# Intramolecular Ene Reaction of the Unsaturated Acyloin 3-(But-3-enyl)-2-hydroxy-3-methylcyclohexanone

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The ene reaction of the title compound takes place readily in decalin solution under reflux and affords the isomeric octahydroinden-4-ones (**6**) and (**7**).

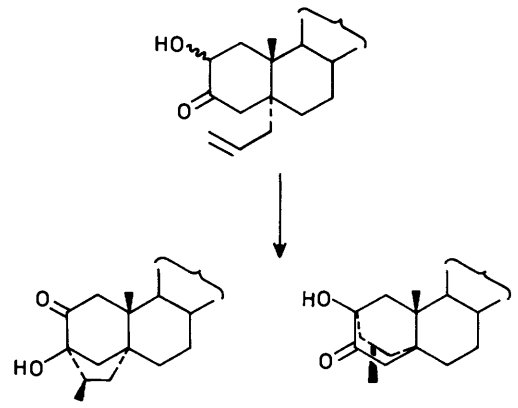
We have recently reported[1,2] that the thermal intramolecular ene reactions of some steroidal unsaturated acyloins (*e.g.* Scheme 1) occur more readily than those of similar unsaturated ketones. The present work demonstrates that the non-steroidal, and accordingly more conformationally mobile, unsaturated acyloins (**3**) and (**4**) are similarly reactive in that they give the ene products (**6**) and (**7**) when heated in decalin under reflux.

Treatment of 3-methylcyclohex-2-enone with the mixed cuprate[3] derived from but-3-enylmagnesium bromide, methyllithium and copper(I) iodide, and trapping[4] of the resultant lithium enolate with trimethylsilyl chloride, gave the *O*-silyl enol (**1**). The i.r. {$\nu_{max.}$ 3 080, 1 640 (-CH=$CH_2$), and 1 660 $cm^{-1}$ [-CH=C(R)OSi$Me_3$]} and $^1$H n.m.r {δ 5.4 – 5.9 (m, -C*H*=$CH_2$), 4.65 – 5.0 (m, -CH=$CH_2$) and 4.50 [s, -C*H*=CH(R)OSi$Me_3$]} spectra confirmed the presence of the terminal alkene and the *O*-silyl enol groups. Oxidation[5] of (**1**) with *m*-chloroperoxybenzoic acid gave the trimethylsilyloxy ketone (**2**), which on hydrolysis gave the acyloins (**3**) and (**4**), purified by flash chromatography. The less polar isomer was assigned the *r*-3-(but-3-enyl)-*t*-2-hydroxy structure (**3**) because the $^1$H n.m.r. signal (δ 0.74) for the 3-methyl group is close to that (δ 0.69) for the 10-methyl group in the seco steroid (**5**).[2] Singlets at δ 4.0 and 3.95 in the $^1$H n.m.r. spectra of the less and more polar isomers, respectively, were assigned to the C-2 methine proton, confirming the regiochemistry of the acyloins, which were also shown to be isomeric by their mass spectra.

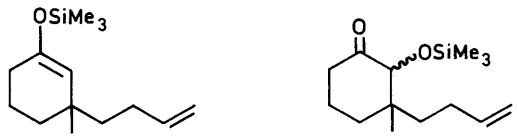
The mixed acyloins (**3**) and (**4**) did not react[2,6] in a deoxygenated solution in t-butyl alcohol containing KOBu$^t$. However, when these isomers were heated under reflux in decalin solution in an atmosphere of argon, two octahydroinden-4-ones (**6**) and (**7**) were isolated by flash chromatography along with a minor unidentified product, possibly (**8**) or (**9**). The i.r. spectra of the octahydroinden-4-ones showed the presence of hydrogen-bonded OH ($\nu_{max.}$ 3 495 $cm^{-1}$) and C=O [$\nu_{max.}$ 1 700 for (**6**) and 1 695 $cm^{-1}$ for (**7**)] groups. The intramolecular hydrogen bonding and thus the *cis*-configuration for the ring junction was supported by the observation of a sharp and dilution independent OH signal in the $^1$H n.m.r. spectra. Further support for the *cis*-assignment was afforded by the angular 7a-methyl singlets in the $^1$H n.m.r. spectra [δ 0.99 for (**6**) and 0.92 for (**7**)], which had chemical shifts similar to those for other *cis*-systems.[7] The $^1$H n.m.r. spectra of solutions in deuteriobenzene provided further evidence in support of the assigned structures. That of (**6**) showed signals at δ 0.93 (7a-Me) and 0.77 (3-Me), upfield of those for (**6**) in $CDCl_3$ by 0.06 and 0.04 p.p.m., respectively. Similar upfield shifts of the signals for the 5-Me (0.09 p.p.m.) and the 7a-Me (0.05 p.p.m.) were observed for (**7**). The larger shift for the 5-Me in (**7**) is indicative of the greater proximity of this methyl group to the carbonyl group, which interacts with the solvating deuteriobenzene. The $^{13}$C n.m.r. data for compounds (**6**) and (**7**) are in accord with the structural assignments (Table 2).

Reduction of the octahydroinden-4-ones (**6**) and (**7**) with sodium borohydride afforded, respectively, the diols (**10**) and (**11**). The $^1$H n.m.r. spectrum of the 3-methyl diol (**10**) showed the 4-H signal as a relatively broad multiplet ($W_{\frac{1}{2}}$ 10 Hz) at δ 3.74, whereas that of its isomer (**11**) showed a broad singlet ($W_{\frac{1}{2}}$ 4 Hz) at δ 3.58, reflecting the single vicinal spin–spin coupling involved in the latter.

Final confirmation of the structure of the octahydroinden-4-one (**7**) came from the *X*-ray crystallographic structure determination of its oxime (**7a**). A drawing of the molecule together



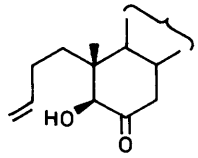

Scheme 1.




(**1**) (**2**)


(**3**) R = O
(**3a**) R = NOH

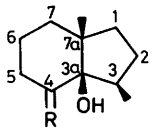
(**4**) R = O
(**4a**) R = NOH



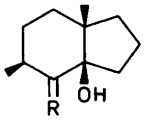

(**5**)

**Table 1.** Atomic co-ordinates and standard deviations for compound (**7a**) ( $\times 10^4$)

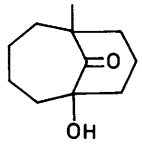
| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| C(1) | 7 440(5) | 3 425(3) | 3 087(4) |
| C(2) | −625(5) | 2 832(3) | 4 061(4) |
| C(3) | −1 071(5) | 1 558(3) | 4 633(5) |
| C(4) | −2 853(6) | 619(3) | 3 167(5) |
| C(5) | 5 155(5) | 1 171(3) | 2 332(5) |
| C(6) | 5 663(5) | 2 409(3) | 1 660(4) |
| C(7) | 6 751(6) | 2 335(4) | 208(5) |
| C(8) | 7 858(6) | 3 708(4) | 222(5) |
| C(9) | 8 077(5) | 4 435(3) | 2 019(5) |
| C(10) | 3 532(6) | 2 888(4) | 962(5) |
| C(11) | −1 618(7) | 1 683(4) | 6 343(5) |
| N(1) | 1 290(4) | 3 507(3) | 4 374(4) |
| O(1) | 2 987(4) | 2 938(2) | 5 379(3) |
| O(2) | 6 560(3) | 3 909(2) | 4 389(3) |



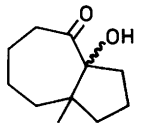
(**6**) R = O
(**6a**) R = NOH
(**10**) R = ⁻OH, H



(**7**) R = O
(**7a**) R = NOH
(**11**) R = ⁻OH, H



(**8**)



(**9**)

with the atom numbering is shown in the Figure and atomic co-ordinates are listed in Table 1. Bond lengths and angles, which are unremarkable, together with thermal parameters, have been deposited with the Cambridge Crystallographic Data Centre.*

The data available for the minor, third product of cyclisation do not allow distinction between the structures (**8**) and (**9**). The i.r. spectrum confirmed that it is a hydroxy ketone ($\nu_{max.}$ 3 495 and 1 712 $cm^{-1}$), the $^1H$ n.m.r. spectrum showed important bands at δ 3.88 (s, OH) and 1.07 (s, Me), and the mass spectrum showed a molecular ion at *m/z* 182, suggesting that the compound was isomeric with the other products but lacked the MeCH group.

The octahydroinden-4-one (**6**) probably arises from the ene reaction of the dienediol (**12**) in conformation **A** (Scheme 2), and the occurrence of its isomer (**7**) may be rationalised by the acyloin rearrangement shown. The dienediol (**12**) may also react[2] in conformation **B** to afford the hydroxybicyclo[4.3.1]-decanones (**8**), which could conceivably undergo acyloin rearrangements to give the hydroxydecalones (**13**) and the hydroxybicyclo[5.3.0]decanones (**9**). The hydroxydecalones (**13**) are excluded because their $^1H$ n.m.r. spectra are different from that of the product obtained.[8]

In one experiment in which the concentration of the acyloin in decalin was approximately twice that in the experiments just described, the major (20%) product was the hexahydroinden-4-

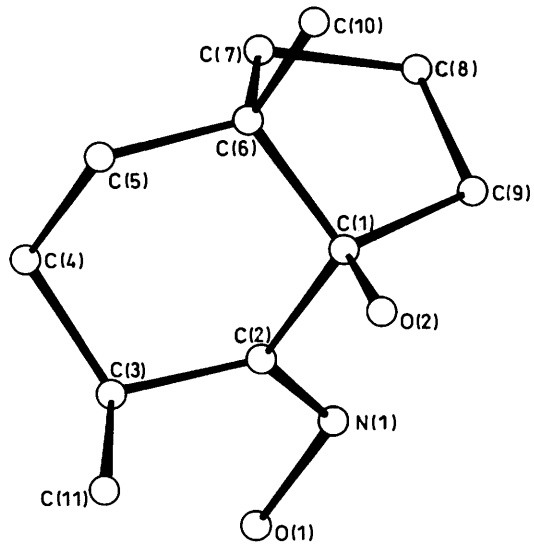
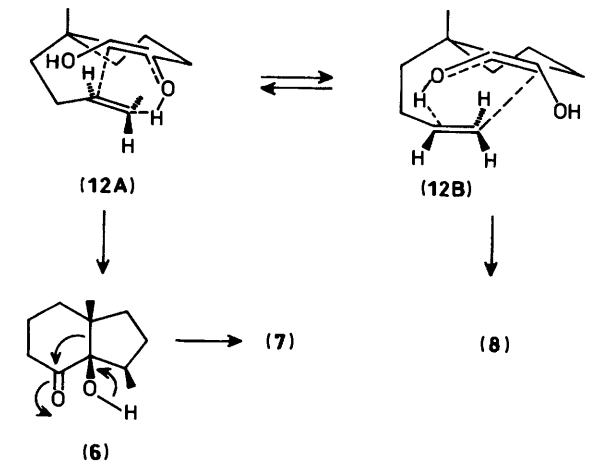
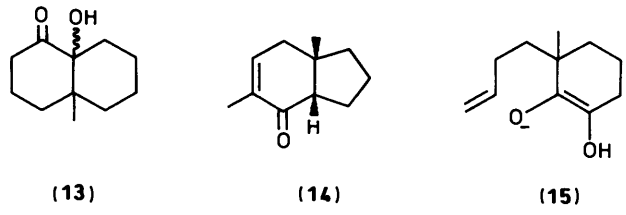


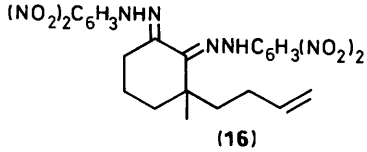
**Figure.** Structure of the oxime (**7a**)



Scheme 2.



(**13**) (**14**) (**15**)



(**16**)

one (**14**), thought to arise by dehydration of (**7**),[2] and identified from its i.r. ($\nu_{max.}$ 1 665 $cm^{-1}$) and $^1H$ n.m.r. {δ 6.47 [m, –C*H*=C(Me)–C=O and 1.78 (br s, –CH=C(*Me*)–C=O]} spectra. The $^{13}C$ n.m.r. spectrum (Table 2) of (**14**) is also in accord with the assigned structure.

The occurrence of the ene reaction of the acyloins (**3**) and (**4**) at the temperature of boiling decalin provides further evidence

* See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1988, Issue 1.

**Table 2.** $^{13}C$ N.m.r. spectra (δ values) of cyclisation products (**6**), (**7**), and (**14**)

| Compd. | C-1 | C-2 | C-3 | C-3a | C-4 | C-5 | C-6 | C-7 | C-7 | 7a-Me | 3-Me | 5-Me |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (**6**) | 36.7 | 30.6 | 42.6 | 89.3 | 215.0 | 38.9 | 23.9 | 36.7 | 54.2 | 19.3 | 13.0 | |
| (**7**) | 34.8 | 21.3 | 39.2 | 88.2 | 214.3 | 39.7 | 33.2 | 39.0 | 54.9 | 18.2 | | 14.5 |
| (**14**) | 34.5 | 22.4 | 28.9 | 57.2 | 201.7 | 133.2 | 142.6 | 39.4 | 44.9 | 26.2 | | 15.9 |

of the greater reactivity of the unsaturated acyloins than of the unsaturated ketone analogues.[1,2] This may be a function of greater electron availability in the ene (enediol) relative to that (enol) in the unsaturated ketones. The conformational constraints in ring *B* in the previously studied seco steroids[2] appear to be relatively unimportant. The failure of KOBu$^t$ to exert a direct effect in the ene reactions of the unsaturated acyloins (**3**)—(**5**)[2] suggests that it has no particularly important catalytic role, notwithstanding the requirement of the acyloins to enolise to the enediols. Also, it seems unlikely that anions such as (**15**) play any major role in these reactions.

## Experimental

Solutions were dried over anhydrous magnesium sulphate and solvents were removed under reduced pressure with a rotary evaporator. Preparative t.l.c. was performed on Kieselgel $60PF_{254}$ and $PF_{360}$. Flash chromatography was carried out with Merck silica gel (230—240 mesh). I.r. spectra were recorded for Nujol mulls (solids) or thin films with a Perkin-Elmer 177 spectrometer. $^1H$ N.m.r. spectra were determined for solutions in $CDCl_3$ with tetramethylsilane as internal standard. Spectra were recorded at 60 (Varian EM360A) or 90 MHz (Perkin-Elmer R32). $^{13}C$ N.m.r. spectra were similarly determined with a Bruker WP80 spectrometer. Mass spectra were recorded with a Kratos MS80 spectrometer, with DS55 data system. M.p.s were determined with a Kofler hot-stage microscope. Deoxygenation of solutions in t-butyl alcohol was achieved by bubbling argon through the solution heated under reflux (4 h).

3-(*But*-3-*enyl*)-3-*methyl*-1-*trimethylsilyloxycyclohexene* (**1**).—To a stirred suspension of copper(I) iodide (0.6 mol equiv.) in tetrahydrofuran (THF) (50 ml) at −40 °C under argon was added a solution of methyl-lithium (17.8 ml, 0.55 mol equiv.) in ether. The yellow suspension of methylcopper was allowed to warm to 0 °C (*ca.* 15 min), then cooled to −40 °C, and a solution of but-3-enylmagnesium bromide (1.2 mol equiv.) in ether was added. The solution was stirred for a further 30 min, after which 3-methylcyclohex-2-enone (6.0 g, 1.0 mol equiv.) in THF (20 ml) was added. The solution was allowed to warm to room temperature and stirring continued for a further 2 h. Trimethylsilyl chloride (12.6 g, 2.2 mol equiv.) in triethylamine (40 ml) was added and the solution stirred for 60 min. The mixture was diluted with light petroleum (b.p. 40—60 °C; 100 ml), washed with aqueous ammonium chloride (2 × 50 ml) and aqueous sodium hydrogen carbonate (50 ml), dried, and evaporated under reduced pressure to give a green liquid (14.3 g). Distillation gave the pure O-*silyl enol* (**1**) (10.6 g, 82%), b.p. 110—115 °C at 1.5 mmHg; $\nu_{max.}$ 3 080 (RCH=$CH_2$), 1 660 (C=C–$OSiMe_3$), and 1 640 $cm^{-1}$ (RCH=$CH_2$); δ 5.4—5.9 (m, 1 H, RC*H*=$CH_2$), 4.65—5.0 (m, 2 H, RCH=C*H*$_2$), 4.50 (s, 1 H, C*H*=CR–$OSiMe_3$), 0.95 (s, 3 H, Me), and 0.18 (s, 9 H, $OSiMe_3$) [Found: *m/z* 238.1768 ($M^{+\cdot}$). $C_{14}H_{26}OSi$ requires *M*, 238.1753].

3-(*But*-3-*enyl*)-2-*hydroxy*-3-*methylcyclohexanones* (**3**) and (**4**).—To a solution of the O-silyl enol (**1**) (13.4 g) in ether (150 ml) were added sodium hydrogen carbonate (7.2 g, 2 mol equiv.) and *m*-chloroperoxybenzoic acid (12.8 g, 1 mol equiv.). The mixture was stirred for 5 h and then filtered. The filtrate was washed with aqueous sodium sulphite (50 ml), aqueous sodium hydrogen carbonate (50 ml), and water (50 ml), dried, and evaporated under reduced pressure to give a white solid (17.4 g). The solid was dissolved in hot hexane (60 ml), and the solution was cooled to 0 °C to afford largely solid 3-chlorophenyl 3-chlorobenzoate, an impurity, which was filtered off. The filtrate was evaporated under reduced pressure to give the crude α-silyloxy ketones (**2**) (11.5 g, 80%).

The α-silyloxy ketones (**2**) were dissolved in ethanol (90 ml) and hydrochloric acid (2M; 20 ml) and stirred at room temperature for 40 min. The solution was diluted with brine (200 ml) and extracted with ether (3 × 50 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate (50 ml) and water (50 ml), dried, and evaporated under reduced pressure. Distillation under reduced pressure gave the isomeric acyloins (**3**) and (**4**) (6.5 g, 63%) (b.p. 100—145 °C at 2 mmHg).

Flash column chromatography [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (8:1 v/v)] gave 3-(but-3-enyl)-3-methylcyclohexanone[3] (0.86 g, 8%), $\nu_{max.}$ 3 080 (RCH=$CH_2$), 1 715 (C=O), and 1 640 $cm^{-1}$ (RCH=$CH_2$); r-3-(*but*-3-*enyl*)-t-2-*hydroxy*-3-*methylcyclohexanone* (**3**) (1.18 g, 12%); $\nu_{max.}$ 3 485 (OH), 3 075 (RCH=$CH_2$), 1 710 (C=O), and 1 640 $cm^{-1}$ (RCH=$CH_2$); δ 5.65—6.13 (m, 1 H, RC*H*=$CH_2$), 4.9—5.2 (m, 2 H, RCH=C*H*$_2$), 4.0 (s, 1 H, 2-H), 3.60 (br s, 1 H, OH; $D_2O$-exchangeable), and 0.74 (s, 3 H, Me) [Found: *m/z*, 182.1306 ($M^{+\cdot}$). $C_{11}H_{18}O_2$ requires *M*, 182.1307], which gave the *oxime* (**3a**), m.p. 132—134 °C [from light petroleum (b.p. 40—60 °C)–ether] (Found: C, 67.0; H, 9.9; N, 7.1. $C_{11}H_{19}NO_2$ requires C, 67.0; H, 9.7; N, 7.1%); a fraction containing a mixture of the isomers (**3**) and (**4**) (1.38 g, 13%); and r-3-(*but*-3-*enyl*)-c-2-*hydroxy*-2-*methylcyclohexanone* (**4**) (0.96 g, 9%); $\nu_{max.}$ 3 490 (OH), 3 075 (RCH=$CH_2$), 1 708 (C=O), and 1 640 $cm^{-1}$ (RCH=$CH_2$); δ 5.59—6.05 (m, 1 H, RC*H*=$CH_2$), 4.85—5.2 (m, 2 H, RCH=C*H*$_2$), 3.95 (s, 1 H, 2-H), 3.78 (br s, 1 H, OH; $D_2O$-exchangeable), and 1.14 (s, 3 H, Me) [Found: *m/z*, 182.1304 ($M^{+\cdot}$). $C_{11}H_{18}O_2$ requires *M*, 182.1307], which gave the *oxime* (**4a**), m.p. 135—136 °C [from light petroleum (b.p. 40—60 °C)–ether] (Found: C, 67.1; H, 10.0; N, 7.0. $C_{11}H_{19}NO_2$ requires C, 67.0; H, 9.7; N, 7.1%), and the 2,4-*dinitrophenylosazone* (**16**), m.p. 193—194 °C (from methanol) (Found: C, 51.3; H, 4.3; N, 20.9. $C_{23}H_{24}N_8O_8$ requires C, 51.1; H, 4.5; N, 20.7%).

*Attempted Cyclisation of* 3-(*But*-3-*enyl*)-2-*hydroxy*-3-*methylcyclohexanone with Potassium t-Butoxide in t-Butyl Alcohol.*—The acyloins (**3**) and (**4**) (0.4 g) were added to a deoxygenated solution of potassium t-butoxide (2 mol equiv.) in t-butyl alcohol (40 ml). The solution was stirred at 50 °C under argon for 4 h, then diluted with water (100 ml), neutralised with hydrochloric acid (2M), and extracted with ether (3 × 25 ml). The combined extracts were washed with water (2 × 25 ml), dried, and evaporated under reduced pressure to give unchanged starting material (0.39 g).

*Cyclisation of* 3-(*But*-3-*enyl*)-2-*hydroxy*-3-*methylcyclohexanone in Decalin.*—A solution of the acyloins (**3**) and (**4**) (1.7 g) in decalin (15 ml) was heated under reflux for 24 h under argon. The solution was flash chromatographed [$SiO_2$; light

petroleum (b.p. 40—60 °C) to remove the decalin, then light petroleum (b.p. 40—60 °C)–ether (8:1 v/v)] to give r-3a-*hydroxy*-c-3,c-7a-*dimethyloctahydroinden*-4-*one* (**6**) (0.32 g, 19%). Preparative t.l.c. [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (3:1 v/v)] gave pure (**6**) (0.150 g, 9%); $\nu_{max.}$ 3 495 (OH) and 1 700 $cm^{-1}$ (C=O); $\delta_H$ 3.7 (s, 1 H, OH; $D_2O$-exchangeable), 0.99 (s, 3 H, 7a-Me), and 0.81 (d, 3 H, 3-Me, *J* 7 Hz), $^{13}C$ see Table 2 [Found: *m/z*, 182.1307. ($M^{+\cdot}$). $C_{11}H_{18}O_2$ requires *M*, 182.1307], which gave the *oxime* (**6a**), m.p. 103—104 °C [from light petroleum (b.p. 40—60 °C)–ether] (Found: C, 66.7; H, 9.8; N, 7.0. $C_{11}H_{19}NO_2$ requires C, 67.0; H, 9.7; N, 7.1%). A second fraction consisted of r-3a-*hydroxy*-c-5,c-7a-*dimethyl*-*octahydro*-4H-*inden*-4-*one* (**7**) (0.55 g, 32%). Preparative t.l.c. [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (3:1 v/v)] gave pure (**7**) (0.318 g, 19%); $\nu_{max.}$ 3 495 (OH) and 1 695 $cm^{-1}$ (C=O); $\delta_H$ 4.02 (s, 1 H, OH; $D_2O$-exchangeable), 1.05 (d, 3 H, 5-Me, *J* 7 Hz), and 0.92 (s, 3 H, 7a-Me), $^{13}C$ see Table 2 [Found: *m/z*, 182.1303 ($M^{+\cdot}$). $C_{11}H_{18}O_2$ requires *M*, 182.1307], which gave the *oxime* (**7a**), m.p. 175—176 °C [from light petroleum (b.p. 40—60 °C)–ether] (Found: C, 67.0; H, 10.0; N, 7.2. $C_{11}H_{19}NO_2$ requires C, 67.0; H, 9.7; N, 7.1%).

The final fraction (0.44 g, 26%) contained a mixture. Preparative t.l.c. [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (3:1 v/v)] gave a further cyclisation product (**8**) or (**9**) (0.08 g, 5%); $\nu_{max.}$ 3 495 (OH) and 1 712 $cm^{-1}$ (C=O); δ 3.88 (s, OH) and 1.07 (s, 3 H, Me) [Found: *m/z*, 182.1307 ($M^{+\cdot}$). Calc. for $C_{11}H_{18}O_2$: *M*, 182.1307), and unchanged starting material (0.138 g, 8%).

r-3a,c-4-*Dihydroxy*-c-3,c-7a-*dimethyloctahydroindene* (**10**).—The ketol (**6**) (140 mg) was dissolved in methanol (10 ml) and sodium borohydride (3 mol equiv.) was added with stirring. After 10 min at room temperature the solution was diluted with water (75 ml) and extracted with ether (3 × 25 ml). The combined extracts were washed with water (25 ml), dried, and evaporated under reduced pressure to give a semi-crystalline gum (0.118 g, 84%). Flash chromatography [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (8:1 v/v)] gave the *diol* (**10**) (0.70 g, 50%), m.p. 94—96 °C (from hexane); $\nu_{max.}$ 3 350 $cm^{-1}$ (br, OH); δ 3.74 (m, 1 H, 4-H, $W_{\frac{1}{2}}$ 10 Hz), 1.08 (d, 3 H, 3-Me, *J* 7 Hz), and 1.0 (s, 3 H, 7a-Me) [Found: *m/z*, 184.1470 ($M^{+\cdot}$). $C_{11}H_{20}O_2$ requires *M*, 184.1463].

r-3a,c-4-2-*Dihydroxy*-c-5,c-7a-*dimethyloctahydroindene* (**11**).—The ketol (**7**) (0.170 g) was treated as in the preceding experiment to give the crude diol (0.140 g) (82%). Flash chromatography [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (8:1 v/v)] gave the *diol* (**11**) (0.097 g, 57%), m.p. 95—96 °C (from hexane); $\nu_{max.}$ 3 500 and 3 460 $cm^{-1}$ (OH); δ 3.58 (br s, 1 H, 4-H, $W_{\frac{1}{2}}$ 4 Hz), 2.54 (br s, 1 H, OH; $D_2O$-exchangeable), 2.31 (br s, 1 H, OH; $D_2O$-exchangeable), 1.07 (s, 3 H, 7a-Me), and 1.0 (d, 3 H, 5-Me, *J* 6.5 Hz) [Found: *m/z*, 184.1455 ($M^{+\cdot}$); C, 72.1; H, 11.2%. $C_{11}H_{20}O_2$ requires *M*, 184.1463; C, 71.7; H, 10.9%).

*Cyclisation of* 3-(*But*-3-*enyl*)-2-*hydroxy*-3-*methylcyclohexanone in Decalin with Product Dehydration.*—A solution of the acyloins (**3**) and (**4**) (3.0 g) in decalin (15 ml) was heated under reflux for 24 h under argon. The solution became cloudy and water droplets appeared in the condenser. Flash column chromatography [$SiO_2$; light petroleum (b.p. 40—60 °C) to remove the decalin, then light petroleum (b.p. 40—60 °C)–ether (8:1 v/v)] gave a fraction containing a mixture of enones (1.25 g, 46%) and starting material (1.1 g, 37%).

The enones were purified by preparative t.l.c. [$SiO_2$; light petroleum (b.p. 40—60 °C)–ether (3:1 v/v)] to give 5,7a-*dimethyl*-1,2,3,3a,7,7a-*hexahydroinden*-4-*one* (**14**) (0.540 g, 20%); $\nu_{max.}$ 1 665 $cm^{-1}$, (C=O); $\delta_H$ 6.47 (m, 1 H, RC*H*=CMe–C=O), 1.78 (br s, 3 H, RCH=C*Me*C=O), and 1.10 (s, 3 H, 7a-Me), $^{13}C$ see Table 2 [Found: *m/z*, 164.1202 ($M^{+\cdot}$). $C_{11}H_{16}O$ requires *M*, 164.1201]; and an unidentified enone (0.131 g, 5%); $\nu_{max.}$ 1 685 (C=O) and 1 620 $cm^{-1}$ (C=C); δ 6.35 (t, RC*H*=CR–C=O, *J* 3 Hz) and 1.04 (s, 3 H, Me).

X-*Ray Crystallography.*—*Crystal data.* $C_{11}H_{19}NO_2$, *M* = 197.2. Triclinic, *a* = 6.544(5), *b* = 10.889(5), *c* = 8.092(5) Å, α = 95.29(5), β = 107.58(5), γ = 99.29(5)°, *V* = 536.35 (by optimisation of axial row reflections), space group $P\bar{1}$ (No. 2), *Z* = 2, $D_x$ = 1.22 g $cm^{-3}$; crystal dimensions 0.76 × 0.21 × 0.06 mm, μ(Mo-$K_\alpha$) = 0.48 $cm^{-1}$.

*Data collection and processing.* Stöe Stadi−2 Weissenberg diffractometer, graphite-monochromated Mo-$K_\alpha$ radiation; 2 419 reflections measured ($2.5 < \theta < 25$), *h* 0 to 7, *k* −14 to 13, *l* −9 to 8, of which 1 283 had $I/\sigma(I) > 3$.

*Structure analysis and refinement.* Direct methods (EEES). Full-matrix least-squares refinement with unit weights. Anisotropic thermal parameters for non-H atoms; H atoms placed from difference map but not refined. Electron density excursions on final difference map ±0.2 e $Å^{-3}$. Max. Shift/error 0.000.

Final *R* value 0.055. Structure solution and refinement using SHELX[9] as implemented at Loughborough University; bond length and angle calculations by the XRAY[10] system implemented at the University of Manchester Regional Computer Centre.

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