Tetrahedron Vol. 48, No. 44, pp. 9725-9734, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

Regiocontrol in the Cyclopropane Ring Cleavage of Tricyclo[4.4.0.$0^{1,3}$]decanes to Hydrindane and Decalin Systems

Adusumilli Srikrishna,* Kathiresan Krishnan and Channabasaveshwar V. Yelamaggad

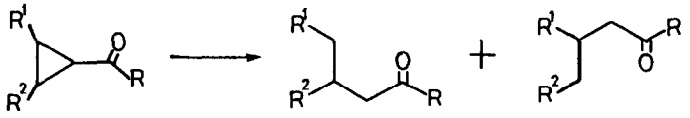
Department of Organic Chemistry, Indian Institute of Science Bangalore - 560 012, INDIA.

(Received in UK 3 August 1992)

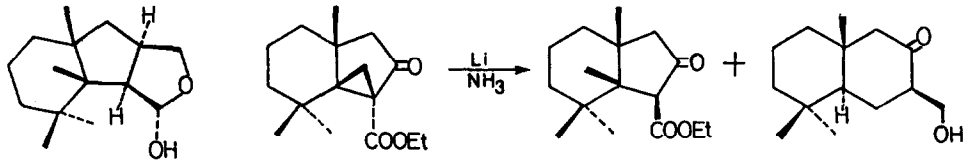
Key Words: Cyclopropanes; Li-liquid ammonia reduction; Hydrindane; Decalin.

***ABSTRACT**: Lithium-liquid ammonia reduction of the cyclopropyl β-ketoester **2** furnished a 1:1 mixture of hydrindane and decalin systems **3** and **4**. Whereas under the same conditions the ketones **5** and **6** furnished the hydrindanones **10** and **13**; and the hydroxy ester **7** furnished the decalin system **14**, via the regiospecific cleavage of either C_3-C_2 bond or C_3-C_1 bond.*

The reduction of organic compounds with alkali metals in liquid ammonia is a well established synthetic operation. Cyclopropyl ketones, when reduced with lithium in liquid ammonia,[1] undergo reductive cleavage of the cyclopropane ring by a mechanism similar to that described for enones, and thus, the developing carbanionic character of the β carbon could be a controlling factor in the ring opening. In fused systems, however, geometrical factors and not electronic factors appear to control the direction of the ring opening, and the bond that cleaves is the one which has the greater overlap with the carbonyl π-system.[2] Whereas in the non-fused systems, where free rotation of the carbonyl moiety is possible, both steric and electronic factors operate depending on the nature of the substitution.[3]

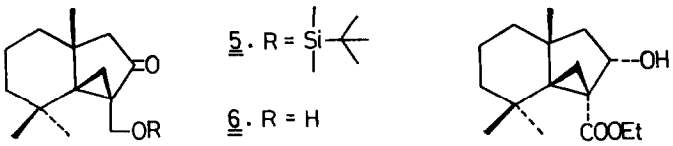


During our recent synthetic studies enroute to first total synthesis[4] of a natural thapsane (**1**), we have employed the tricyclo[4.4.0.$0^{1,3}$]decane system **2** as a precursor to the key intermediate **3**. The compound **2** contains an interesting cyclopropane moiety which is conjugated to a ketone which is part of a fused system; as well as to the ester carbonyl which is not fused in nature. The reductive cleavage of the cyclopropane ring in the keto-ester **2** with lithium in liquid ammonia at −33°C furnished a 1:1 mixture of the hydrindanone **3** and the decalin **4**. The formation of the two products **3** and **4**



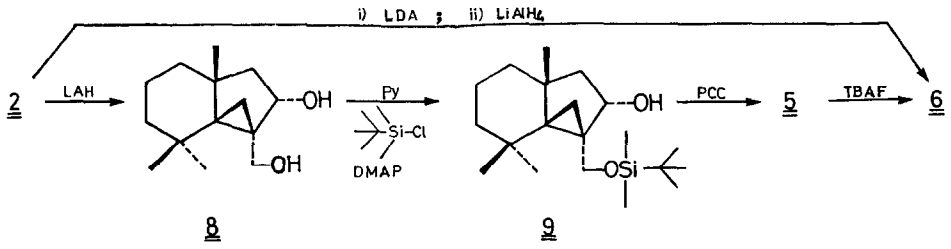
1 2 3 4

can be explained by the selective cleavage of either the C_3–C_2 bond or the C_3–C_1 bond of the cyclopropane. Transfer of electron to the ketone carbonyl results in the cleavage of the C_3–C_2 bond leading to the hydrindanone 3 analogous to those systems[5] containing either a hydrogen or a methyl group in the place of ester group. On the other hand transfer of electron to the ester carbonyl results in the cleavage of C_3–C_1 bond, because in the sterically less hindered conformation, the C_3–C_1 bond has better overlap with the π-system of the carbonyl of the ester similar to that in *cis* 2-methylacetylcyclopropane,[3] followed by further reduction leading to the decalin 4. This is further supported by the fact that a primary alcohol was obtained from the ester, analogous to the lithium-liquid ammonia reduction of α,β-unsaturated esters to the corresponding primary alcohols.[6] In order to establish this hypothesis we have investigated the reduction of related compounds 5, 6 and 7, each containing only one carbonyl system conjugated to cyclopropane, anticipating regiospecificity in the cleavage of cyclopropane ring during lithium-liquid ammonia reduction resulting either hydrindane or decalin systems exclusively.



7

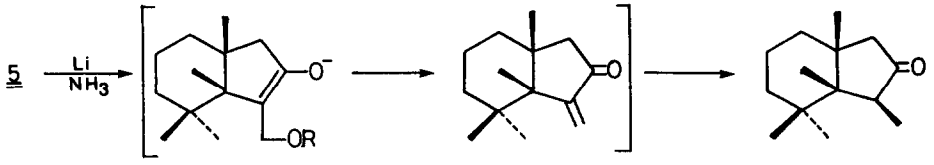
The keto-ester 2 was converted to the TBDMS ether 5 via the diol 8. Thus, $LiAlH_4$ reduction of the ketoester 2 in ether at 0°C furnished the diol 8 in 76% yield. Selective protection of the primary hydroxyl by treatment with one equivalent of TBDMS–Cl in pyridine and a catalytic amount of 4-dimethylaminopyridine (DMAP) afforded the hydroxy ether 9 in 85% yield. Oxidation



8 9

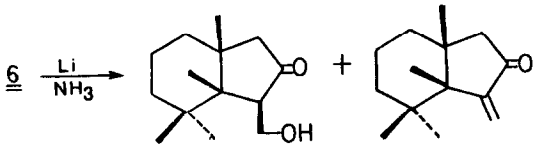
of the hydroxy ether 9 with PCC in methylene chloride furnished the keto ether 5 in 70% yield. Treatment of the keto ether 5 with tetra-n-butylammonium fluoride (TBAF) in THF furnished the keto alcohol 6, m.p.118-120°C, in 90% yield. Interestingly, the keto alcohol 6 was obtained from the β-ketoester 2 in a single operation, via the protection of the ketone carbonyl as its enolate.[7] Thus, treatment of the β-ketoester 2 with LDA in THF at −78°C followed by addition of $LiAlH_4$ furnished the keto alcohol 6 in 81% yield. The structures of both the ketones 5 and 6 were established from their spectral data (see experimental section).

Cleavage of the cyclopropane ring in 5 with lithium in liquid ammonia furnished regiospecifically the hydrindanone 10, which was identified by spectral comparison (IR and ^{1}H NMR) with the authentic sample. The formation of the hydrindanone 10 can be rationalised as depicted below via the enone 12. The regiospecific cleavage of the cyclopropane ring followed by elimination of the β-silyloxy group from the intermediate enolate 11, generates the enone 12. Further reduction of the enone 12 furnishes the hydrindanone 10.



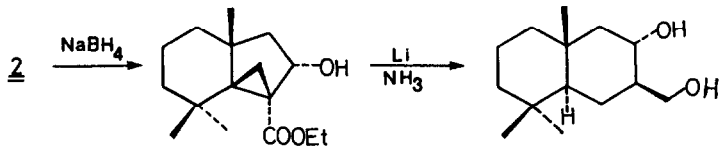
11 12 10

To overcome the side reaction, the reaction was carried out with the keto alcohol 6. Lithium-liquid ammonia reduction of keto alcohol 6 furnished the keto alcohol 13, m.p. 102-105°C, and the enone 12, m.p. 85-88°C, in a 3:1 ratio, in 84% yield, whose structures were delineated from their spectral data. The keto alcohol 13 showed characteristic bands due to the hydroxyl at ν_{max} 3490 and an intramolecular hydrogen bonded cyclopentanone at 1725 cm^{-1}. The ^{1}H NMR spectrum showed peaks due to CH_2OH [δ 3.8 (2 H, m) and 3.44 (1 H, dd, J = 10, 2.8 Hz)], a methine α to carbonyl [2.69 (dd, J = 8.3, 3.6)], a methylene α to carbonyl [2.38 and 1.96 (AB q)] and in particular four methyl singlets (1.19, 1.03, 0.94 and 0.89 ppm); and the ^{13}C NMR spectrum exhibited resonances due to a cyclopentanone carbonyl at 223.9, a CH_2OH at 62.5 (t), a methine α to carbonyl at 55.7 (d), a methylene α to carbonyl at 54.1 (t),



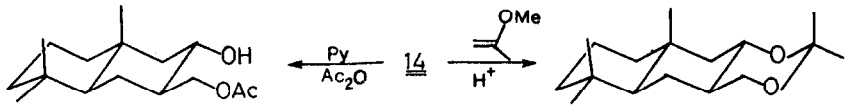
13 12

four methyl quartets at 29.2, 25.0, 22.1 and 13.2; and in particular three quaternary carbon singlets at 47.9, 40.0 and 36.1, confirming the structure. The enone 12 showed a molecular ion peak at 206 in the mass spectrum. The IR spectrum showed bands at ν_{max} 1731 and 1640 cm^{-1} due to the α methylene cyclopentanone. In the ^1H NMR spectrum the presence of resonances due to exo methylene at δ 6.07 (1 H, s) and 5.16 (1 H, s), methylene α to carbonyl (2.78 and 1.84, AB q), four methyl singlets at 1.1, 0.88, and 0.86 (2 x Me) established the structure which is further supported by its ^{13}C NMR spectrum (see experimental). Enone 12, was obviously formed during the workup.



7 14

In other direction, lithium-liquid ammonia reduction of the hydroxy ester 7 was expected to furnish regiospecifically the decalin derivative via the cleavage of the C_3-C_1 bond. Treatment of the β-ketoester 2 with sodium borohydride in methanol at 0°C furnished the hydroxy ester 7. The stereochemistry of the hydroxyl group was assigned as *endo* based on the approach of the hydride from the less hindered *exo* face of the molecule which was further supported by the shift in the ester carbonyl band (ν_{max} 1689 cm^{-1}) in the IR spectrum due to the intramolecular hydrogen bonding of hydroxy and carbonyl groups.[8] Lithium-liquid ammonia reduction of the hydroxy ester 7, as anticipated, furnished exclusively the decalin derivative 14, m.p. 145-146°C, in 63% yield. The absence of ester functionality in the IR and ^1H NMR spectra and the presence of resonances due to CHOH and CH_2OH [3.6-3.8 (3 H, m)] and in particular three methyl singlets at 0.92, 0.87 and 0.76 established the structure. The trans stereochemistry of the decalin was assigned based on the thermodynamic considerations and in analogy to the well established octalone reductions.[9] In order to establish the stereochemistry of the hydroxymethyl group, first the diol 14 was converted to its acetonide 15 with 2-methoxypropene in the presence of a catalytic amount of p-toluenesulfonic acid. However, in the ^1H NMR spectrum of the acetonide 15, resonances due to both the methine and methylene protons attached to oxygen atoms came as a multi-



16 15

plet. Hence the diol 14 was converted to its monoacetate 16, m.p. 82-83°C, in a conventional manner. In the ^{1}H NMR spectrum, presence of the doublets of an AB quartet signals (δ 4.04 and 4.43) due to the diastereotopic acetoxymethyl protons, and in particular the presence of a doublet of a triplet (due to two trans-diaxial and one axial-equatorial couplings) at 3.57 ppm (J = 14.6, 4.4 Hz) for the axial proton attached to the carbon bearing the hydroxy group confirmed the equatorial stereochemistry of the acetoxymethyl group in the compound 16, which in turn confirmed the stereochemistry of the diol 14.

In conclusion, we have demonstrated the control of the regiospecificity in the opening (C_2–C_3 bond or C_1–C_3 bond) of the cyclopropane ring present in tricyclo[4.4.0.0^{1,3}]decane system using lithium in liquid ammonia reduction conditions, either to a *cis* hydrindane system or to a *trans* decalin system.

EXPERIMENTAL SECTION

IR spectra were recorded on a Hitachi 270-50 spectrophotometer. ^{1}H (90, 200, 270 MHz) and ^{13}C NMR (22.5, 67.5 MHz) spectra were recorded on Jeol FX-90Q, Brucker ACF-200 and WH-270 spectrometers. The chemical shifts (δ ppm) and the coupling constants (Hz) are reported in the standard fashion using either internal tetramethylsilane (for ^{1}H) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C) as reference. In the ^{13}C NMR spectra off-resonance multiplicities, when recorded, are given in parentheses. Low and High resolution mass measurements were carried out with a Jeol JMS-DX 303 GC-MS instrument using a direct inlet mode. Elemental analyses were carried out using a Carlo Erba 1106 analyser. All the moisture sensitive reactions were carried out using standard syringe-septum techniques. Acme's silica gel (100-200 mesh) was used for column chromatography. Methylene chloride was distilled over P_2O_5. Dry THF was obtained by distillation over sodium benzophenone ketyl. Ammonia was obtained in cylinders from Mysore Ammonia Co. and was distilled over sodium prior to use. ^{n}BuLi and lithium (rods) were obtained from E-Merck.

3a,4a,6β-3-Hydroxymethyl-6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]decan-4-ol (8): To an ice cold, magnetically stirred suspension of $LiAlH_4$ (114 mg, 3 mmol) in dry ether (5 ml) was added a solution of the β-keto ester 2 (528 mg, 2 mmol) in dry ether (3 ml), and the reaction mixture was slowly brought to room temperature and stirred for 3 hr. The excess $LiAlH_4$ was decomposed by careful addition of ethyl acetate (0.5 ml). The reaction was quenched with water (5 ml) and 5% aqueous H_2SO_4 (3 ml), and extracted with ether (15 ml x 3). The ether extract was washed with saturated aqueous $NaHCO_3$ solution (5 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel (5 g) column using ethyl acetate-hexane (1:5) as eluent afforded the diol 8 (336 mg, 76%) as a viscous oil. IR (neat): ν_{max} 3375, 3060, 1180, 1150, 1045, 1010, 980, 745 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$):

δ 4.34 and 3.66 (2 H, AB q, J = 12 Hz, $C\underline{H}_2OH$), 4.25 (1 H, d, J = 5 Hz, C<u>H</u>OH), 2.26 (2 H, br s, OH), 1.15-2.05 (8 H, m), 1.09 (3 H, s), 1.05 (3 H, s), 0.9 (3 H, s), 0.47 and 0.30 (2 H, AB q, J = 5.3 Hz, cyclopropane CH_2). ^{13}C NMR (22.5 Mhz, $CDCl_3$): δ 79.4 (d, <u>C</u>HOH), 65.5 (t, $\underline{C}H_2OH$), 47.7 (t, C-5), 45.0 (s, C-1), 42.8 (2 C, s, C-6 & 10), 40.4 (t), 39.0 (t), 33.1 (s, C-3), 28.9 (q), 27.9 (q), 25.2 (q), 19.4 (t, C-8), 13.8 (t, C-2). Mass: m/e 224 (M^+, 3%), 206 (58), 173 (52), 123 (100), 122 (40), 121 (40), 119 (74), 107 (47), 94 (48), 93 (45), 91 (42). HRMS: m/e Calcd. for $C_{14}H_{24}O_2$, 224.1776; Found, 224.1787.

3α,4α,6β-3-t-Butyldimethylsilyloxymethyl-6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]-decan-4-ol (<u>9</u>): To a magnetically stirred solution of the diol <u>8</u> (336 mg, 1.5 mmol) in pyridine (2 ml) was added t-butyldimethylchlorosilane (241 mg, 1.6 mmol) and DMAP (catalytic). The reaction mixture was stirred for 3 hr at room temperature, diluted with water (5 ml) and extracted with methylene chloride (10 ml x 3). The organic extract was washed with 5% aqueous Hcl followed by saturated aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel (3 g) column using ethyl acetate-hexane (1:20) as eluent afforded the TBDMS ether <u>9</u> (430 mg, 85%) as an oil. IR (neat): ν_{max} 3514, 1392, 1377, 1365, 1257, 1149, 1047, 1026, 1005, 837, 813, 777 cm^{-1}. ^1H NMR (90 Mhz, $CDCl_3$): δ 4.31 and 3.8 (2 H, AB q, J = 11 Hz, $C\underline{H}_2OTBDMS$), 4.18 (1 H, d, J = 4.3 Hz, C<u>H</u>OH), 1.2-2.18 (9 H, m), 1.11 (3 H, s), 1.07 (3 H, s), 0.85 (3 H, s), 0.95 (9 H, s, t-Bu), 0.36 (2 H, close AB q, J = 5 Hz, cyclopropane CH_2), 0.13 (3 H, s, Si-Me), 0.09 (3 H, s, Si-Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 79.6 (CHOH), 65.7 (CH_2OSi), 47.9, 45.1, 42.9, 40.5, 39.2, 33.1, 29.8, 29.1, 28.0, 25.8, 25.2, 19.5 (C-8), 13.8 (H-2), -3.5 ($SiMe_2$). Mass: m/e 207 (M^+-OTBDMS, 35%), 206 (55), 189 (73), 123 (85), 122 (55), 120 (60), 107 (60), 105 (100), 95 (75), 93 (90).

3α,6β-3-t-Butyldimethylsilyloxymethyl-6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]-decan-4-one (<u>5</u>): To a magnetically stirred suspension of PCC (388 mg, 1.8 mmol) in methylene chloride (4 ml) was added the alcohol <u>9</u> (406 mg, 1.2 mmol) in methylene chloride (2 ml). The reaction mixture was stirred for 3 hr at room temperature and filtered through a short silica gel (5 g) column using methylene chloride as eluent. Evaporation of the solvent furnished the ketone <u>5</u> (282 mg, 70%) as a colourless viscous liquid. IR (neat): ν_{max} 1728, 1392, 1362, 1338, 1257, 1227, 1176, 1158, 1125, 1095, 1005, 777 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.61 and 3.32 (2 H, AB q, J = 11.1 Hz, CH_2O), 1.24-2.05 (10 H, m), 1.21 (3 H, s), 1.19 (3 H, s) and 0.92 (3 H, s) (3 x tert. Me), 0.87 (9 H, s, t-Bu), 0.09 (6 H, s, $SiMe_2$). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 212.5 (s, C=O), 59.5 (t, CH_2OSi), 49.6 (t, $CO\underline{C}H_2$), 48.4 (s, C-1), 39.4 (t), 37.8 (s), 33.6 (s), 29.1 (q), 27.5, 26.0 (3 C, CMe_3), 23.6 (q), 19.6, 19.1, 18.3 (s, Si-C), -5.1 (q) and -5.5 (q) ($SiMe_2$). Mass: m/e 279 (M^+-^{t}Bu, 100%), 131 (12), 123 (62). HRMS: m/e Calcd. for $C_{16}H_{27}O_2Si$ (M^+-^{t}Bu), 279.1780; Found, 279.1799.

3α,6β-3-Hydroxymethyl-6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one (6): *From the keto ether 5:* To a magnetically stirred solution of the keto ether 5 (235 mg, 0.7 mmol) in THF (2 ml) was added tetrabutylammonium fluoride trihydrate (253 mg, 0.8 mmol) and stirred at room temperature for 5 hr. The reaction mixture was diluted with water (5 ml) and extracted with ether (10 ml x 3). The ether extract was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (4 g) column using ethyl acetate-hexane (1:5) as eluent afforded the keto alcohol 6 (140 mg, 90%) as a colourless solid, which was recrystallised from ether. m.p.: 118-120°C. IR (neat): ν_{max} 3442, 1716, 1475, 1385, 1335, 1080, 1035 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.33 and 3.64 (2 H, AB q, J = 12.4 Hz, CH_2OH), 2.06 and 1.69 (2 H, AB q, J = 17.4 Hz, CH_2CO), 1.2-1.8 (9 H, m), 1.22 (3 H, s), 1.18 (3 H, s) and 0.86 (3 H, s) (3 x Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 214.8 (s, carbonyl), 59.9 (t, CH_2OH), 51.3 (s, C-1), 49.2 (t, $COCH_2$), 48.4 (s, C-3), 39.7 (t), 39.3 (t), 37.9 (s), 33.5 (s), 28.7 (q), 28.4 (q) and 23.5 (q) (3 x tert. Me), 20.1 (t, cyclopropane CH_2), 18.6 (t, C-8). Mass: m/e 222 (M^+, 8%), 134 (29), 123 (45), 122 (100), 121 (27), 107 (27), 95 (20). HRMS: m/e Calcd. for $C_{14}H_{22}O_2$, 222.1620; Found, 222.1626. Anal. Calcd. for $C_{14}H_{22}O_2$, C:75.63, H:9.97%; Found, C:75.85, H:10.20%.

From β-keto ester 2: To a magnetically stirred, cold (-78°C, alcohol-liquid N_2 bath) solution of diisopropyl amine (0.17 ml, 1.2 mmol) in dry THF (3 ml) under nitrogen atmosphere, was added a solution of n-butyllithium (0.62 ml, 1.6 M in hexane, 1 mmol) dropwise. To the LDA, thus formed was added a solution of the β-keto ester 2 (264 mg, 1 mmol) in THF (1 ml) and stirred at the same temperature for 1 hr. A suspension of LAH (38 mg, 1 mmol) in THF (2 ml) was added in one portion and the reaction mixture was warmed up to -20°C and stirred for 10 minutes. The excess LAH was decomposed by careful addition of ethyl acetate (0.5 ml). The reaction mixture was poured into 5% aqueous HCl (10 ml) and extracted with ether (15 ml x 3). The ether extract was washed with saturated aqueous $NaHCO_3$ solution followed by brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on a silica gel (5 g) column using ethyl acetate-hexane (1:5) as eluent furnished the keto alcohol 6 (180 mg, 81%).

Li-liquid ammonia reduction of the cyclopropyl ketone 5: To a magnetically stirred, freshly distilled (over sodium) ammonia (20 ml) in a three necked flask equipped with a Dewar condenser, was added the cyclopropyl ketone 5 (84.5 mg, 0.25 mmol) in 2 ml of dry ether followed by freshly cut lithium (9 mg, 1.3 mmol). The blue colour reaction mixture was stirred at -33°C for 10 min, quenched with solid NH_4Cl, and ammonia was evaporated slowly. The residue was taken in water (10 ml) and extracted with ether (10 ml x 3). The ether extract was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of

the solvent and purification of the product on a silica gel (3 g) column using ethyl acetate-hexane (1:20) as eluent furnished the 1β,6β,9β-1,2,2,6,9-pentamethylbicyclo[4.3.0]nonan-8-one (10, 35 mg, 68%), and was identified by comparison (TLC, IR, ^{1}H NMR spectra) with the authentic[5] sample. m.p.: 119-123°C. IR (neat): ν_{max} 1740, 1400, 1385, 1270, 1190, 1025, 985 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.61 (1 H, q, J = 7.2 Hz, CHCO), 2.26 and 1.9 (2 H, AB q, J = 18.2 Hz, CH_2CO), 1.2-1.7 (6 H, m), 1.08 (3 H, d, J = 7.2 Hz, C_9–Me), 1.21 (3 H, s), 1.04 (3 H, s) and 0.88 (6 H, s) (4 x tert. Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 221.4 (s, carbonyl), 54.0 (t, $\underline{C}H_2CO$), 48.8 (d, $\underline{C}HCO$), 48.1 (s, C-1), 39.8 (s, C-6), 37.9 (t), 37.4 (t), 36.3 (s, C-2), 29.7 (q), 25.5 (q), 22.9 (q), 18.5 (t, C-4), 13.4 (2 C, q). Mass: m/e 208 (M^+, 15%), 193 (10), 137 (24), 125 (40), 124 (77), 123 (25), 109 (30). HRMS: m/e Calcd. for $C_{14}H_{24}O$, 208.1827; Found, 208.1825.

1β,6β,7β-7-Hydroxymethyl-1,5,5,6-tetramethylbicyclo[4.3.0]nonan-8-one (13) and 1β,6β-7-methylene-1,5,5,6-tetramethylbicyclo[4.3.0]-nonan-8-one (12): Reduction of the cyclopropyl keto alcohol 6 (444 mg, 2 mmol) with lithium (70 mg, 10 mmol) in liquid ammonia (40 ml) and dry THF (2 ml) for 10 min as described above and purification of the product mixture on a silica gel (7 g) column using ethyl acetate-hexane (1:20) as eluent first afforded the enone 12 (87 mg, 21%) as a colourless solid. m.p.:102-105°C. IR (neat): ν_{max} 1731, 1640, 1263, 1092, 1020, 798 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.07 (1 H, s) and 5.16 (1 H, s) (exo methylene), 2.78 and 1.84 (2 H, AB q, J = 19.1 Hz, $COCH_2$), 1.0-1.7 (6 H, m), 1.1 (3 H, s), 0.88 (3 H, s) and 0.86 (6 H, s) (4 x tert. Me). ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 207.7 (s, carbonyl), 153.5 (s, $\underline{C}=CH_2$), 116.6 (t, $C=\underline{C}H_2$), 58.4 (s, C-6), 50.1 (s, C-5), 49.6 (t, $CO\underline{C}H_2$), 40.1 (s, C-1), 36.9 (t), 33.5 (t), 30.2 (q), 28.6 (q), 27.0 (q), 16.9 (q), 18.4 (t, C-3). Mass: m/e 206 (M^+, 18%), 191 (52), 124 (100), 123 (70), 122 (65), 107 (15), 94 (40). HRMS: m/e Calcd. for $C_{14}H_{22}O$, 206.1671; Found, 206.1675.

Further elution of the column using ethyl acetate-hexane (1:5) as eluent afforded the hydrindanone 13 (282 mg, 63%) as a viscous liquid. Crystallization from petroleum ether furnished a colourless solid. m.p.:85-88°C. IR (neat): ν_{max} 3490, 1725, 1385, 1290, 1260,1050, 1010 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.8 (2 H, m, $C\underline{H}_2OH$), 3.44 (1 H, dd, J = 10, 2.8 Hz, OH), 2.69 (1 H, dd, J = 8.3, 3.6 Hz, CHCO), 2.38 (1 H, ½ AB q, J = 18.6 Hz) and 1.96 (1 H, d of ½ AB q, J = 18.6, 1.6 Hz) ($COCH_2$), 1.2-1.7 (6 H, m), 1.19 (3 H, s), 1.03 (3 H, s), 0.94 (3 H, s) and 0.89 (3 H, s) (4 x tert. Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 223.9 (s, carbonyl), 62.5 (t, CH_2OH), 55.7 (d, $\underline{C}HCO$), 54.1 (t, $\underline{C}H_2CO$), 47.9 (s, C-6), 40.0 (s, C-5), 37.3 (2 C, t, C-2 and 4), 36.1 (s, C-1), 29.2 (q), 25.0 (q), 22.1 (q) and 13.2 (q) (4 x Me), 18.3 (t, C-3). Mass: m/e 224 (M^+, 21%), 206 (10), 141 (80), 140 (82), 138 (55), 123 (60), 122 (100), 110 (63), 95 (87). HRMS: m/e Calcd. for $C_{14}H_{24}O_2$, 224.1776; Found, 224.1774.

Anal. Calcd. for $C_{14}H_{24}O_2$, C:74.95; H:10.78%; Found, C:74.15; H:10.91%.

3α,4α,6β-Ethyl 6,10,10-trimethylbicyclo[4.4.0.0^{1,3}]nonan-4-ol-3-carboxylate (7): To magnetically stirred, ice cold solution of β-ketoester 2 (100 mg, 0.38 mmol) in dry methanol (6 ml) was added sodium borohydride (19 mg, 0.5 mmol) and stirred for 2 hrs at room temperature. Methanol was evaporated under reduced pressure. The residue was taken in 5% aqueous HCl (10 ml) and extracted with methylene chloride (5 ml x 3). The organic extract was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel (4 g) column using ethyl acetate-hexane (1:10) as eluent furnished the hydroxy ester 7 (99 mg, 98%) as an oil. IR (neat): ν_{max} 3478, 1689, 1392, 1377, 1320, 1290, 1272, 1236, 1203, 1173, 1134, 1089, 1071, 1050, 1029 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.2 (1 H, d, J = 5.4 Hz, CHOH), 4.1 and 4.05 (2 H, q of AB q, J = 11.1, 7.2, OCH_2CH_3), 1.22-1.32 (10 H, m), 1.29 (3 H, t, J = 7.2 Hz, OCH_2CH_3), 1.06 (3 H, s), 1.05 (3 H, s) and 0.63 (3 H, s) (3 x tert. Me). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 174.7 (s, carbonyl), 74.3 (d, CHOH), 61.3 (t, OCH_2CH_3), 52.0 (s, C-1), 47.0 (t, C-5), 42.6 (2 C, s, C-6 and 10), 40.0 (t), 38.1 (t), 33.1 (s, C-3), 28.8 (q), 27.1 (q) and 24.8 (q) (3 x Me), 19.0 (t, cyclopropane CH_2), 13.8 (2 C, t and q, C-8 and OCH_2CH_3). Mass: m/e 266 (M^+, 12%), 249 (60), 248 (77), 220 (56), 175 (65), 129 (58), 123 (70), 122 (96), 119 (65), 105 (100), 91 (64). HRMS: m/e Calcd. for $C_{16}H_{26}O_3$, 266.1882; Found, 266.1870.

1β,3α,4β,6α-4-Hydroxymethyl-1,7,7-trimethylbicyclo[4.4.0]decan-3-ol (14): Reduction of the hydroxy ester 7 (50 mg, 0.19 mmol) with lithium (≈7 mg, 1 mmol) in liquid ammonia (30 ml) and dry THF (2 ml) for 10 min as described above and purification of the product over a silica gel (3 g) column using ethyl acetate-hexane (1:4) as eluent furnished the diol 14 (28 mg, 66%) as a colourless solid. m.p.:145-146°C. IR (nujol): 3202, 1380, 1158, 1119, 1098, 1080, 1044, 1026, 999 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.6-3.8 (3 H, m, CHOH and CH_2OH), 0.98-1.65 (13 H, m), 0.92 (3 H, s), 0.87 (3 H, s) and 0.76 (3 H, s) (3 x tert. Me). Mass: m/e 226 (M^+, 6%), 208 (94), 193 (34), 177 (30), 137 (100), 123 (40), 109 (37), 95 (48). HRMS: m/e Calcd. for $C_{14}H_{26}O_2$, 226.1933; Found, 226.1943.

4aα,5aα,9aβ,10aβ-2,2,6,6,9a-Pentamethylperhydronaphtho[2,3-c](1,3)-dioxane (15): To a magnetically stirred solution of the diol 14 (32 mg, 0.14 mmol) in dry methylene chloride (2 ml) was added 2-methoxypropene (15 mg, 0.21 mmol) and a catalytic amount of p-toluenesulphonic acid and stirred for 1.5 hr at room temperature. The reaction mixture was diluted with methylene chloride (10 ml), washed with saturated aqueous $NaHCO_3$ followed by brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel (5 g) column using ethyl acetate-hexane (1:10) as eluent furnished the acetonide 15 (24 mg, 64%) as an oil. IR (neat): ν_{max} 1590, 1383,

1188, 1155, 1025, 1098, 1065, 1041, 843 cm-1. 1H NMR (270 MHz, $CDCl_3$): δ 3.55-3.8 (3H, m, OCH_2 and OCH), 0.9-1.7 (12 H, m), 1.46 (3 H, s), 1.37 (3 H, s), 0.98 (3 H, s), 0.85 (3 H, s), 0.77 (3 H, s) (5 x Me).

1β,3a,4β,6a-4-Acetoxymethyl-1,7,7-trimethylbicyclo[4.4.0]decan-3-ol (16): To a magnetically stirred solution of the diol **14** (32 mg, 0.14 mmol) in dry methylene chloride (2 ml) was added acetic anhydride (21 mg, 0.21 mmol) and one drop of pyridine, and stirred at room temperature for 4 hr. The reaction mixture was diluted with methylene chloride (10 ml) and washed with 10% aqueous HCl followed by saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel (5 g) column using ethyl acetate-hexane (3:20) as eluent furnished the monoacetate **16**, which was recrystallised from hexanes (8 mg, 21%). m.p.: 82-83°C. IR (CCl_4): ν_{max} 3412, 1734, 1518, 1383, 1125, 1107, 1038, 846 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 4.43 (1 H, dd, J = 11.1, 4.5 Hz) and 4.04 (1 H, dd, J = 11.1, 4 Hz) (CH_2—OAc), 3.57 (1 H, dt, J = 14.6, 4.4 Hz, CH—OH), 2.27 (1 H, br s, OH), 2.09 (3 H, s, $COCH_3$), 0.9-1.85 (12 H, m), 0.91 (3 H, s), 0.87 (3 H, s) and 0.78 (3 H, s) (3 x tert. Me).

ACKNOWLEDGEMENTS: We thank the C.S.I.R., New Delhi for the financial support.

REFERENCES AND NOTES

1. Volkenburgh, R.V., Greenlee, K.W., Derfer, J.M. and Boord, C.E. *J. Am. Chem. Soc.*, **1949**, *71*, 3595.
2. Norin, T. *Acta Chem. Scand.*, **1963**, *17*, 738; and **1965**, *19*, 1289; Imanishi, T, Yamashita, M., Matsui, M., Ninbari, F., Tanaka, T. and Iwata, C. *Chem. Pharm. Bull.*, **1988**, *36*, 1351.
3. Dauben, W.G. and Deviny, E.J. *J. Org. Chem.*, **1966**, *31*, 3794; Dauben, W.G. and Wolf, R.E. *J. Org. Chem.*, **1970**, *35*, 374 and 2361.
4. Srikrishna, A. and Krishnan, K. *J. Chem. Soc., Chem. Commun.*, **1991**,1693.
5. Srikrishna, A. and Krishnan, K. *Tetrahedron Lett.*, **1989**, *30*, 6577.
6. Mirrington, R.N. and Schmalzl, K.J. *J. Org. Chem.*, **1972**, *37*, 2871.
7. Kraus, G.A. and Frazier, K. *J. Org. Chem.*, **1980**, *45*, 4262.
8. Chen, E.Y. *Tetrahedron Lett.*, **1982**, *23*, 4769.
9. Stork, G. and Darling, S.D. *J. Am. Chem. Soc.*, **1960**, *82*, 1912; and **1964**, *86*, 1761; Stork, G., Uyeo, S., Wakamatsu, T., Grieco, P. and Labovitz, J. *J. Am. Chem. Soc.*, **1971**, *93*, 4945; Janaki, S. and Subba Rao, G.S.R. *Indian J. Chem.*, **1988**, *27B*, 505.