Condensed Cyclic and Bridged-ring systems. Part 13.[1] Synthesis of the Insect Attractant Hydrocarbon, 9a-Carbamorphinan, and *X*-Ray Structural Analyses of 9a-Carbamorphinan-10-one and 9a-Carba-14α-morphinan-10-one

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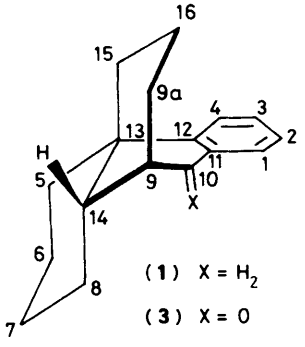
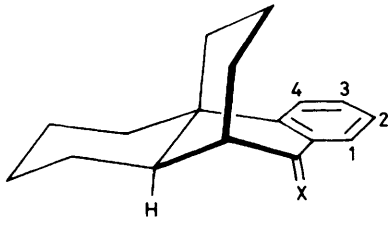
The insect attractant bridged hydrocarbon, (±)-9a-carbamorphinan (**1**) and its inactive epimer, (±)-9a-carba-14α-morphinan (**2**), have been synthesized through (±)-9a-carbamorphinan-10-one (**3**), and (±)-9a-carba-14α-morphinan-10-one (**4**), prepared by polyphosphoric acid-catalysed cyclization of the double-bond isomeric benzyloctalins (**7**), derived from Huang-Minlon reduction of 1-benzyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (**6**), followed by the benzylic oxidation with chromic acid. The reduction of the easily accessible (±)-9a-carbamorphinan-16-one (**10**), the orthophosphoric acid-induced cyclization product of (**6**), provides an efficient alternative route to (**1**). The structures of the epimeric ketones (**3**) and (**4**) have been established by *X*-ray analysis.

In conjunction with our interest in bridged-ring carbocyclic compounds[2] we synthesized (±)-9a-carbamorphinan (**1**) and (±)-9a-carba-14α-morphinan (**2**). Quite early in the work we observed compound (**1**) to be attractive to some insects, tentatively identified‡ as members of the family *Dolichopodidae*, Thyrpticus. In a systematic study[3] using an olfactometer designed for the economically important coconut rhinoceros beetle, *Oryctes rhinoceros*(L), the hydrocarbon (**1**), but not its stereoisomer (**2**), was found to be a strong attractant for adult rhinoceros beetles. We now present a detailed account of our synthetic studies of (**1**) and (**2**), and *X*-ray structural determinations of 9a-carbamorphinan-10-one (**3**) and 9a-carba-14α-morphinan-10-one (**4**).



(**1**) X = H_2

(**3**) X = O



(**2**) X = H_2

(**4**) X = O

Results and Discussion

Alkylation of the octalone (**5**) with benzyl chloride in the presence of potassium t-pentyl oxide in t-pentyl alcohol and benzene gave the desired monoalkylated product (**6**)[4] (Scheme 1). Huang-Minlon reduction[5] of (**6**) led to a mixture of benzyloctalins (**7**), which on cyclization[6] with polyphosphoric acid gave a mixture of (**1**) and (**2**), along with an isomeric hydrocarbon of undetermined structure, in a ratio of *ca.* 50:33:17 (g.l.c.) in excellent yield. Oxidation of the cyclised hydrocarbon mixture with chromium trioxide in aqueous acetic acid[2c] cleanly eliminated the third hydrocarbon and afforded a mixture of the partly unchanged hydrocarbon (**1**) and the ketones (**3**) and (**4**) in a ratio of *ca.* 9:40:51 (g.l.c.) in the neutral fraction. The crystalline pure epimeric ketones (**3**) and (**4**) and the hydrocarbon (**1**) were separated by fractional crystallization and chromatography. Each of the ketones on reduction[5] gave the corresponding crystalline hydrocarbons (**1**) and (**2**).

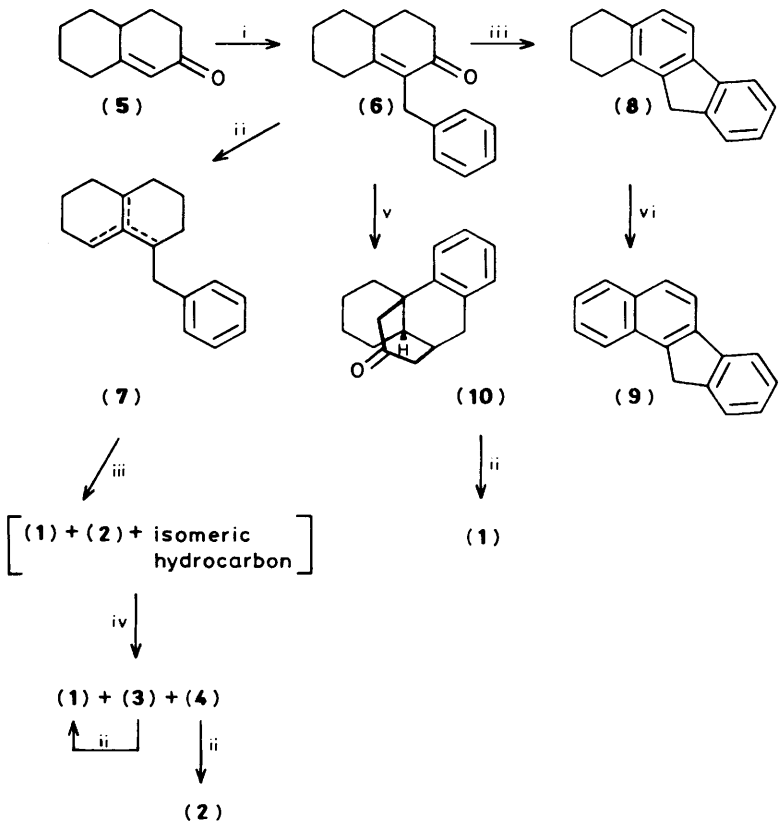
Attempted polyphosphoric acid cyclizations of the octalone (**6**) led to complex mixtures of hydrocarbons. In some of the experiments the partially aromatized hydrocarbon (**8**) was isolated, the structure of which was confirmed by its smooth transformation into (**9**).[7] While these experiments were in progress, Stork briefly mentioned in a lecture[4] the angular cyclization with orthophosphoric acid of (**6**), prepared in a moderate yield by enamine alkylation, to the bridged ketone (**10**)§ (20% yield). We have now substantially improved the yield of (**10**) (see Experimental section) by repeating Stork's method.¶ The ketone (**10**) is smoothly converted into the

