Tetrahedron Vol 49, No 44, pp 10123-10132, 1993
Printed in Great Britain

0040-4020/93 $6 00+.00

Studies on the Friedel Crafts Acylation of Hydrindane

Gordon R. Davison,* Judith A. K. Howard and Nigel A. Pitchford

Department of Chemistry, University of Durham, Durham, DH1 3LE, U.K.

Alan M. Jones, Jack W. Rasburn and Anthony J. Simpson

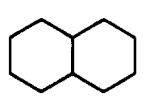
Department of Chemical & Life Sciences, University of Northumbria at Newcastle upon Tyne, Newcastle upon Tyne, NE1 8ST, U.K.

(*Received in UK* 23 *July* 1993; *accepted* 27 *August* 1993)

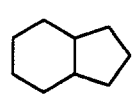
Abstract: Products arising from Friedel Crafts acylation of hydrindane have been isolated and characterised. Novel compounds obtained include two isomeric vinyl ethers **6** and **7**, and their corresponding hydrolysis products, hydroxyketones **12** and **13**. Unsaturated diketones **14** and **23**, and chlorodiketone **15** were also isolated. The X-ray crystal structure of the chlorodiketone **15** has been solved. Mechanistic proposals explaining the formation of all products are put forward.

Friedel Crafts acylation of the saturated hydrocarbon decalin **1** (4:4:0 decane) has been studied quite extensively.[1-4] We were interested in extending the reaction to the homologous hydrindane **2** (4:3:0 nonane) to compare reactivities and products isolated. The decalin and hydrindane systems themselves are of fundamental importance due to their ubiquitous occurrence in natural products such as the sesqui-, di- and triterpenes and steroids.[5] Novel methods of functionalising these ring systems may therefore find applications in natural product total synthesis.

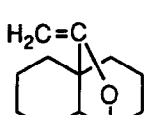
In previous studies on decalin, the most notable product isolated from reaction under Friedel Crafts conditions was the vinyl ether **3**, obtainable in yields of 35-40%.[2] The vinyl ether species was postulated to have arisen via formation of an intermediate oxonium ion of the type **4**.[3] Supporting evidence for this intermediate was later provided by the isolation of the saturated ether **5** following reductive work-up of the crude reaction mixtures with lithium aluminium hydride [6] Attempts by others[7] to isolate analogous hydrindane vinyl ethers have thus far proved unsuccessful.



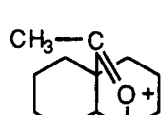
1



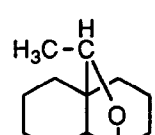
2



3



4



5

RESULTS AND DISCUSSION

Reaction Details. Typical initially employed acylation conditions are described in Table 1. These stoichiometries and reaction conditions were derived from the decalin studies.[2] Following aqueous work-up of the reaction mixtures, products were separated by fractional vacuum distillation. Extensive use of ^{13}C nmr techniques was required to determine the structures of reaction products, including COSY[8] and INADEQUATE[9] experiments. The products were mainly oils and their high solubility in deutero-chloroform facilitated the ability to collect data quite rapidly in less sensitive experiments.

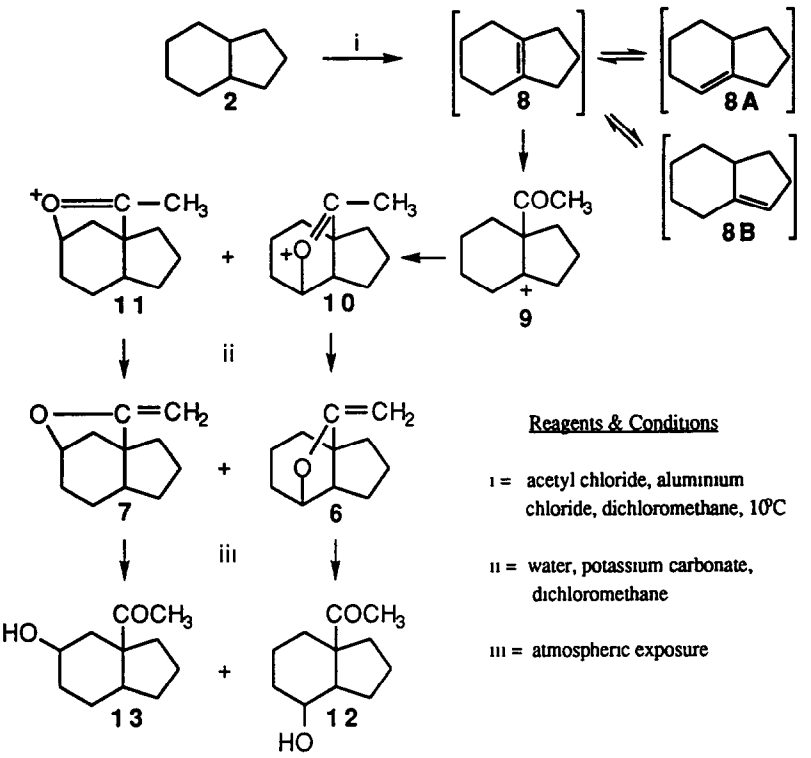
Table 1. Typical Initial Acylation Conditions.

Stoichiometries		Conditions	Products & Yields	
hydrindane	1.0M	80 - 130 mins	vinyl ether **6**	1.0 - 2.6%
aluminium chloride	2.5M	6 - 18°C	vinyl ether **7**	1.8 - 4.0%
acetyl chloride	3.5M		unsaturated diketone **14**	4 - 13%
			chlorodiketone **15**	0 - 4.0%

Products isolated and characterised include two vinyl ether isomers **6** and **7**. In accordance with decalin studies,[10] the mechanism of formation is proposed as initial hydride abstraction by the Friedel-Crafts complex, followed by deprotonation to yield intermediate bicycloalkene **8** (Scheme 1). Alkene **8**, under the acidic reaction conditions, is likely to be in equilibrium with alkenes **8A** and **8B**. However, species **8** is the thermodynamically more stable isomer and other workers[11] have shown that it is likely to be the predominant form. This alkene is then attacked by a second mole of the acylating complex to give tertiary carbocation intermediate **9**. Single or concerted hydride shifts then occur, prior to cyclisation, to yield the intermediate oxonium ions **10** and **11**. These oxonium ions are thought to be stabilised by complexation as tetrachloroaluminate salts under the reaction conditions. Indeed, a correlation was found between aluminium chloride concentration and increased monoacyl product isolation, salt formation thus reducing the tendency for multiple acylations to occur.

Deprotonation of species **10** and **11** then occurs during work-up to yield the vinyl ethers **6** and **7** respectively. The six-membered ring of hydrindane is known to exist in a deformed chair conformation[12] and examination of molecular models shows that vinyl ether **6**, arising from a single 1,2-hydride shift, takes up a particularly strain-free structure in the chair conformation. Both vinyl ethers were found to be moisture sensitive, complete hydrolysis to the corresponding hydroxyketones **12** and **13** occurred in less than one hour, on exposure to atmospheric conditions. In our hands, the analogous decalin vinyl ether, **3**, appeared to be more stable with respect to hydrolysis, perhaps due to conformational differences. Bearing in mind the susceptibility of the vinyl ethers **6** and **7** to hydrolysis, and the aqueous work-up conditions employed, it seems likely that these vinyl ethers, isolated by fractional distillation, are obtained via dehydration of their hydroxyketone counterparts **12** and **13** upon heating. This is not the case with **3**, however, which is found in worked-up reaction mixtures prior to distillation.

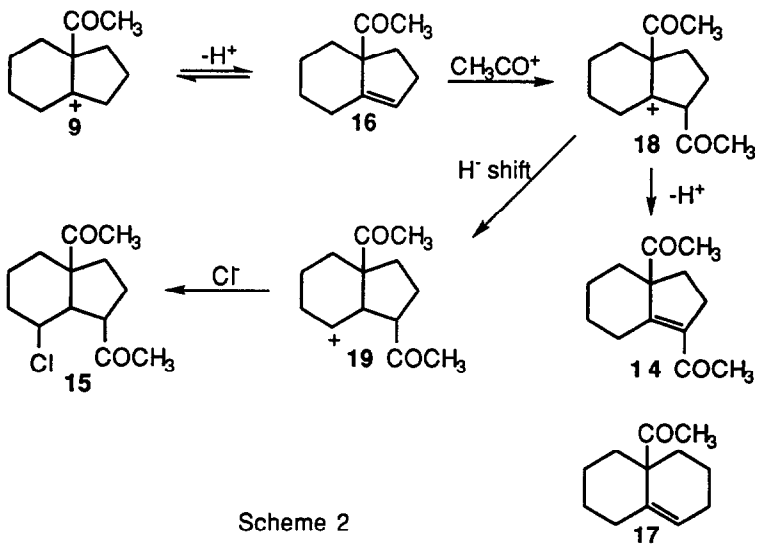
Initial experiments under conditions described in Table 1 also yielded the novel diketones **14** and **15**



Scheme 1

as shown in Scheme 2. The formation of these two classes of compound is most unusual in the Friedel-Crafts acylation of alkane substrates and has no precedent in the earlier decalin studies cited.[1-4] The mechanism postulated for diketone formation involves an unsaturated ketone intermediate such as **16**. This intermediate is believed to arise via deprotonation of cationic species **9**. As stated above, complexation of cationic intermediates as aluminate salts confers stability and prevents deprotonation to the corresponding unsaturated ketones. The role of unsaturated ketones as intermediates to diacylated products is suggested. Thus, the observation that higher aluminium chloride concentrations gave higher yields of monoacylated products is explained. Unsaturated ketone **17** has been isolated from decalin acetylation reactions.[1] No analogous species such as **16** has been observed in the current hydrindane reactions, perhaps indicating the greater reactivity of these species with respect to a second acylation step. Secondary acylation of intermediate **16** may yield tertiary carbocation **18** which could then either deprotonate to give the isolated compound **14** or rearrange, via a 1,2-hydride migration, to intermediate **19**. Nucleophilic attack by chloride ion on **19** may then furnish the isolated chlorodiketone **15**.

Yields of vinyl ethers **6** and **7**, and diketones **14** and **15**, were disappointing under the initial reaction conditions (Table 1). Despite many efforts to modify these conditions, no significant improvement of the vinyl ether yields could be effected. However, acetylation of hydrindane under more aggressive conditions led to much improved yields of the unsaturated diketone **14** and chlorodiketone **15** (Table 2).



Scheme 2

Table 2. Modified Reaction Conditions.

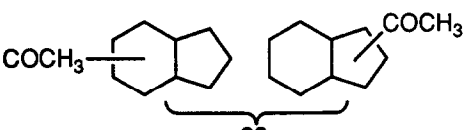
Stoichiometries		Conditions	Products & Yields	
hydrindane	1M	95 mins	unsaturated diketone **14**	31%
aluminium chloride	4M	34 - 36°C	chlorodiketone **15**	12%
acetyl chloride	6M			

A comparison between the reactivity of hydrindane and decalin was also carried out under conditions approximating to those described in Table 1. Separate experiments on both alkanes, under identical reaction conditions, appeared to show that hydrindane was almost 50% more reactive than decalin, based on recovered starting materials. This would be a striking result, bearing in mind the similarity of the two alkane systems. The greater reactivity of hydrindane also appeared to lead to a larger diversity of minor products than was the case with decalin. Gas chromatography of crude product mixtures from hydrindane reactions revealed the presence of perhaps seventy or more minor reaction products. However, despite the observed higher reactivity of hydrindane, it could not be acylated in the presence of stannic chloride as catalyst, a feature common to decalin.[13]

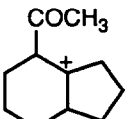
More detailed analysis may explain this perceived difference in reactivity between hydrindane and decalin. Both alkanes were obtained and used as *cis/trans* isomeric mixtures. Nmr evidence was obtained for the more reactive nature of the *cis* isomers of both alkanes. *Trans* isomer enrichment was noted in recovered unreacted alkanes. It would, however, be inappropriate to attempt quantification of this observation since aluminium halides have been shown to act as isomerisation catalysts.[14] The greater reactivity of the decalin *cis* isomer under Friedel-Crafts conditions has been reported previously.[13,15] The *cis:trans* ratios of hydrindane (ca. 8:1) and decalin (ca. 1:1) as supplied and used are therefore likely to have a bearing on displayed

reactivity. Hydrindane, being significantly higher in *cis* isomer content, would be expected to be more reactive overall.

We found some evidence for the existence of saturated ketones of the type **20** in low yield (< 3%). This species was only observed in reactions employing reverse-addition, with the acylating agent being added to the hydrindane. Isomerisation of the intermediate alkene **8** under the acidic reaction conditions to an alkene where the double bond resides in one of the rings, **8A** or **8B**, followed by acylation to give a cationic intermediate such as **21** is proposed. Reduction of **21** to **20** via hydrindane acting as hydride source may then occur. There is precedent for hydrocarbons to behave as hydride donors under Friedel-Crafts conditions.[1,16] The absolute structure of **20** was not determined as the material resisted purification.



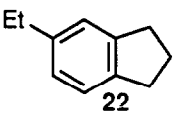
20



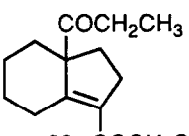
21

In an attempt to isolate analogous hydrindane saturated ethers of the type **5**, experiments were conducted using reductive work-up with lithium aluminium hydride. Whilst no hydrindane saturated ethers were found, a quantity of 5-ethylindane **22** (2.4%) was isolated. This compound is believed to be formed by acetylation of indane, the indane being formed as a by-product of hydrindane acting as a hydride donor, as described above, with subsequent aromatisation. The reduction of ketones to alkanes by lithium aluminium hydride in the presence of aluminium chloride has been documented.[17]

A further noteworthy product is the unsaturated diketone **23**. This compound was obtained by acylation of hydrindane with propionyl chloride in the presence of aluminium chloride at 0°C for 1.1h. Yield of **23** was 17%. Interestingly, no mono-acylated products or chlorodiketone analogues were isolated from this reaction.



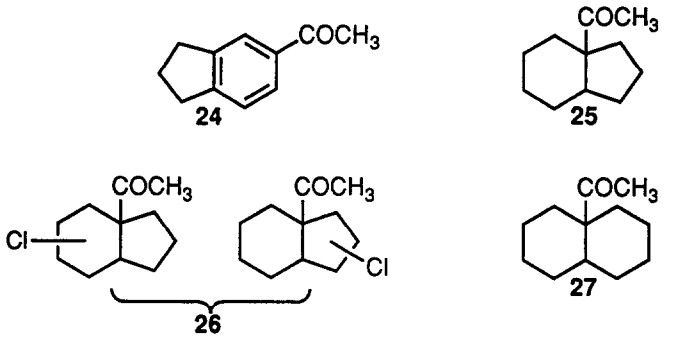
22



23 $COCH_2CH_3$

Comparison of our results for the acetylation of hydrindane with those of Tardella and Campana[7] is warranted. These workers observed three product types, namely, 5-acetyl indane **24** (11%), saturated ketone **25** (10%) and chloroketones of the type **26** (69%). Isolation of 5-acetyl indane **24** parallels our own isolation of 5-ethylindane **22** when we employed reductive work-up. Saturated ketone **25** has the acetyl function located on the ring junction, in accord with the previously isolated decalin saturated ketone **27**.[1] However, saturated ketone **20**, isolated during the current work, has the acetyl function sited off the ring junction and presumably, therefore, results from acetylation of one of the alkene isomers **8A** or **8B**. The isolation by Tardella *et al* of the chloroketones **26** as the major reaction product is more surprising. We could find no evidence for the existence of these species, much less as the major products of reaction. Additionally, Tardella and Campana do not report the diacyl species **14** and **15** which we found to predominate when repeating their reaction conditions (5.5h at 0°C). One possible explanation for these different findings is that their work-up

and product isolation conditions are not described in detail. Differing procedures may influence the outcome of products formed.



X-ray Crystal Structure Analysis of Chlorodiketone Derivative **15**. A view of the crystal structure of compound **15** is shown in Figure 1 and selected bond lengths, angles and torsion angles are presented in Tables 3, 4 and 5. The six-membered ring of the molecule exists in the symmetrical C_2 chair conformation, as described by Hendrickson.[18] The five-membered ring conforms to the parameters first postulated by Pitzer and Donath,[19] describing the C_s 'envelope' conformation. The tip of the envelope can be seen to be at the ring juncture atom C(9), with the four remaining carbon atoms of the ring (C8-C1-C2-C3) being co-planar. Both rings can be considered to be in their minimum energy conformations, as confirmed by recent studies,[20] although the envelope is formally the saddle point on a zero-energy pseudorotation pathway between two twist conformations.

Compound **15** has *cis* ring-junction configuration, whereas decalin vinyl ether **3** has been determined[3] as having *trans* configuration. These findings are in accord with the thermodynamically most stable configurations of hydrindane and decalin derivatives which bear ring-junction substituents.[12] The confirmed siting of an acetyl function on C(1) of the five-membered ring lends support to the proposal of unsaturated ketones of the type **16** acting as precursors to diacylated products **14**, **15** and **23**.

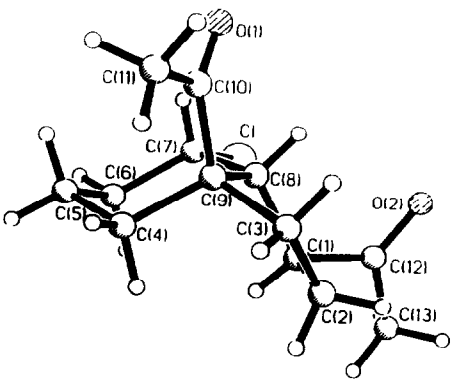


Figure 1. X-ray Crystal Structure of Compound **15**.

EXPERIMENTAL

General. Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1760X Fourier-transform spectrophotometer; samples were either embedded in KBr discs or measured neat as thin films between KBr plates, as indicated. ^{1}H nmr and ^{13}C nmr spectra were recorded on a Jeol JNM-GX270 instrument, operating at 270.05 MHz for protons and 67.80 MHz for carbon nuclei. Chemical shifts, quoted in ppm, are relative to tetramethylsilane (tms) as internal standard. All coupling constants, J, are quoted in Hz. Bonding states of carbon nuclei, as determined by off-resonance and INEPT[21] experiments, are quoted as s, d, t and q for non-protonated, methine, methylene and methyl carbons respectively. Mass spectra were obtained on a VG 7070E instrument, operating at 70 eV, with ionisation modes as indicated. Elemental analyses were performed on a Carlo-Erba Strumentazione Model 1106. Gas chromatography was carried out on a Perkin-Elmer F17 instrument, equipped with Carbowax 20M or SP1000 polyethylene glycol columns and LDC/Milton Roy CI-10 integrator. Hydrindane used was technical grade, supplied as a *cis:trans* (ca. 8:1) isomeric mixture, by the Aldrich Chemical Company. Decalin used was general purpose reagent grade, supplied as a *cis:trans* (ca. 1:1) isomeric mixture, by BDH Ltd. All other reagents and solvents were general purpose reagent grade and used as supplied. Yields are quoted as mole percent isolated, with respect to hydrindane.

Typical Experimental Procedure. To a stirred suspension of anhydrous aluminium chloride (40.0 g, 0.3 mol) in dichloromethane (100 ml) was added acetyl chloride (33.0 g, 0.42 mol) over 0.2 h. The resultant dark yellow solution was rapidly filtered through a glass wool plug into the reaction flask. The flask contents were cooled (ice/water bath) to 6°C and hydrindane (14.9 g, 0.12 mol) added dropwise with stirring over 0.5 h at 6-10°C. The temperature was then slowly raised to 18°C for a total reaction time of 2 h. The reaction mixture was then poured slowly, with stirring, onto ice/water (ca. 500 ml). The organic layer was separated and washed with potassium carbonate solution (10%, 10 x 200 ml) to remove acidic by-products. The organic layer was dried ($MgSO_4$) and solvent removed *in-vacuo* in the presence of potassium carbonate. Reaction products were separated by fractional vacuum distillation across a Vigreaux column and collected via a single arm collection tube. The glassware was dismantled and rinsed with acetone between fractions in order to minimise cross contamination of distillates

Characterisation of Reaction Products Thus Obtained

5-Ethylindane **22**. Compound **22** (420 mg, 2.4%) was obtained as a colourless oil and authenticated by comparison of proton and carbon nmr data with those quoted in the literature.[22]

1',4β-Epoxy-8β-vinylhydrindane **6**. Compound **6** (510 mg, 2.6%) was obtained as a pale yellow pleasant smelling oil, b.pt. 95-105°C at 6 mm Hg; δ_H ($CDCl_3$) 4.36 (1H, d, J=4.5), 4.16 (1H, m, fine), 3.69 (1H, d, J=1.4) and 2.30-1.20 (13H, complex pattern due to overlap) ppm; δ_C ($CDCl_3$) 168.5 (s), 78.8 (d), 76.5 (t), 55.1 (s), 54.8 (d), 35.6 (t), 33.5 (t), 30.3 (t), 26.5 (t), 22.3 (t) and 18.5 (t) ppm; m/z (EI) 164 (M^+); (CI) 165 (M^+ +1); high resolution MS (EI) found: 164.11801, requires 164.12011

1',6β-Epoxy-8β-vinylhydrindane **7**. Compound **7** (790 mg, 4.0%) was obtained as a pale yellow pleasant smelling oil, b.pt. 90-100°C at 4 mm Hg; δ_H ($CDCl_3$) 4.45 (1H, m), 3.95 (1H, dd, J=1.6 + 1.0), 3.70 (1H, d, J=1.6) and 2.60-1.20 (13H, complex pattern due to overlap) ppm; δ_C ($CDCl_3$) 169.2 (s), 75.5 (d), 73.4 (t), 50.0 (s), 46.5 (d), 35.4 (t), 32.9 (t), 32.7 (t), 28.0 (t), 24.1 (t) and 21.7 (t) ppm; m/z (EI) 164 (M^+);

(CI) 165 (M^+ +1); high resolution MS (EI) found: 164.11847, requires 164.12011.

8-Acetyl-4-hydroxyhydrindane **12**. Compound **12** (220 mg, quantitative) was obtained as a colourless oil by spontaneous hydrolysis of vinyl ether **6**; ν_{max} (neat) 3420, 2920, 1685, 1445, 1350, 1235, 1155 and 960 cm^{-1}; δ_H ($CDCl_3$) 5.35 (1H, s, broad), 4.07 (1H, s) and 3.10-0.90 (16H, complex pattern due to overlap) ppm; δ_C ($CDCl_3$) 216.9 (s), 66.2 (d), 60.5 (s), 50.9 (d), 36.5 (t), 34.9 (t), 34.3 (t), 25.5 (q), 22.6 (t), 19.8 (t) and 18.1 (t) ppm; m/z (CI) 183 (M^+ +1); high resolution MS (CI) found: 183.14286, requires 183.13848.

8-Acetyl-6-hydroxyhydrindane **13**. Compound **13** (520 mg, quantitative) was obtained as a colourless oil by spontaneous hydrolysis of vinyl ether **7**; ν_{max} (neat) 3430, 2840, 1710, 1460, 1360, 1280, 1185 and 1150 cm^{-1}; δ_H ($CDCl_3$) 3.89 (1H, heptet), 3.45 (1H, s, broad), 2.36 (1H, m), 2.20 (3H, s) and 2.15-1.20 (12H, complex pattern due to overlap) ppm; δ_C ($CDCl_3$) 213.2 (s), 65.7 (d), 58.0 (s), 38.8 (d), 36.1 (t), 33.4 (t), 29.8 (t), 28.3 (t), 24.6 (q), 22.7 (t) and 20.8 (t) ppm; m/z (EI) 182 (M^+); (CI) 183 (M^+ +1); high resolution MS (CI) found: 183.14728, requires 183.13848.

1,9-Diacetylhydrind-1(8)-ene **14**. Compound **14** (7.7 g, 31%) was obtained as a pale yellow oil, b.pt. 138-154°C at 4 mm Hg; ν_{max} (neat) 2960, 1725, 1640, 1460, 1380, 1290, 1245 and 1185 cm^{-1}; δ_H ($CDCl_3$) 3.43 (1H, d, J=14.3), 2.30 (3H, s), 2.12 (3H, s) and 2.80-1.20 (11H, complex pattern due to overlap) ppm; δ_C ($CDCl_3$) 208.2 (s), 197.1 (s), 155.1 (s), 135.3 (s), 66.1 (s), 36.6 (t), 33.2 (t), 31.7 (t), 29.8 (q), 26.6 (t), 26.4 (t), 25.2 (q) and 22.8 (t) ppm; m/z (EI) 206 (M^+); (CI) 207 (M^+ +1); high resolution MS (CI) found: 207.14069, requires 207.13849.

1β,9β-Diacetyl-7α-chloro-cis-hydrindane **15**. Compound **15** (3.5 g, 12%) was obtained as a white crystalline solid recrystallised from hexane, m.pt. 85-87°C (Found: C, 64.7; H, 8.1; Cl, 14.3. $C_{13}H_{19}ClO_2$ requires C, 64.3; H, 7.9; Cl, 14.6%); ν_{max} (KBr disc) 2945, 2870, 1710, 1690, 1415, 1360, 1210 and 740 cm^{-1}; δ_H ($CDCl_3$) 4.33 (1H, dt, J=12.2 + 5.1), 3.43 (1H, dd, J=5.1 + 9.9), 3.24 (1H, dt, J=4.8 + 9.8), 2.25 (3H, s), 2.14 (3H, s), 2.30-1.50 (8H, complex pattern due to overlap), 1.49 (1H, dt, J=3.2 + 13.8) and 1.22 (1H, tt, J=3.4 + 13.7) ppm; δ_C ($CDCl_3$) 210.3 (s), 210.3 (s), 61.6 (s), 58.8 (d), 49.5 (d), 48.9 (d), 36.3 (t), 31.6 (t), 29.7 (q), 27.9 (t), 26.0 (t), 25.6 (q) and 22 8 (t) ppm; m/z (CI) 243 + 245 (M^+ +1, isotopes).

1,9-Dipropionylhydrind-1(8)-ene **23**. Compound **23** (4.8 g, 17%) was obtained as a pale yellow oil, b.pt. 152-156°C at 1 mm Hg (Found: C, 77.0; H, 9.6. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); ν_{max} (neat) 2935, 1705, 1620, 1460, 1355, 1030, 980 and 920 cm^{-1}; δ_H ($CDCl_3$) 3.42 (1H, d, J = 14.3), 2.69 (1H, dt, J = 3.8 + 9.0), 2.54 (2H, q, J=7.1), 2.37 (2H, q, J=7.5), 1.05 (3H, t, J=7.5), 1.02 (3H, t, J=7.3) and 2.34-1.10 (10H, complex pattern due to overlap) ppm; δ_C ($CDCl_3$) 209.7 (s), 198.9 (s), 154.0 (s), 134.6 (s), 65.2 (s), 36.3 (t), 34.5 (t), 33.2 (t), 31.0 (t), 29.8 (t), 26.2 (t), 26.1 (t), 22.5 (t), 6.9 (q) and 6.4 (q) ppm; m/z (EI) 234 (M^+); (CI) 235 (M^+ +1).

X-Ray Crystal Structure Analysis of Compound **15**. Crystal data: ($C_{13}H_{19}ClO_2$), M=242.7, monoclinic, space group $P2_1/c$, a=10.867(1), b=10.334(2), c=11.869(1)Å, U=1300.6(3)$Å^3$, