Synthetic Studies towards Complex Diterpenoids. Part VIII.† Stereocontrolled Synthesis of (±)-2-Methoxy-11β-methyl-4bα*H*-gibba-1(10a),2,4-trien-8-one and Related Compounds through Intramolecular Alkylations of γδ-Unsaturated α'-Diazomethyl Ketones

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Like the corresponding 1-demethyl analogues, the α'-diazomethyl ketones 2β-diazoacetyl-7-methoxy-1β-methyl-1,2,3,4-tetrahydrofluorene and -1,2,3,4,9,10-hexahydrophenanthrene (1a and b) undergo smooth intramolecular oxocarbenoid addition and boron trifluoride–ether-catalysed cyclisation, leading to the cyclopropyl ketones 2-methoxy-11β-methyl-4bβ,9-cyclogibba-1(10a),2,4-trien-8-one (2a) and 3-methoxy-14β-methyl-9β,15-cyclo-17,18,19,20-tetranorphylloclada-1(10),2,4-trien-16-one (2b) and the tetracyclic ketones 2-methoxy-11β-methylgibba-1(10a),2,4,4b-tetraen-8-one (3a) and 3-methoxy-14β-methyl-17,18,19,20-tetranorphylloclada-1(10),2,4,9(11)-tetraen-16-one (3b), respectively. Catalytic hydrogenation of the cyclopropyl ketones (2a and b) and of the unsaturated ketones (3a and b) produced 2-methoxy-11β-methyl-4bα*H*-gibba-1(10a),2,4-trien-8-one (4a) and 3-methoxy-14β-methyl-9α*H*-17,18,19,20-tetranorphylloclada-1(10),2,4-trien-16-one (4b).

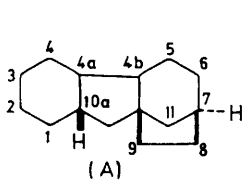
PREVIOUSLY we have reported [1] two simple routes for producing the bicyclo[3.2.1]octan-6-one unit fused within reduced fluorene and phenanthrene systems *via* intramolecular alkylations of γδ-unsaturated α'-diazomethyl ketones. These reactions have been extended [2] to the synthesis of several 4bα*H*- and 4bβ*H*-gibbane derivatives. We now report on the evaluation of the conformational effect of a 1β-methyl substituent ‡ in the diazoketones (1a and b) on the courses of intramolecular oxocarbenoid addition and BF_3–Et_2O catalysed cyclisations,[3] and on the stereoselectivities of catalytic hydrogenation of the derived pentacyclic ketones (2a and b) and tetracyclic ketones (3a and b). Stereoselective formation of the 11β-methyl gibbane (4a) and the 14β-methylphylllocladane (4b) ring systems § illustrate the general applicabilities of these methods.[1,2]

The known unsaturated acids (9a) [4] and (9b) [5] were prepared in improved yields (see Experimental section)

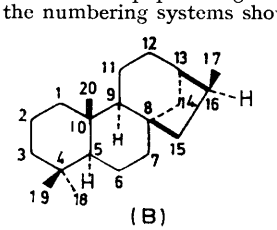
† Part VII, U. R. Ghatak, R. Dasgupta, and J. Chakravarty, *Tetrahedron*, 1974, **30**, 187.

‡ All structures represent racemic mixtures.

§ The parent ring systems described in this paper are gibbane (A) and phyllocladane (B), with the numbering systems shown.



(A)



(B)

[1] (*a*) S. K. Dasgupta, R. Dasgupta, S. R. Ghosh, and U. R. Ghatak, *Chem. Comm.*, 1969, 1253; (*b*) P. N. Chakrabortty, R. Dasgupta, S. K. Dasgupta, S. R. Ghosh, and U. R. Ghatak, *Tetrahedron*, 1972, **28**, 4653.

