeared. The cooled solution was filtered through neutral alumina (5 g) and the column was eluted with Et_2O-petroleum (1:3). Evaporation of the combined organic layers gave **8** (20 mg, 56%). Recrystallisation once from Et_2O-petroleum gave analytically pure **8**, mp 107-108°C identical (mixed mp, IR, ^1H NMR, GC) with the sample prepared earlier.

(±)-1-Diazo-3-(4'-methyl-2',3',9',9a'-tetrahydro-1'H-fluoren-9a'-yl)propan-2-one (2a). The acid **14a**[13] (1.05 g, 4.3 mmol), prepared from **13a**[4], was converted to the diazoketone **2a** (1.00 g, 87%) as a light yellow solid, mp 75°C [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 **1**. IR (KBr) 2105 (CHN_2), 1615 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.20-2.60 (total 8H, m, $COCH_2$ and 3 x CH_2), 1.96 (3H, s, C=C-Me), 2.74 (δ_A) and 3.42 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 5.14 (1H, br s, CHN_2), 7.14-7.44 (3H, m, ArH), 7.44-7.58 (1H, m, either $C_{5'}$-ArH or $C_{8'}$-ArH). Anal. calcd. for $C_{17}H_{18}ON_2$: C, 76.66; H, 6.81. Found : C, 76.82; H, 6.70%.

(±)-1-Diazo-3-(7'-methoxy-4'-methyl-2',3',9',9a'-tetrahydro-1'H-fluoren-9a'-yl)propan-2-one (2b). The crude diazoketone, prepared from 1.09 g (4.0 mmol) of the acid **14b**[13] following the aforementioned procedure, was filtered through neutral alumina (15 g) with Et_2O-petroleum (3:7) as eluant to furnish 920 mg (78%) of pure **2b**, mp 120°C; IR (KBr) 2100 (CHN_2), 1640 (CO) and 1625 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.18-2.52 (total 8H, m, $COCH_2$ and 3 x CH_2), 1.91 (3H, s, C=C-Me), 2.62 (δ_A) and 3.30 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 3.80 (3H, s, ArOMe), 5.13 (1H, br s, CHN_2), 6.74-6.95 (2H, m, ArH), 7.39 (1H, d, J = 8 Hz, $C_{5'}$-ArH). Anal. calcd. for $C_{18}H_{20}O_2N_2$: C, 72.95; H, 6.80. Found : C, 72.80; H, 6.97%.

Carbenoid Decomposition of the Diazoketones 2a and 2b : (i) (±)-2,3-Benzo-9α-methyltetracyclo-[5,3,3,$0^{1,9}$,$0^{1,10}$]dodec-2-en-11-one (15a). A solution of the diazoketone **2a** (260 mg, 0.98 mmol) in anhydrous cyclohexane (100 ml) was stirred and refluxed for 6 h with 'activated copper oxide' catalyst (1 g, 12.5 mmol) under irradiation as described for **5**. Usual work-up followed by chromatography on neutral alumina (15 g) and elution with Et_2O-petroleum (1:3) afforded the cyclopropyl ketone **15a** (180 mg, 78%); mp 124°C (Et_2O-petroleum), homogeneous in GC (R_t 4.04 min at 230°C); IR (KBr) 1705 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.22-1.86 (6H, m, 3 x CH_2), 1.52 (3H, s, Me), 1.90 (1H, s, COCH), 2.50 (δ_A) and 2.68 (δ_B) (2H, ABq, J = 18 Hz, $COCH_2$), 3.19 (δ_A) and 3.31 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 7.14-7.24 (4H, m, ArH); MS, m/e (relative intensity) 238 (M^+, 24), 196 (193), 181 (100), 165 (44), 152 (26), 141 (34), 128 (27), 115 (25). Anal. calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.87; H, 7.83%.