† To receive any correspondence on *X*-ray work.

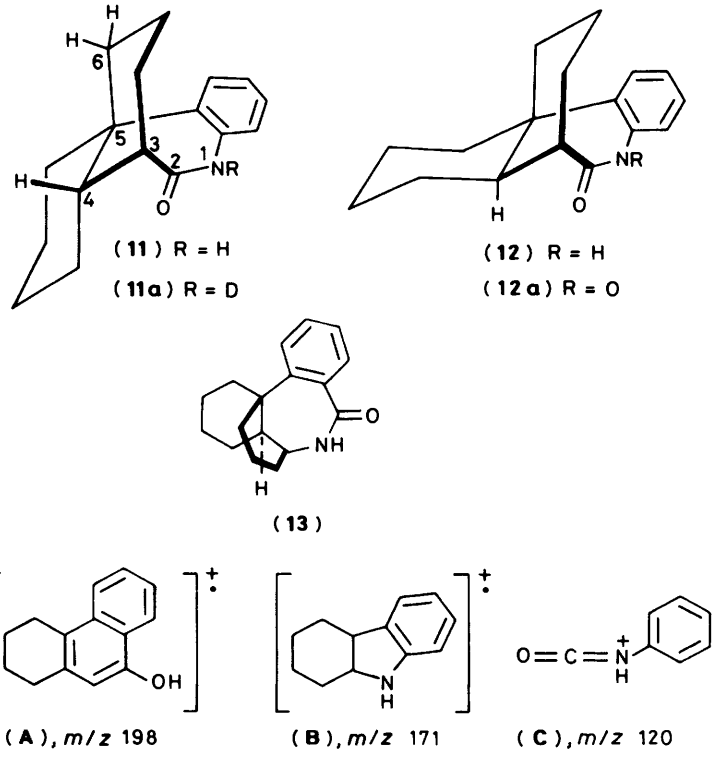
‡ Dr. P. T. Cherian, personal communication, Zoological Survey of India, Calcutta; Identification Report No. 8/74, June 29, 1974.

§ The basis of its stereochemical assignment was not discussed (ref. 4).

¶ We thank Professor G. Stork for forwarding the experimental method.



Scheme. *Reagents*: i, KOC_5H_{13}-t, $PhCH_2Cl$,C_6H_6; ii, $NH_2{\cdot}NH_2{\cdot}H_2O$ (99%), KOH, diethylene glycol; iii, PPA; iv, CrO_3, H_2O, HOAc; v, H_3PO_4; vi, Pd–C(10%), Heat



hydrocarbon (**1**), thus providing a simple preparative route to this important insect attractant in sufficient quantity for field studies.

While the gross structures of the epimeric hydrocarbons (**1**) and (**2**), and the corresponding 10-oxo-compounds (**3**) and (**4**), were elucidated from the spectral and elemental analyses, it was not possible to assign the stereochemistry of these compounds from those data. However, the use of high resolution mass

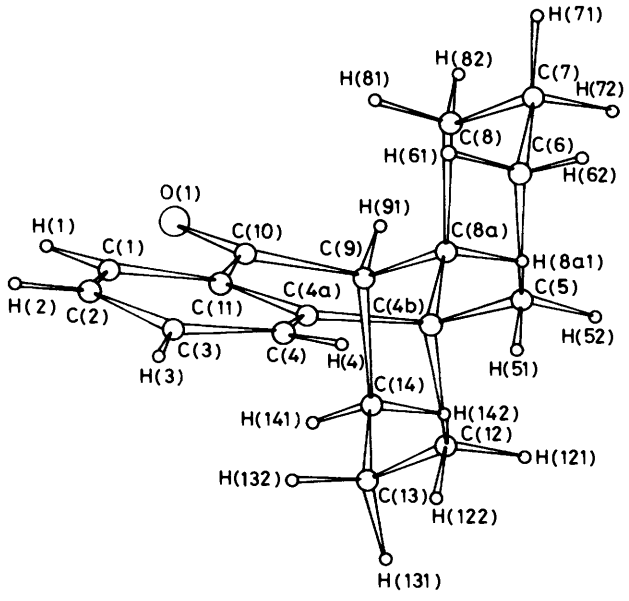


Figure 1. Perspective view of 9a-carbamorphinan-10-one (**3**), showing the crystallographic numbering scheme used

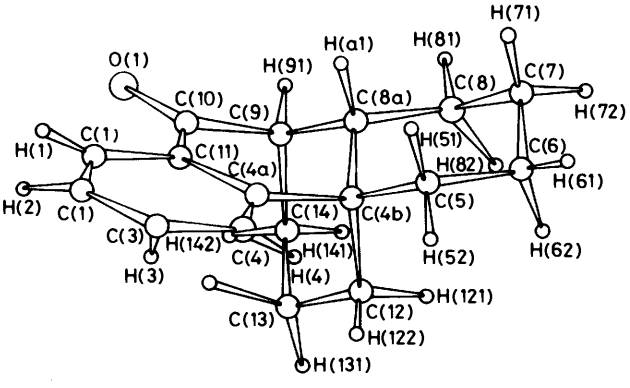


Figure 2. Perspective view of 9a-carba-14α-morphinan-10-one (**4**), showing the crystallographic numbering scheme used

spectrometry first allowed us a reliable differentiation of the epimeric ketones (**3**) and (**4**) and the lactams (**11**) and (**12**) derived from these, details of which have been reported separately.[8] In the mass spectrum of (**3**) a very intense peak, assignable to (**A**), was observed at *m/z* 198, with an accompanying metastable ion at *m/z* 163.5 for loss of propene from the molecular ion, which was of negligible intensity in the spectrum of the epimer (**4**). More noteworthy were the dramatic differences observed in the mass spectra of the lactams (**11**) and (**12**) obtained by treatment of the ketones (**3**) and (**4**), respectively, with sodium azide in sulphuric acid,[9] along with the corresponding isomeric lactam (**13**) in the latter case.

The mass spectrum of (**11**) exhibited its most intense fragment ion at *m/z* 171 [shifted to *m/z* 172 for the respective deuteriated derivative (**11a**)] and a metastable ion at *m/z* 114.8, which corresponds to the loss of propylketene from the molecular ion and the formation of the tetrahydrocarbazole ion (**B**). The *m/z* ion was small in the spectrum of (**12**) but showed a prominent fragment ion, actually the most intense one, at *m/z* 120, assigned as (**C**) [shifted to *m/z* 121 for (**12a**)] and a metastable ion at *m/z* 56.5 which were absent in the spectrum of (**11**). The C-4 proton of (**12**) is in close proximity to C-6 and presumably the *m/z* 120 ion is formed by transfer of the C-4 proton to C-6 in the molecular ion, followed by cleavage of two bonds (between C-5 and C-6, and C-2 and C-3) to form the octalinyl radical ion (**C**).

Finally, the complete structure and stereochemistry of each of these epimeric ketones (**3**) and (**4**) has now been determined by *X*-ray crystal structure analysis and their perspective drawings are shown in Figures 1 and 2. With the establishment of the stereochemistry of (**3**) and (**4**) the stereochemistry of the hydrocarbons (**1**) and (**2**) and that of Stork's ketone (**10**)[4] are now confirmed.

Experimental

The compounds described are all racemates. I.r. spectra were recorded on a Perkin-Elmer model PE 298 spectrometer. U.v. spectra were recorded on a Beckmann DU spectrometer for solutions in 95% ethanol. Unless otherwise specified, ^{1}H n.m.r. and ^{13}C n.m.r. spectra were recorded on a Varian XL-200 spectrometer using tetramethylsilane as an internal standard. High resolution mass measurements were obtained (at 70 eV) by the Battelle High Resolution Mass Spectrometry Center, U.S.A. through the courtesy of Professor R. E. Moore, University of Hawaii, Honolulu, U.S.A. G.l.c. was performed on a Hewlett Packard 5730A Chromatograph equipped with a flame-ionization detector (20 × 1/8 in, 10% UCW-982) at a column temperature of 190 °C with N_2 as the carrier gas. Elemental analyses were performed by Mrs. C. Dutta and Mr. P. P. Bhattacharyya of this laboratory. Petroleum and light petroleum refer to fractions of b.p. 60—80 °C and 40—60 °C, respectively.

1-*Benzyl*-4,4a,5,6,7,8-*hexahydronaphthalen*-2(3H)-*one* (**6**).—4,4a,5,6,7,8-Hexahydronaphthalen-2(3*H*)-one (**5**) (15.0 g, 100 mmol) was added slowly with stirring to an ice-cold suspension of dry potassium t-pentyl oxide prepared from potassium metal (3.9 g, 86 mg-atom), in dry thiophene-free benzene (100 ml) under N_2 and was refluxed for 1 h. Benzyl chloride (18.0 g, 142 mmol) was added dropwise to the ice-cold dark brown solution, and the reaction mixture was allowed to stand at room temperature (*ca.* 25 °C) for 15 min, before being heated under reflux for 3 h and then acidified with 6M-HCl in the cold. The organic layer was separated and the aqueous layer was extracted with benzene; the extract was washed with water, dried (Na_2SO_4), and the solvent removed. The residual oil was carefully fractionated to afford (**6**) (10.0 g, 42%), b.p. 157—160 °C (0.2 mmHg) (a considerable amount of thick brown by-product, possibly the dialkylated product, was left in the distilling flask); homogeneous in g.l.c. $\nu_{max.}$(neat) 1 665 and 1 620 cm^{-1}; $\lambda_{max.}$ 248 nm (ε 10 470); δ_H($CDCl_3$) 0.88—3.50 (complex m, 12 H), 3.74 (m, 2 H), and 7.10—7.28 (m, 5 H, ArH) (Found: C, 84.5; H, 8.7. Calc. for $C_{17}H_{20}O$: C, 84.95; H, 8.4%); and its 2,4-*dinitrophenylhydrazone*, m.p. 149 °C (EtOAc–MeOH) (Found: C, 65.5; H, 5.6. $C_{23}H_{24}N_4O_4$ requires C, 65.7; H, 5.75%).

1-*Benzyloctahydronaphthalenes* (**7**).—A suspension of the ketone (**6**) (7.2 g, 30 mmol) in hydrazine hydrate (7.2 ml, 99%) and diethylene glycol (100 ml) was heated at 140—145 °C for 1 h under N_2. The reaction mixture was cooled to 100 °C and to it was added KOH (5.2 g). Water was then distilled off by heating the reaction mixture until the temperature rose to 200—210 °C and maintaining it at that temperature for 2 h while a slow but constant flow of N_2 was passed through it. The cold reaction mixture was diluted with ice–water, acidifed with 6M HCl, and extracted with Et_2O (4 × 75 ml). The extract was washed with brine, dried (Na_2SO_4), and evaporated and the residue distilled to afford the *benzyloctalins* (**7**) as a colourless liquid (5.4 g, 80%), b.p. 132—135 °C (0.2 mmHg); g.l.c. showed the presence of three components in a ratio of *ca.* 3:2:1 with R_t values of 3, 3.7, and

4.5 min respectively; $\nu_{max.}$(neat) 1 610 cm^{-1} (Found: C, 89.7; H, 9.8. $C_{17}H_{22}$ requires C, 90.2; H, 9.8%).

9a-*Carbamorphinan*-10-*one* (**3**) *and* 9a-*Carba*-14α-*morphinan*-10-*one* (**4**).—The aforementioned mixture of benzyloctalins (**7**) (4.52 g, 20.0 mmol) was added to a well-stirred solution of PPA [prepared from P_2O_5 (40.0 g), and H_3PO_4 24 ml, 89%)] and heated in an oil-bath at 150 °C for 1 h. The cold reaction mixture was decomposed with crushed ice (*ca.* 200 g) and extracted with Et_2O (4 × 74 ml); the extract was washed with Na_2CO_3, dried (Na_2SO_4), and evaporated to afford a colourless liquid (3.84 g, 85%), b.p. 128—134 °C (0.2 mmHg); $\lambda_{max.}$ 267 (log ε 2.94) and 274 nm (log ε 2.89) (Found: C, 90.5; H, 9.7. $C_{17}H_{22}$ requires C, 90.2; H, 9.8%). G.l.c. analyses showed it to be a mixture of (**1**), (**2**), and an unknown compound in a ratio of *ca.* 50:33:17 with R_t values of 3.0, 3.7, and 4.5 min by co-injection with pure samples of (**1**) and (**2**).

To a stirred solution of the aforementioned hydrocarbon mixture (3.39 g, 15.0 mmol) in acetic acid (40 ml) was added a solution of CrO_3 (5.0 g, 5 mmol) in water (15 ml) and acetic acid (35 ml). It was stirred at room temperature (*ca.* 25—30 °C) for 18 h and then heated on a steam-bath for 30 min. The mixture was diluted with water (100 ml) and extracted with Et_2O (75 ml × 4) after saturation with NaCl. The combined ethereal extracts were successively washed with ice-cold NaOH solution (5%) until alkaline and then with brine, dried (Na_2SO_4), and evaporated to leave a thick yellow oil (2.55 g); $\nu_{max.}$(neat) 1 690 cm^{-1}. G.l.c. analyses revealed it to be a mixture of (**1**), (**3**), and (**4**) in a ratio of *ca.* 9:40:51 with R_t values of 3, 5, and 8 min, respectively by co-injection with the pure samples. The mixture was dissolved in light petroleum and left for 2—3 h in an ice-box. The partly solidified product (1.44 g, overall 30%), m.p. 114—116 °C, was recrystallized to afford (**4**) as small transparent cubes, m.p. 117—118 °C; homogeneous in g.l.c. (R_t 8.0 min); $\lambda_{max.}$ 254 nm (log ε 4.08); $\nu_{max.}$(KBr) 1 690, 1 590, and 769 cm^{-1}; $\delta_H(CDCl_3)$ 1.06—2.38 (complex m, 15 H), 2.54 (br s, 1 H), 7.32—7.61 (m, 3 H), and 8.12 (d, *J* 8 Hz, 1 H); $\delta_C(CDCl_3)$ 202.6 (C-10), 152.6 (C-12), 134.0 and 133.8 (C-11 and/or C-1), 126.2, 126.1, 124.4, and 49.0 (C-9), 42.7 (C-14), 37.5 (C-13), 36.7 (C-5), and 28.7, 26.1, 25.9, 22.7, 22.3, and 19.2 (C-16); *m/z* 240 (M^+, 100%), 198 (50), 197 (43), 142 (33), 129 (25), 128 (35), and 115 (43) (Found: C, 84.6; H, 8.5. $C_{17}H_{20}O$ requires C, 84.95; H, 8.4%); the 2,4-*dinitrophenylhydrazone*, m.p. 239—240 °C (EtOAc) (Found: C, 66.0; H, 5.9. $C_{23}H_{24}N_4O_4$ requires C, 65.7; H, 5.75%).