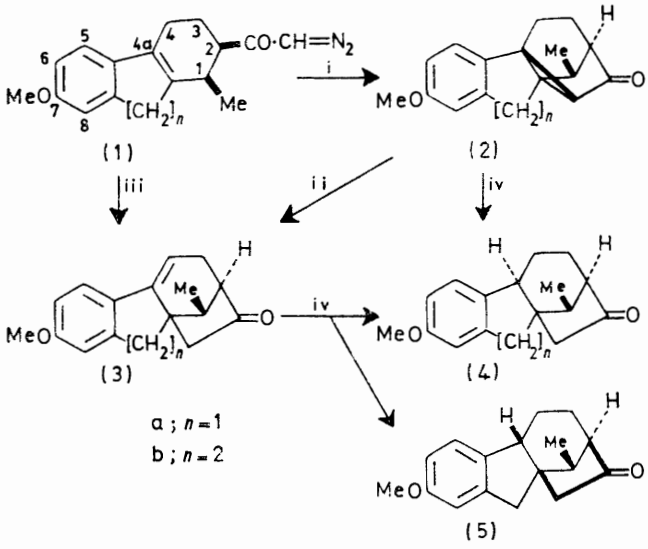
[2] U. R. Ghatak, P. C. Chakraborti, B. C. Ranu, and B. Sanyal, *J.C.S. Chem. Comm.*, 1973, 548.

[3] *Inter alia*, D. J. Beames, T. R. Klose, and L. N. Mander, *Chem. Comm.*, 1971, 773; W. F. Erman and L. C. Stone, *J. Amer. Chem. Soc.*, 1971, **93**, 2821.

[4] R. A. Barnes and M. S. Sedlak, *J. Org. Chem.*, 1962, **27**, 4562.

[5] J. A. Hogg, *J. Amer. Chem. Soc.*, 1948, **70**, 161.

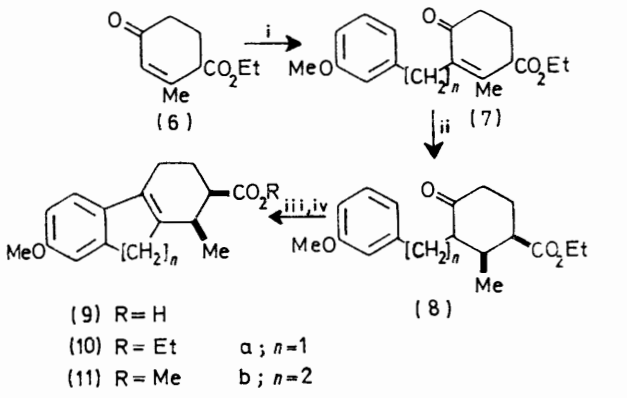
following the sequence shown in Scheme 2 starting from Hagemann's ester (6).



SCHEME 1

Reagents: i, 'Activated Cu–CuO'; ii, $CHCl_3$–HCl; iii, BF_3–Et_2O, CH_2Cl_2; iv, H_2, Pd–C (10%), EtOH

The relative stereochemistry of the methyl and carboxy-groups in the unsaturated acids (9a and b) has been assigned as *cis*. This arrangement originates in the keto-esters (8a and b), produced from the unsaturated

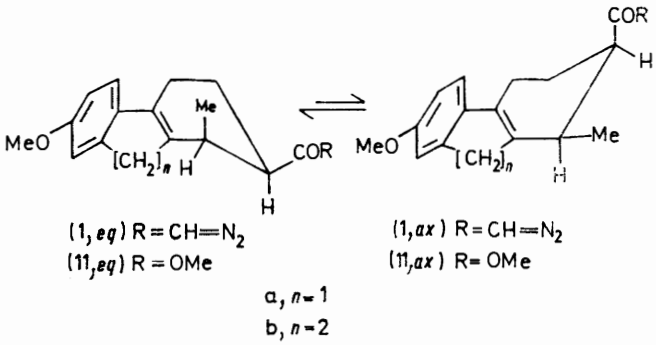


SCHEME 2

Reagents: i, *m*-$MeOC_6H_4CH_2Cl$, Bu^tOK–Bu^tOH; ii, H_2, Pd–C (10%), EtOH; iii, *p*-TsOH; iv, KOH, H_2O–diethylene glycol

esters (7a and b) by catalytic hydrogenation of the double bond from the less hindered side:[4,6] studies[7] with bicyclic and tricyclic systems have indicated that catalytic hydrogenation of βγ-unsaturated esters usually occurs from the side opposite the ester function. The stereochemical homogeneity of the acids (9a and b) was further confirmed by the sharp OMe and CO_2Me singlets in the 220 MHz ^1H n.m.r. spectra of their methyl esters (11a and b). If the stereochemistry assigned to (11a) is correct, then owing to the $A^{1,2}$ effect[8] this should exist predominantly in the conformation (11a, *eq*) with quasi-axial methyl group and equatorial carboxy-group. The axial nature of the methyl group has been indicated by the upfield solvent shift[9] of the methyl doublet [$\delta(CDCl_3) - \delta(C_6D_6) = 0{\cdot}087$ p.p.m.] in the 220 MHz ^1H n.m.r. spectra. A similar solvent shift (0·027 p.p.m.) for the methyl doublet in (11b), although not as pronounced as in (11a), indicates the conformational preference for (11b, *eq*) over (11b, *ax*).

The unsaturated acids (9a and b) were converted *via* the acyl chlorides into the diazoketones (1a and b) in the usual manner,[1] in excellent yield. Thermal decomposition of the diazoketones (1a and b) with copper catalysts[1b] such as anhydrous copper(II) sulphate and copper-bronze afforded the cyclopropyl ketones (2a and



b) in 35—45% yields. The best yields of the cyclopropyl ketones (50—60%) were obtained by thermal decomposition of the diazoketones (1a and b) in the presence of 'activated CuO catalyst'[2] in cyclohexane–tetrahydrofuran. Unlike the demethyl analogues, decomposition of these diazoketones under irradiation with a tungsten lamp did not improve[2] the yields of the intramolecular addition products. Fragmentation of the cyclopropyl ketones (2a and b) on treatment with dry hydrogen chloride in chloroform[2] afforded the tetracyclic unsaturated ketones (3a and b) in 85—90% yields: these ketones were also obtained in 70—75% yields by direct BF_3–Et_2O catalysed cyclisations[2] of the diazoketones (1a and b). The spectral data are consistent with the assigned structures. It is noteworthy that the introduction of a 1β-methyl group in the unsaturated diazoketones (1a and b), which might influence[8] the conformational preference of (1, *eq*) with an equatorial diazoketone group over (1, *ax*) with the diazoacetyl group axial, as required for these reactions, has little influence in the intramolecular cyclisation process described above.

[6] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985, and other papers in this series.

[7] U. R. Ghatak, N. R. Chatterjee, A. K. Banerjee, J. Chakravarty, and R. E. Moore, *J. Org. Chem.*, 1969, **34**, 3739, and references cited therein.

[8] F. Johnson, *Chem. Rev.*, 1968, **68**, 375.

[9] N. S. Bhacca and D. H. Williams, 'Applications of N.m.r. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, p. 169; R. S. Matthews, P. K. Hyer, and E. A. Folkers, *Chem. Comm.*, 1970, 38; M. Miyano and C. R. Dorn, *J. Org. Chem.*, 1972, **37**, 259.

In accord with our previous findings [2] with the demethyl analogues, high stereo- and regio-selectivities were observed in the catalytic hydrogenolysis of the cyclopropyl ketones (2a and b) in the presence of Pd–C (10%) in ethanol, affording the 4bα*H*-gibbane (4a) and the 9α*H*-phyllocladane (4b) derivatives in excellent yields, as the only isolable products. The stereochemistry of the ketones (4a and b) is assigned by analogy with similar cases.[1b,2]

As observed with the demethyl analogues,[1b] catalytic hydrogenation [with Pd–C (10%) (in ethanol)] of the 9,11-double bond in (3b) produced only the 9α*H*-ketone (4b). On the other hand, the gibbane (3a) on similar reduction produced a mixture of 4bα*H*- and 4bβ*H*-ketones (4a) and (5) in a ratio of *ca.* 75 : 25 as determined from n.m.r. The pure 4bα*H*-ketone (4a) was isolated in 45% yield by fractional crystallisation. However, attempts to isolate the 4bβ*H*-ketone have failed. The proportion of 4bα*H*-ketone (4a) in the reduction of (3a) is higher than observed in the hydrogenation of the corresponding de-11β-methyl ketone, where the 4bα*H*- and 4bβ*H*-ketones were produced [1b] in a ratio of 69 : 31. The increase in stereoselectivity in the reduction of (3a) indicates the influence of the 11β-methyl group in the hydrogenation of the Δ^{4b}-gibbene system.[2]

EXPERIMENTAL

The compounds described are racemic forms: the terms α and β refer to the relative orientation of substituent groups according to the steroid convention. M.p.s were taken in open capillaries in a sulphuric acid-bath. The homogeneity of all compounds was checked by t.l.c. on *ca.* 0·2 mm silica gel-G (Merck), using benzene–methanol and benzene–ethyl acetate as solvent systems. Spots were located by exposing the dried plates in I_2 vapour. U.v. spectra were determined in 95% ethanol solutions on a Beckmann DU spectrometer and i.r. spectra were determined in chloroform solutions on a Perkin-Elmer model 21 spectrometer by Mr. A. Ghosal. 60 MHz N.m.r. spectra were recorded on Varian HA-60 and T-60 instruments and 220 MHz n.m.r. spectra were obtained from Varian Associates' Analytical Instrument Division, Palo Alto, California. Analyses were performed by Mrs. C. Dutta of this laboratory. Light petroleum and petroleum refer to the fractions b.p. 40—60° and 60—80° respectively.

1β-*Methyl*-7-*methoxy*-1,2,3,4-*tetrahydrofluorene*-2β-*carboxylic Acid* (9a).—This was prepared according to the method of Barnes *et al.*[4] with the following modifications. Hagemann's ester (6) (120 g) was alkylated * with *m*-methoxybenzyl chloride (93 g) in the presence of potassium t-butoxide in t-butyl alcohol, prepared from potassium metal (23·2 g), following the procedure described previously [10] for alkylation with benzyl chloride. The alkylated product was fractionated twice to afford ethyl 3-(*m*-methoxybenzyl)-2-methyl-4-oxocyclohex-2-enecarboxylate (7a) (139 g, 67%), b.p. 170—172° at 0·1 mmHg, as a pale yellow oil. Catalytic hydrogenation of (7a) (5 g) in 95% ethanol (40 ml) in the presence of 10% palladium–charcoal (0·3 g) at atmospheric pressure and temperature yielded ethyl 3-(*m*-methoxybenzyl)-2-methyl-4-oxocyclohexanecarboxylate (8a) (4·6 g, 91%), b.p. 175° at 0·2 mmHg (lit.,[4] 150° at 0·05 mmHg); $\lambda_{max.}$ 274 nm (log ε 3·3) (Found: C, 70·8; H, 8·2. Calc. for $C_{18}H_{24}O_4$; C, 71·0; H, 8·0%). In our hands, cyclisation of (8a) with polyphosphoric acid according to the published method [4] afforded ethyl 1β-methyl-7-methoxy-1,2,3,4-tetrahydrofluorene-2β-carboxylate (10a) in only 50—55% yields: the following method, however, gave consistently higher yields of the cyclised ester. To a solution of the oxo-ester (8a) (5 g) in dry benzene (300 ml) was added toluene-*p*-sulphonic acid (0·5 g) and the mixture was heated under reflux (*ca.* 6 h) under a Dean–Stark water separator. The usual work-up gave an oil, b.p. 168° at 0·2 mmHg, which crystallised on standing. Recrystallisation from ethanol afforded the ester (10a) as needles (4·0 g, 85%), m.p. 90—91° (lit.,[4] 87—88°); $\lambda_{max.}$ 266 nm (log ε 4·2) (Found: C, 75·9; H, 7·9. Calc. for $C_{18}H_{22}O_3$: C, 76·1; H, 8·0%).

The ethyl ester (10a) (1·3 g) was saponified by gently heating under reflux for 1 h with potassium hydroxide (1 g) in water (1 ml) and diethylene glycol (8·5 ml) under nitrogen. The cooled mixture was diluted with water, acidified (6N-hydrochloric acid), and the product was taken up in ethyl acetate and thoroughly extracted with 2% sodium hydroxide solution. The regenerated acidic product, obtained on acidification of the combined alkaline washings, was taken up in ethyl acetate, washed with water, and dried (Na_2SO_4). Evaporation of the solvent yielded a white solid, which on recrystallisation from ethyl acetate–light petroleum afforded the acid (9a) (0·7 g, 62%), m.p. 192° (lit.,[4] 193°); $\lambda_{max.}$ 266 nm (log ε 4·2), $\nu_{max.}$ 1710 cm^{-1} (Found: C, 74·1; H, 7·0. Calc. for $C_{16}H_{18}O_3$: C, 74·3; H, 7·0%). The acid (9a) was esterified with an excess of ethereal diazomethane solution and the *methyl ester* (11a) was crystallised from light petroleum, m.p. 107—108°; $\lambda_{max.}$ 266 nm (log ε 4·24); $\nu_{max.}$ 1730 and 1612 cm^{-1}; δ ($CDCl_3$; 220 MHz) 1·06 (3H, d, *J* 8 Hz), 2·20 (4H, m), 2·89 (2H, m), 3·26 (2H, q, $\delta_A - \delta_B$ 54·55 Hz, J_{AB} 25 Hz), 3·75 (3H, s), 3·82 (3H, s), and 7·00—7·02 (3H, m) (Found: C, 74·85; H, 7·5. $C_{17}H_{20}O_3$ requires C, 74·95; H, 7·4%).

1β-*Methyl*-7-*methoxy*-1,2,3,4,9,10-*hexahydrophenanthrene*-2β-*carboxylic Acid* (9b).—Ethyl 3-(*m*-methoxyphenethyl)-2-methyl-4-oxocyclohexanecarboxylate (8b) (5 g), prepared by catalytic hydrogenation of ethyl 3-(*m*-methoxyphenethyl)-2-methyl-4-oxocyclohex-2-enecarboxylate (7b) [11] in the presence of palladium–charcoal in ethanol, was cyclised by refluxing for *ca.* 10 h in benzene (300 ml) containing toluene-*p*-sulphonic acid (0·5 g). Work-up gave the unsaturated ethyl ester (10b) (3·9 g, 82%), b.p. 170—175° at 0·2 mmHg. This ester (2·5 g) was saponified by refluxing for 2 h with potassium hydroxide (1·9 g) in water (1 ml) and diethylene glycol (16 ml) under nitrogen. The usual work-up and recrystallisation from ethyl acetate–light petroleum afforded the acid (9b) (1·8 g, 79%), m.p. 191—192° (lit.,[5] 192—193°), $\lambda_{max.}$ 270 nm (log ε 4·3), $\nu_{max.}$ 1710 cm^{-1} (Found: C, 74·85; H, 7·65. Calc. for $C_{17}H_{20}O_3$: C, 74·95; H, 7·5%). The *methyl ester* (11b), prepared by esterification of acid (9b) with ethereal diazomethane, was recrystallised from light petroleum, m.p. 112—113°, $\lambda_{max.}$ 270 nm (log ε 4·29); $\nu_{max.}$ 1735 and 1610 cm^{-1};

* We thank Dr. R. Dasgupta for this experiment.

[10] U. R. Ghatak, J. Chakravarty, and A. K. Banerjee, *Tetrahedron*, 1968, **24**, 1577.

[11] U. R. Ghatak and N. R. Chatterjee, *Indian J. Chem.*, 1971, **9**, 804.

δ ($CDCl_3$; 220 MHz) 1·045 (3H, d, *J* 8 Hz), 1·82—2·78 (10H, complex m), 3·73 (3H, s), 3·79 (3H, s), and 6·98—7·0 (3H, m) (Found: C, 75·55; H, 7·9. $C_{18}H_{22}O_3$ requires C, 75·5; H, 7·75%).

2β-*Diazoacetyl*-1β-*methyl*-7-*methoxy*-1,2,3,4-*tetrahydrofluorene* (1a).—The acid (9a) (2 g) in methanol (100 ml) was neutralised with a *ca.* 10% solution of sodium methoxide in methanol using phenolphthalein as indicator. The solvent was evaporated under reduced pressure. To the sodium salt, dry benzene (3 × 30 ml) was added and distilled off (3 times) to remove traces of methanol. To a rapidly stirred, ice-cold suspension of the sodium salt in dry benzene (100 ml) and pyridine (0·2 ml), oxalyl chloride (2·5 ml) was added dropwise. The mixture was stirred at room temperature for 30 min and finally warmed at *ca.* 60° for 1 h. The resulting precipitate was filtered off and the filtrate concentrated under reduced pressure. The dark red solid residue was dissolved in anhydrous ether (100 ml) and added to a stirred solution of an excess of cold ethereal diazomethane solution [prepared from *N*-methylnitrosourea (6 g)] and left overnight at room temperature. Evaporation of the solvent yielded a yellow solid which was dissolved in benzene and chromatographed on neutral alumina (50 g). Elution with ether–light petroleum (1 : 1) gave the *diazoketone* (1a) as a pale yellow solid (1·6 g, 73%), m.p. 116—119° (decomp.) (from ether); $\nu_{max.}$ 2115 cm^{-1} (Found: C, 72·0; H, 6·4. $C_{17}H_{18}N_2O_2$ requires C, 72·3; H, 6·45%).

2β-*Diazoacetyl*-1β-*methyl*-7-*methoxy*-1,2,3,4,9,10-*hexahydrophenanthrene* (1b).—The acid (9b) (2 g) was converted into the *diazoketone* (1b) (1·7 g, 75%), m.p. 135—137° (decomp.) (from ether), following the procedure described above; $\nu_{max.}$ 2115 cm^{-1} (Found: C, 73·1; H, 6·9. $C_{18}H_{20}N_2O_2$ requires C, 72·95; H, 6·8%).

Carbenoid Addition of the Diazoketone (1a).—A solution of the diazoketone (1a) (850 mg) in anhydrous tetrahydrofuran–cyclohexane (3 : 7; 250 ml) was heated and stirred under reflux over ' activated Cu–CuO catalyst ' [2] (2·5 g) for 6 h, filtered, and evaporated to dryness under reduced pressure. The residue was chromatographed on neutral alumina (20 g) and 2-*methoxy*-11β-*methyl*-4bβ,9-*cyclogibba*-1(10a),2,4-*trien*-8-*one* (2a) eluted with benzene–petroleum (2 : 8). Recrystallisation from petroleum gave pure material (450 mg, 59%), m.p. 115°; $\lambda_{max.}$ 248 nm (log ε 4·02); $\nu_{max.}$ 1715 cm^{-1}; δ ($CDCl_3$) 1·15 (3H, d, *J* 7 Hz), 1·42 (1H, s), 2·00—2·17 (6H, m, complex), 3·13br (2H, s), 3·75 (3H, s), and 6·95 (3H, m, complex) (Found: C, 80·1; H, 7·05. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·15%).

Carbenoid Addition of the Diazoketone (1b).—Thermal decomposition of the diazoketone (1b) (600 mg) in anhydrous tetrahydrofuran–cyclohexane (3 : 7; 200 ml) in the presence of ' activated Cu–CuO catalyst ' [2] (1·8 g) as described above, yielded 3-*methoxy*-14β-*methyl*-9β,15-*cyclo*-17,18,19,20-*tetranorphylloclada*-1(10),2,4-*trien*-16-*one* (2b) (280 mg, 51%), m.p. 120—121°, after chromatography on neutral alumina and recrystallisation from petroleum, $\lambda_{max.}$ 245 nm (log ε 4·05), $\nu_{max.}$ 1710 cm^{-1}; δ ($CDCl_3$) 1·10 (3H, d, *J* 7 Hz), 1·80—1·83 (9H, m, complex), 2·50 (2H, q, complex), 3·77 (3H, s), and 7·0 (3H, m, complex) (Found: C, 80·6; H, 7·45. $C_{18}H_{20}O_2$ requires C, 80·55; H, 7·55%).

2-*Methoxy*-11β-*methylgibba*-1(10a),2,4,4b-*tetraen*-8-*one* (3a).—(a) *Cleavage of the cyclopropyl ketone* (2a). Through a solution of (2a) (270 mg) in anhydrous chloroform (50 ml), dry HCl gas was bubbled for *ca.* 1·5 h. The wine-red solution was evaporated under reduced pressure and the residual solid filtered through a short column of neutral alumina in petroleum. The *unsaturated ketone* (3a) (240 mg, 89%), m.p. 104°, was recrystallised from petroleum; $\lambda_{max.}$ 268 nm (log ε 4·3); $\nu_{max.}$ 1740, 1640, and 1610 cm^{-1}; δ ($CDCl_3$) 1·07 (3H, d, *J* 7 Hz), 2·98 (2H, m), 3·80 (3H, s), and 5·68 (1H, m) (Found: C, 80·2; H, 7·2. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·15%).

(b) BF_3–Et_2O-*Catalysed intramolecular alkylation of the diazoketone* (1a). To a stirred solution of the diazoketone (1a) (500 mg) in anhydrous methylene chloride (70 ml), cooled in an ice–salt bath (*ca.* −10°), freshly distilled BF_3–Et_2O (0·3 ml) was added. After 1 h, the dark yellow solution was washed with water, 5% sodium carbonate solution, water, and dried (Na_2SO_4). Removal of solvent under reduced pressure and chromatography of the residue on neutral alumina (10 g) with benzene–petroleum (1 : 10) as eluant afforded the ketone (3a) (320 mg, 71%), m.p. and mixed m.p. 104°, after recrystallisation from petroleum.

3-*Methoxy*-14β-*methyl*-17,18,19,20-*tetranorphylloclada*-1(10),2,4,9(11)-*tetraen*-16-*one* (3b).—(*a*) Cleavage of the cyclopropyl ketone (2b) (200 mg) in anhydrous chloroform (50 ml) with dry HCl for *ca.* 1 h and purification of the product by chromatography on neutral alumina, followed by recrystallisation from light petroleum afforded the *unsaturated ketone* (3b) (170 mg, 85%), m.p. 109—110°, $\lambda_{max.}$ 266 nm (log ε 4·24); $\nu_{max.}$ 1735, 1640, and 1610 cm^{-1}; δ ($CDCl_3$) 1·05 (3H, d, *J* 7 Hz), 2·78 (2H, q), 3·80 (3H, s), and 6·07 (1H, t) (Found: C, 80·6; H, 7·6. $C_{18}H_{20}O_2$ requires C, 80·55; H, 7·55%).

(*b*) The diazoketone (1b) (360 mg) in methylene chloride (60 ml) was cyclised with BF_3–Et_2O (0·3 ml) as described above. The crude product on chromatography and recrystallisation from light petroleum gave the ketone (3b) (240 mg, 73%), m.p. and mixed m.p. 110°.

2-*Methoxy*-11β-*methyl*-4bαH-*gibba*-1(10a),2,4-*trien*-8-*one* (4a).—(a) *Catalytic hydrogenolysis of the cyclopropyl ketone* (2a). The ketone (2a) (120 mg) in ethanol (20 ml) was hydrogenated in the presence 10% palladium–charcoal (30 mg). The uptake of hydrogen was very fast and complete within 10—15 min. The usual work-up gave a solid which on recrystallisation from light petroleum afforded the 4bαH-*ketone* (4a) (110 mg, 91%), m.p. 119—120°; $\lambda_{max.}$ 228 (log ε 3·8) and 278 nm (3·4); $\nu_{max.}$ 1735 cm^{-1}; δ ($CDCl_3$) 1·02 (3H, d, *J* 7 Hz), 2·93 (3H, m, complex), and 3·77 (3H, s) (Found: C, 79·4; H, 7·9. $C_{17}H_{20}O_2$ requires C, 79·65; H, 7·85%).

(b) *Catalytic hydrogenation of the unsaturated ketone* (3a). The unsaturated ketone (3a) (850 mg) in ethanol (50 ml) was hydrogenated in the presence of 10% palladium–charcoal (50 mg). The uptake of hydrogen was complete within 30 min. The catalyst was filtered off and the solvent evaporated under reduced pressure to afford a solid (850 mg), m.p. 90—100° (Found: M^+, 256. Calc. for $C_{17}H_{20}O_2$: *M*, 256). T.l.c. in benzene–ethyl acetate (4 : 1) showed two close spots. ^1H N.m.r. of this mixture ($CDCl_3$ at 100 MHz) showed two OMe singlets separated by *ca.* 1·5 Hz. From the integration and comparison with the spectrum of (4a), the ratio of (4a) and the 4bβ*H*-gibbane (5) was determined to be *ca.* 75 : 25. From the reduction product the pure 4bα*H*-epimer (4a) could be isolated (*ca.* 45% yield) by fractional crystallisation from methanol, m.p. and mixed m.p. 119—120° (identified by t.l.c. and i.r. comparison). Column chromatography or p.l.c. under various conditions failed to resolve the mixture.

3-*Methoxy*-14β-*methyl*-9αH-17,18,19,20-*tetranorphyllo*-

clada-1(10),2,4-*trien*-16-*one* (4b).—(*a*) Catalytic hydrogenolysis of the cyclopropyl ketone (2b) (200 mg) in ethanol (30 ml) in the presence of 10% palladium–charcoal (50 mg) afforded a solid (180 mg, 91%), m.p. 86—88°, recrystallised once from light petroleum to give the 9αH-*ketone* (4b), m.p. 88°; $\lambda_{max.}$ 275 nm (log ε 3·67); $\nu_{max.}$ 1735 cm^{-1}; δ ($CDCl_3$) 0·93 (3H, d, *J* 7 Hz) and 3·77 (3H, s) (Found: C, 79·9; H, 8·2. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%).

(*b*) Catalytic hydrogenation of the unsaturated ketone (3b) (160 mg) in ethanol (30 ml) in presence of 10% palladium–charcoal (30 mg) gave the product, m.p. 86—88° Recrystallisation from light petroleum afforded pure 9α*H*-ketone (4b) (144 mg, 89%), m.p. and mixed m.p. 88° (identical by t.l.c. and i.r. comparison).

We thank Dr. A. J. Baker, Glasgow University, and Dr. L. F. Johnson, Varian Associates, Palo Alto, for the 100 and 220 MHz ^1H n.m.r. spectra, and the C.S.I.R., New Delhi, for a senior fellowship (to S. C.).

[4/656 *Received*, 1*st April*, 1974]