(ii) (±)-2,3-(4'-Methoxybenzo)-9α-methyltetracyclo-[5,3,3,$0^{1,9}$,$0^{1,10}$]dodec-2-en-11-one (15b). The diazoketone **2b** (250 mg, 0.84 mmol) was decomposed with 'activated CuO' catalyst for 7 h under the condition described for 5 to yield the crude cyclopropyl ketone **15b** which was chromatographed on neutral alumina (15 g) with Et_2O-petroleum (3:7) as eluant to afford pure **15b** (170 mg, 75%); mp 92°C (Et_2O-petroleum), homogeneous in GC (R_t 8.17 min at 230°C); IR (KBr) 1705 (CO) and 1620 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) 1.10-2.24 (6H, m, 3 x CH_2), 1.46 (3H, s, Me), 1.78 (1H, s, COCH), 2.45 (δ_A) and 2.63 (δ_B) (2H, ABq, J = 16 Hz, $COCH_2$), 3.10 (δ_A) and 3.22 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 3.76 (3H, s, ArOMe), 6.64-6.92 (2H, m, ArH), 7.02 (1H, d, J = 10 Hz, C_2,-ArH); MS, m/e (relative intensity) 268 (M^+, 24), 240 (11), 226 (100), 211 (28), 197 (10), 175 (27), 165 (10), 153 (9), 115 (12). Anal. calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found : C, 80.59; H, 7.70%.

Acid-catalyzed Intramolecular Alkylation Reaction of the Diazoketone 2a : (±)-4-Methyl-1,2,9,9a-tetrahydro-4aβ,9aβ-propano-4aH-fluoren-11-one (16a). The diazoketone **2a** (200 mg, 0.75 mmol) in CH_2Cl_2 (20 ml) was cyclized with TFA (0.4 ml, 0.52 mmol) and 70% aqueous $HClO_4$ (0.1 ml, 0.17 mmol) in CH_2Cl_2 (10 ml) under the same conditions as described for **6**. The crude product containing **16a** (68% by GC) on column chromatography over neutral alumina (15 g) and elution with Et_2O-petroleum (1:4) furnished pure **16a** (20 mg, 11%), mp 97-98°C (Et_2O-petroleum), homogeneous in GC (R_t 3.22 min at 230°C); IR (KBr) 1735 (CO) cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) 1.20-2.32 (4H, m, 2 x CH_2), 1.64 (3H, m, C=C-Me), 2.24 (2H, s, $COCH_2$), 2.49 (δ_A) and 2.97 (δ_B) (2H, ABq, J = 18 Hz, $COCH_2$), 2.61 (δ_A) and 3.23 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 5.40 (1H, br t, C=CH), 7.08-7.40 (4H, m, ArH). Anal. calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.77; H, 7.69%.

Acid-catalyzed cyclisation of the diazoketone **2b** under identical conditions as above, afforded, along with a number of other compounds, the unsaturated bridged ketone **16b** [evident from the IR carbonyl band at 1740 cm^{-1} and a signal for the olefenic proton at δ5.42 (br t) in the ^1H NMR spectrum] which could not be isolated in pure form.

Acid-catalyzed Fragmentation of the Cyclopropyl ketones 15a and 15b : (i) (±)-4aβ-Hydroxy-4α-methyl-2,3,4,4a,9,9a-hexahydro-4β,9aβ-propano-1H-fluoren-11-one (17). Through a solution of the cyclopropyl ketone **15a** (140 mg, 0.59 mmol) in anhydrous $CHCl_3$ (50 ml) was bubbled a stream of dry HCl at 0°C for 1 h. The organic layer was washed successively with water, $NaHCO_3$ aq. (5%), water and dried ($CaCl_2$). Removal of the solvent followed by chromatography of the resultant semi-solid mass on silica gel (10 g) and elution with Et_2O-petroleum (3:17) afforded the 4aβ-hydroxy cyclohexanone **17** (110 mg, 73%), mp 172-173°C (Et_2O-petroleum), homogeneous in GC (R_t 5.25 min at 230°C); IR (KBr) 3480 (OH), 1695 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.28-1.70 (total 7H, m, 3 x CH_2 and C_{4a}-O<u>H</u> which appeared at δ 1.64 was exchangeable with D_2O),

1.47 (3H, s, Me), 2.27 (δ_A) and 2.95 (δ_B) (2H, ABq, J = 16 Hz, $COCH_2$), 2.52 (δ_A) and 3.22 (δ_B) (2H, ABq, J = 16 Hz, $COCH_2$), 2.56 (δ_A) and 3.22 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 7.24-7.44 (3H, m, ArH), 7.62-7.70 (1H, m, either C_5-ArH or C_8-ArH); MS, m/e (relative intensity) 256 (M^+, 61), 196 (100), 181 (28), 158 (35), 145 (62), 128 (23), 115 (28), 91 (21). Anal. calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found : C, 79.80; H, 7.45%.

(ii) (±)-7-Methoxy-4-methyl-1,2,9,9a-tetrahydro-4aβ,9aβ-propano-4aH-fluoren-3-en-2-one (18). Acid-catalyzed fragmentation of the cyclopropyl ketone **15b** (100 mg, 0.37 mmol) under identical conditions as above, afforded, after removal of the solvent, a faint yellow liquid which showed the presence of the bridged propellenone **18** (73% by GC) which on column chromatography over silica gel (5 g) and elution with Et_2O-petroleum (1:4) furnished pure **18** (20 mg, 20%), homogeneous in GC (R_t 9.50 min at 230°C); UV (EtOH) λ_{max} 231 nm (log ε 4.69) and 2.90 nm (log ε 4.29); IR (neat) 1665 (C=C-CO) and 1620 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.06-2.52 (total 6H, m, 3 x CH_2), 1.97 (3H, s, C=C-Me), 2.56 (2H, s,C=C-$COCH_2$), 2.82 (δ_A) and 2.88 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 3.80 (3H, s, ArOMe), 5.80 (1H, s, C=CH), 6.78-6.90 (2H, m, ArH), 7.27 (1H, d, J = 8 Hz, C_5-ArH). MS^{19}, m/e (relative intensity) 268.3399 (M^+, 45, calcd. for $C_{18}H_{20}O_2$, 268.3400), 240 (13), 226 (100), 21 (25), 197 (10).

(±)-4α-Methyl-2,3,4,4aα,9,9a-hexahydro-4β,9aβ-propano-1H-fluoren-11-one (19a). Method (A): Catalytic Hydrogenation of the Hydroxyketone 17 in the presence of Acid : To a solution of the hydroxyketone **17** (20 mg, 0.08 mmol) in EtOH (5 ml) was added 70% aqueous $HClO_4$ (0.1 ml). The solution was hydrogenated at room temperature and atmospheric pressure in the presence of Pd-C (10%, 10 mg) for 24 h after which it was cautiously neutralised with solid Na_2CO_3 and the catalyst was filtered off. Removal of the solvent followed by chromatography on neutral alumina (5 g) with Et_2O-petroleum (1:3) as eluant afforded the bridged ketone **19a** (18 mg, 96%), mp 124-125°C (Et_2O-petroleum), homogeneous in GC (R_t 3.21 min at 230°C); IR (KBr) 1705 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.32-1.88 (total 6H, m, 3 x CH_2), 1.42 (3H, s, Me), 2.06 (δ_A) and 2.12 (δ_B) (2H, ABq, J = 16 Hz, $COCH_2$), 2.21 (δ_A) and 2.41 (δ_B) (2H, ABq, J = 16 Hz, $COCH_2$), 2.61 (δ_A) and 2.73 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 2.80 (1H, s, ArCH), 7.14-7.40 (3H, m, ArH), 7.40-7.60 (1H, m, either C_5-ArH or C_8-ArH). Anal. calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.95; H, 8.68%.

Method (B) : Catalytic Hydrogenolysis of the Cyclopropylketone 15a : A solution of the cyclopropyl ketone **15a** (100 mg, 0.42 mmol) in EtOH (20 ml) was hydrogenated over Pd-C (10%, 70 mg). The uptake of hydrogen was completed within 15-20 min. Usual work-up as described for the preparation of **8** afforded the bridged ketone **19a** (90 mg, 89%), mp and mixed mp 124-125°C, identical with the sample described above in all respect (^1H NMR, IR, GC).

(±)-4α-Methyl-2,3,4,4aβ,9,9a-hexahydro-4β,9aβ-propano-1H-fluoren-11-one (20a). Method (A): Hydrogenolysis of the 4aβ-hydroxycyclohexanone 17 with Li-NH_3 : Reduction of the hydroxy ketone **17** (50 mg, 0.19 mmol) in dry ether (10 ml) and anhydrous NH_3 (80 ml) with freshly scrapped Li-wire (30 mg, 4.3 mg atom) was carried out as described for compound **7**, with stirring for an additional 15 min. After work-up, it was oxidized with Jones reagent. The crude product was chromatographed on neutral alumina (5 g) and elution with Et_2O-petroleum (3:17) afforded the ketone **20a** (45 mg, 96%), mp 100°C (Et_2O-petroleum), homogeneous in GC (R_t 3.24 min at 230°C); IR (KBr) 1705 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 1.22-2.24 (total 6H, m, 3 x CH_2), 1.43 (3H, s, Me), 2.32 (2H, s, $COCH_2$), 2.59 (δ_A) and 2.73 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 2.65 (2H, br s, $COCH_2$), 3.12 (1H, s, ArCH), 7.18-7.38 (3H, m, ArH), 7.38-7.62 (1H, m, either C_5-ArH or C_8-ArH). Anal. calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found : C, 84.91; H, 8.41%.

Method (B) : Hydrogenolysis of the Cyclopropylketone 15a with Li-NH_3 : Reduction of the cyclopropyl ketone **15a** (100 mg, 0.42 mmol) in dry ether (15 ml) and anhydrous NH_3 (125 ml) with Li-wire (60 mg, 8.57 mg atom) followed by oxidation with Jones reagent and chromatography on neutral alumina (10 g) with Et_2O-petroleum (3:17) as eluant afforded **20a** (95 mg, 94%), mp and mixed mp 100°C, identical with the sample described above in all respect (^1H NMR, IR, GC).

(±)-7-Methoxy-4α-methyl-2,3,4,4aβ,9,9a-hexahydro-4β,9aβ-propano-1H-fluoren-11-one (20b). Method (A) : Hydrogenolysis of the Cyclopropylketone 15b with Li-NH_3 : Reduction of the cyclopropyl ketone **15b** (100 mg, 0.37 mmol) in dry ether (15 ml) and anhydrous NH_3 (150 ml) with Li-wire (119 mg, 17 mg atom) was carried out as described for compound **7**. Oxidation with Jones reagent followed by usual work-up gave a semi-solid mass which showed the presence of the two epimeric ketones **20b** and **19b** in the ratio of ca 70:30 (by GC and ^1H NMR). The IR spectrum showed a single carbonyl band at 1695 cm^{-1}. The ^1H NMR spectrum of the crude product showed signals at δ 1.42, 1.38 (two methyl singlets) and δ 3.82, 3.76 (two methoxy singlets), the latter values in both the sets corresponding to the minor epimer **19b**. Column chromatography over neutral alumina (10 g) and elution with Et_2O-petroleum (2:3), the major epimer **20b** (40 mg, 40%) was obtained, mp 100-101°C (Et_2O-petroleum), homogeneous in GC (R_t 8.76 min at 230°C); IR (KBr) 1695 (CO) and 1615 cm^{-1} ; ^1H NMR (200 MHz, $CDCl_3$) 1.18-2.14 (total 6H, m, 3 x CH_2), 1.42 (3H, s, Me), 2.32 (2H, m, $COCH_2$), 2.57 (δ_A) and 2.71 (δ_B) (2H, ABq, J = 16 Hz, $ArCH_2$), 2.60 (2H, s, $COCH_2$), 3.08 (1H, s, ArCH), 3.82 (3H, s, ArOMe), 6.72-6.94 (2H, m, ArH), 7.32-7.38 (1H, m, C_5-ArH). Anal. calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found : C, 80.02; H, 8.11%.

The minor epimer **19b** could not be obtained in pure form.

Method (B) : Catalytic Hydrogenolysis of the Cyclopropylketone 15b : A solution of the cyclopropyl ketone **15b** (100 mg, 0.42 mmol) in ethanol (20 ml) was hydrogenated over Pd-C (10%, 70 mg). The uptake of hydrogen was completed within 15-20 min. Usual work-

up afforded the epimeric ketones **19b** and **20b** in a ratio of ca 1:1 (by GC and ^{1}H NMR) which could not be separated by column chromatography.

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