The mother liquor after separation of (**4**) was left in the ice-box for several days when colourless plates (790 mg), m.p. 68—71 °C separated out. This, on recrystallization from light petroleum afforded (**3**), m.p. 72 °C; homogeneous in g.l.c. (R_t 5.0 min); $\lambda_{max.}$ 255 nm (log ε 4.16); $\nu_{max.}$(KBr) 1 695, 1 600, and 762 cm^{-1}; $\delta_H(CDCl_3)$ 1.92—1.94 (m, 14 H), 2.40 (br d, *J* 13 Hz, 1 H), 2.54 (br s, 1 H), 7.29—7.63 (m, 3 H), and 8.09 (d, *J* 8 Hz, 1 H); δ_C ($CDCl_3$) 202.1 (C-10), 134.8 and 134.4 (C-11 and/or C-1), 146.3 (C-12), 126.2, 126 × 2, and 49.9 (C-9), 48.1 (C-14), 40.8, 40.0 (C-13), 37.2 (C-5), 30.3, 28.5, 26.6, 21.8, and 19.3 (C-16); *m/z* 240 (M^+, 69), 198 (100), 197 (39), 141 (21), 129 (11), 128 (21), and 115 (21) (Found: C, 84.6; H, 8.3. $C_{17}H_{20}O$ requires C, 84.95; H, 8.4%); the 2,4-*dinitrophenylhydrazone*, m.p. 209—210 °C (EtOAc–MeOH) (Found: C, 65.4; H, 5.7. $C_{23}H_{24}N_4O_4$ requires C, 65.7; H, 5.75).

The semi-solid mother liquor after separation of (**3**) was chromatographed on acid-washed alumina (25 g) using petroleum as eluant to afford first the hydrocarbon (**1**) (*ca.* 95 mg) (identified by g.l.c.) followed by the ketone (**3**) (*ca.* 200 mg, overall 25%), m.p. and mixed m.p. 72 °C.

(±)-9a-*Carbamorphinan* (**1**).—(*a*) A suspension of the ketone (**3**) (240 mg, 1.0 mmol) in hydrazine hydrate (2.5 ml, 99%) and diethylene glycol (18 ml) was heated at 140—145 °C for 1 h under N_2, cooled to 100 °C, and KOH (1.4 g) was added. Water was distilled off by heating the reaction mixture until the temperature rose to 200—210 °C, and maintaining it at the same temperature for 2 h while a slow but constant flow of N_2 was passed through it. The cooled reaction mixture was diluted with water (30 ml), acidified with 6M HCl, and extracted with Et_2O (4 × 30 ml). The ethereal extract was washed with water, dried (Na_2SO_4), and evaporated to afford a gummy mass (210 mg), which on chromatography over neutral alumina (4.0 g) and elution with petroleum afforded the hydrocarbon (**1**) (194 mg, 86%), m.p. 57—58 °C (light petroleum), homogeneous by g.l.c. (R_t 3.0 min); $\delta_H(CDCl_3)$ 1.30—2.42 (m, 14 H), 2.38—2.70 (m, 3 H), 3.16—3.28 (m, 1 H), and 7.34—7.50 (m, 4 H); $\delta_C(CDCl_3)$ 141.1 (C-12), 138.8 (C-11), 127.9, 125.8, 125.3, and 124.9, 45.3 (C-14), 43.3 (C-15), 39.1 (C-13), 37.2 (C-5), 35.6 (C-10), 33.0 (C-9), 32.7, 28.5, 27.1, 22.3, and 19.4 (C-16) (Found: C, 90.4; H, 9.8. $C_{17}H_{22}$ requires C, 90.2; H, 9.8%).

(*b*) By adopting the following method of Stork[4] the ketone (**10**) was prepared. The benzyl ketone (**6**) (6 g, 25 mmol) was heated with orthophosphoric acid (36 ml, 85%) under N_2 at 140—150 °C for 4 h. After the usual work-up and extraction with Et_2O the crude cyclized product was chromatographed on basic alumina (60 g). The initial petroleum eluates (*ca.* 300 ml) gave mostly the unchanged ketone (**6**) (2.58 g, 43%) (as revealed by g.l.c.) followed by the cyclized product (**10**) (2.82 g, 47%), m.p. 122—124 °C. This, on recrystallization from petroleum, gave a pure sample of (**10**), m.p. 124—125 °C. Reduction of the ketone (**10**) (2.51 g, 10 mmol) using hydrazine hydrate (25 ml, 99%), diethylene glycol (175 ml), and KOH (14 g) following the procedure described above afforded (**1**) (2.03 g, 86%), m.p. and mixed m.p. 57—58 °C (identical by i.r. and ^1H n.m.r. spectroscopy and by g.l.c.) after chromatography on neutral alumina (40 g) using petroleum as the eluant.

(±)-9a-*Carba*-14α-*morphinan* (**2**).—Reduction of the ketone (**4**) (240 mg, 1.0 mmol) by an identical procedure to that described above, followed by chromatographic purification of the product, afforded the hydrocarbon (**2**) (192 mg, 85%), m.p. 70 °C (light petroleum), homogeneous by g.l.c. (R_t 3.7 min); $\delta_H(CDCl_3)$ 1.33—1.93 (m, 13 H), 2.11—2.28 (m, 3 H), 2.64—2.73 (m, 1 H), 3.17—3.29 (m, 1 H), and 7.05—7.22 (m, 4 H, ArH) (Found: C, 90.3; H, 9.75. $C_{17}H_{22}$ requires C, 90.2; H, 9.8%).

Cyclization of (**6**) *with PPA:* 1,2,3,4-*Tetrahydrobenzo*[a]*fluorene* (**8**).—To a well-stirred homogeneous solution of PPA, prepared from P_2O_5 (20 g) and H_3PO_4 (12 ml, 89%) was added (**6**) (2.4 g, 100 mmol) and the mixture was heated in an oil-bath at 150 °C for 2 h. The cooled deep brown reaction mixture was decomposed with crushed ice (100 g) and extracted with Et_2O (4 × 50 ml). The Et_2O extract was washed with 5% aqueous Na_2CO_3 and brine, dried (Na_2SO_4), and evaporated; distillation of the residue afforded a colourless liquid (1.65 g), b.p. 170—175 °C (0.4 mmHg); g.l.c. showed it to be mixture of at least six compounds with R_t values 2.6 (4%), 3.0 (34%), 4.0 (15%), 72 (4%), 10.0 (23%), and 11.0 (20%) min. The mixture was dissolved in petroleum and left in an ice-box when a colourless solid separated out, which on recrystallization from light petroleum afforded (**8**) (440 mg, 20%), m.p. 132—133 °C; homogeneous by g.l.c., R_t 10.0 min; $\lambda_{max.}$ 259 nm (log ε 4.06); $\delta_H(CDCl_3)$ 1.88 (br s, 4 H), 2.80—2.86 (m, 4 H), 3.70 (s, 2 H), and 7.14—7.80 (m, 6 H, ArH) (Found: C, 92.45; H, 7.45. $C_{17}H_{16}$ requires C, 92.68; H, 7.3%). A mixture of (**8**) (220 mg, 1.0 mmol) and Pd–C (100 mg, 10%) was heated in a metal-bath at 310 °C for 15 h and the reaction product chromatographed on neutral alumina (5.0 g) with petroleum as eluant to afford benzo[*a*]fluorene (**9**) (165 mg, 76%) as a white solid, m.p. 183—184 °C

Table 1. Positional parameters of non-hydrogen atoms in the asymmetric unit of the ketone (**3**) (Figure 1) with their e.s.d.'s in parentheses

Atom	$x(\times 10^3)$	$y(\times 10^4)$	$z(\times 10^4)$
C(1)	658(1)	−1 814(5)	3 842(6)
C(2)	816(1)	−2 047(5)	3 697(7)
C(3)	920(1)	−1 444(5)	3 096(7)
C(4)	864(1)	−566(5)	2 740(6)
C(4a)	705(1)	−308(4)	2 878(5)
C(4b)	645(1)	660(5)	2 432(5)
C(5)	765(1)	1 443(6)	2 476(8)
C(6)	822(1)	1 689(6)	3 754(8)
C(7)	673(1)	1 967(6)	4 489(8)
C(8)	542(1)	1 233(6)	4 445(8)
C(8a)	492(1)	951(5)	3 166(6)
C(9)	365(1)	−218(6)	3 115(7)
C(10)	428(1)	−706(5)	3 643(6)
C(11)	595(1)	−938(4)	3 434(5)
C(12)	586(1)	520(5)	1 142(6)
C(13)	445(1)	−173(6)	1 015(6)
C(14)	308(1)	34(6)	1 804(8)
O(1)	333(1)	−1 245(5)	4 138(6)

Table 2. Bond distances (Å) and angles (°) in the asymmetric unit of the ketone (**3**) with e.s.d.'s in parentheses

(a) Bond distances

C(1)–C(2)	1.35(1)	C(4b)–C(12)	1.55(1)
C(1)–C(11)	1.42(1)	C(12)–C(13)	1.54(1)
C(2)–C(3)	1.39(1)	C(13)–C(14)	1.46(1)
C(3)–C(4)	1.39(1)	C(9)–C(14)	1.58(1)
C(4)–C(4a)	1.37(1)	C(4b)–C(5)	1.49(1)
C(4a)–C(11)	1.42(1)	C(5)–C(6)	1.56(1)
C(4a)–C(4b)	1.55(1)	C(6)–C(7)	1.54(2)
C(9)–C(10)	1.53(1)	C(7)–C(8)	1.50(1)
C(10)–C(11)	1.44(1)	C(8)–C(8a)	1.56(1)
C(8a)–C(9)	1.47(1)	O(1)–C(10)	1.23(1)
C(4b)–C(8a)	1.57(1)		

(b) Bond angles

C(2)–C(1)–C(11)	121.7(7)	C(7)–C(8)–C(8a)	113.6(7)
C(1)–C(2)–C(3)	120.2(7)	C(4b)–C(8a)–C(8)	110.2(6)
C(2)–C(3)–C(4)	119.2(7)	C(8)–C(8a)–C(9)	114.0(7)
C(3)–C(4)–C(4a)	121.8(7)	C(4b)–C(8a)–C(9)	111.3(6)
C(4)–C(4a)–C(11)	119.5(6)	C(8a)–C(9)–C(10)	110.6(6)
C(4)–C(4a)–C(4b)	120.7(6)	C(8a)–C(9)–C(14)	112.4(7)
C(11)–C(4a)–C(4b)	119.8(5)	C(10)–C(9)–C(14)	109.0(6)
C(4a)–C(4b)–C(5)	116.1(6)	C(11)–C(10)–C(9)	117.1(6)
C(4a)–C(4b)–C(8a)	108.8(5)	C(11)–C(10)–O(1)	122.8(6)
C(4a)–C(4b)–C(12)	107.0(5)	C(9)–C(10)–O(1)	119.9(7)
C(5)–C(4b)–C(8a)	108.7(6)	C(1)–C(11)–C(4a)	117.4(7)
C(5)–C(4b)–C(12)	109.5(6)	C(4a)–C(11)–C(10)	122.8(6)
C(8a)–C(4b)–C(12)	106.4(6)	C(1)–C(11)–C(10)	119.8(6)
C(4b)–C(5)–C(6)	113.6(7)	C(4b)–C(12)–C(13)	114.0(6)
C(5)–C(6)–C(7)	108.3(8)	C(12)–C(13)–C(14)	113.4(7)
C(6)–C(7)–C(8)	112.4(8)	C(9)–C(14)–C(13)	112.2(7)

(light petroleum) (lit.,[7] 183—184 °C); picrate, m.p. 127—128 °C (lit.,[7] 127—127.5 °C).

Schmidt Rearrangement of the Ketone (**3**): *Lactam* (**11**).—To a magnetically stirred solution of (**3**) (500 mg, 2.08 mmol) in dry thiophene-free benzene (3.3 ml) was added sulphuric acid (1.1 ml, 93%), followed by sodium azide (235 mg, 3.6 mmol) in small portions during 9 h at 55—60 °C (water-bath) when the colour of the mixture turned pink. The reaction mixture was cooled and the benzene layer was decanted off and discarded. The acidic layer was decomposed with ice and extracted repeatedly with $CHCl_3$; the extract was washed with saturated aqueous Na_2CO_3 and water, dried (Na_2SO_4), and evaporated under reduced pressure to give a pink solid (490 mg, 93%), m.p. 196—198 °C, which on repeated recrystallization from EtOAc–petroleum gave the lactam (**11**), m.p. 199 °C; homogeneous by g.l.c. (R_t 17.5 min); $\nu_{max.}(CHCl_3)$ 1 655 and 1 665sh cm^{-1}; $\delta(CDCl_3)$ 1.29—1.90 (complex m, 13 H), 2.3 (br d, *J* 10 Hz, 1 H), 2.52 (br d, *J* 10 Hz, 1 H), 2.94 (br s, 1 H), 6.82 (d, *J* 7.5 Hz, 1 H), 7.04—7.22 (m, 2 H), 7.45 (d, 1 H, *J* 7.5 Hz), and 8.39 (br s, 1 H); *m/z* 255 (M^+, 100%), 183 (38), and 171 (100) (Found: C, 79.65; H, 8.4. $C_{17}H_{21}NO$ requires C, 79.95; H, 8.3%).

Table 3. Positional parameters ($\times 10^4$) of non-hydrogen atoms in the asymmetric unit of the ketone (**4**) (Figure 2) with e.s.d.'s in parentheses

Atom	*x*	*y*	*z*
C(1)	351(2)	2 005(1)	2 283(2)
C(2)	35(2)	2 931(2)	1 747(2)
C(3)	769(2)	3 409(1)	1 151(2)
C(4)	1 968(2)	2 976(1)	1 109(2)
C(4a)	2 404(2)	2 044(1)	1 663(2)
C(4b)	3 714(2)	1 563(1)	1 597(2)
C(5)	4 904(2)	2 312(2)	1 812(2)
C(6)	6 347(2)	1 862(2)	2 028(3)
C(7)	6 855(2)	1 119(2)	3 256(3)
C(8)	5 725(2)	351(2)	3 010(2)
C(8a)	4 303(2)	8 000(1)	2 832(2)
C(9)	3 124(2)	50(1)	2 620(2)
C(10)	1 904(2)	551(1)	2 807(2)
C(11)	1 555(2)	1 559(1)	2 245(2)
C(12)	3 220(2)	1 054(1)	94(2)
C(13)	2 092(2)	278(2)	145(2)
C(14)	2 576(2)	446(2)	1 108(2)
O(1)	1 230(2)	148(1)	3 398(2)

Schmidt Rearrangement of the Ketone (**4**): *the Lactams* (**12**) *and* (**13**).—The reaction of (**4**) (500 mg, 2.08 mmol) in dry benzene (3.3 ml) and sulphuric acid (1.1 ml, 93%) with sodium azide (235 mg, 6.5 mmol) was carried out as described for (**3**). The crude product (500 mg, 94%), m.p. 171—172 °C; $\nu_{max.}$ 1 657s and 1 631s cm^{-1}, was chromatographed on silica gel (15 g) and eluted with benzene to afford a white solid (450 mg), which on rechromatography over silica gel (15 g) afforded the lactam (**12**) (150 mg, 28%), m.p. 223 °C (EtOH) in the earlier eluates (*ca.* 180 ml); homogeneous by g.l.c. (R_t 22.0 min); $\nu_{max.}(CHCl_3)$ 1 657 cm^{-1}; $\delta_H(CDCl_3)$ 1.19—2.34 (complex m, 15 H), 2.71 (br s, 1 H), 6.76 (d, *J* 7 Hz, 1 H), 7.0—7.12 (m, 2 H), 7.43 (d, *J* 7 Hz, 1 H), and 8.16 (br s, 1 H); *m/z* 255 (M^+, 100), 171 (18), and 120 (52) (Found: C, 79.65; H, 8.1. $C_{17}H_{21}NO$ requires C, 79.95; 8.3%).

Further elutions with benzene (*ca.* 120 ml) gave a mixture of the isomeric lactams (**12**) and (**13**). The slower moving fractions (*ca.* 260 ml) afforded pure (**13**) (200 mg, 38%) m.p. 205—208 °C (EtOH); $\nu_{max.}(CHCl_3)$ 1 631 cm^{-1} (Found: C, 79.65; H, 8.1. $C_{17}H_{21}NO$ requires C, 79.95; H, 8.3%).

Crystallographic Analysis of the Ketone (**3**).—*Crystal data.* $C_{17}H_{20}O$, M = 240, orthorhombic, space group $P2_12_12_1$, a = 8.24(2), b = 14.19(4), c = 11.30(3) Å, Z = 4, D_c = 1.21 g cm^{-3}, D_m = 1.24 g cm^{-3}, $F(000)$ = 520, μ(Cu-K_α) = 5.69 cm^{-1}, m.p. = 72 °C. 972 Reflections were observed on a Weissenberg goniometer using Cu-K_α radiation and their intensities were visually measured. The structure was solved by MULTAN-78[10] and refined by the full-matrix least-square method to R = 0.103. A view of the asymmetric unit of (**3**) along the *a*-axis is shown in Figure 1. Positional parameters are shown in Table 1 and bond distances and angles in Table 2.

Table 4. Bond distances (Å) and angles (°) in the asymmetric unit of the ketone (**4**) with e.s.d.'s in parentheses

(a) Bond distances

C(1)–C(2)	1.377(3)	C(4b)–C(12)	1.548(2)
C(1)–C(11)	1.392(3)	C(12)–C(13)	1.517(3)
C(2)–C(3)	1.372(3)	C(13)–C(14)	1.518(3)
C(3)–C(4)	1.381(3)	C(9)–C(14)	1.543(3)
C(4)–C(4a)	1.396(2)	C(4b)–C(5)	1.540(3)
C(4a)–C(11)	1.405(2)	C(5)–C(6)	1.532(2)
C(4a)–C(4b)	1.522(2)	C(6)–C(7)	1.518(4)
C(9)–C(10)	1.507(3)	C(7)–C(8)	1.510(3)
C(10)–C(11)	1.484(3)	C(8)–C(8a)	1.522(3)
C(8a)–C(9)	1.534(3)	O(1)–C(10)	1.219(2)
C(4b)–C(8a)	1.545(2)		

(b) Bond angles

C(2)–C(1)–C(11)	120.7(2)	C(7)–C(8)–C(8a)	111.4(2)
C(1)–C(2)–C(3)	119.3(2)	C(4b)–C(8a)–C(8)	113.6(2)
C(2)–C(3)–C(4)	120.7(2)	C(8)–C(8a)–C(9)	113.7(2)
C(3)–C(4)–C(4a)	121.6(2)	C(4b)–C(8a)–C(9)	109.1(2)
C(4)–C(4a)–C(11)	116.9(2)	C(8a)–C(9)–C(10)	108.6(2)
C(4)–C(4a)–C(4b)	121.5(2)	C(8a)–C(9)–C(14)	112.0(2)
C(11)–C(4a)–C(4b)	121.5(2)	C(10)–C(9)–C(14)	110.4(2)
C(4a)–C(4b)–C(5)	111.3(2)	C(11)–C(10)–C(9)	117.4(2)
C(4a)–C(4b)–C(8a)	108.3(2)	C(11)–C(10)–O(1)	121.1(2)
C(4a)–C(4b)–C(12)	107.9(2)	C(9)–C(10)–O(1)	121.5(2)
C(5)–C(4b)–C(8a)	108.9(2)	C(1)–C(11)–C(4a)	120.8(2)
C(5)–C(4b)–C(12)	110.8(2)	C(4a)–C(11)–C(10)	120.7(2)
C(8a)–C(4b)–C(12)	109.6(2)	C(1)–C(11)–C(10)	118.5(2)
C(4b)–C(5)–C(6)	114.1(1)	C(4b)–C(12)–C(13)	112.9(2)
C(5)–C(6)–C(7)	111.7(2)	C(12)–C(13)–C(14)	111.7(2)
C(6)–C(7)–C(8)	111.2(2)	C(9)–C(14)–C(13)	112.2(2)

Crystallographic Analysis of the Ketone (**4**).—*Crystal data.* $C_{17}H_{20}O$, $M = 240$, monoclinic, space group $P2_1/c$, $a = 10.243(3)$, $b = 13.771(4)$, $c = 10.070(3)$ Å, $\beta = 114.84(2)°$, $Z = 4$, $D_c = 1.24$ g cm^{-3}, $D_m = 1.26$ g cm^{-3}, $F(000) = 520$, μ (Cu-K_α) = 5.83 cm^{-1}, m.p. = 118 °C. 1 551 observed reflections with $|F| \geqslant 46|F|$ and $\theta \leqslant 57°$ were measured on CAD-4 diffractometer using graphite monochromated Cu-K_α radiation. The structure was solved by MULTAN-78 [10] and refined by the full-matrix least squares method to $R = 0.04$. A view of the asymmetric unit of the molecule along the b axis is shown in Figure 2. Positional parameters are shown in Table 3 and bond distances and angles in Table 4. Tables of thermal parameters are available as a Supplememtary Publication [SUP No. 56533 (5 pp.)]. Structure factor tables are available on request from the Editorial office.*

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* For details of the Supplementary Publications Scheme, see Instructions for Authors (1986), *J. Chem. Soc., Perkin Trans. 1*, 1986, Issue 1.

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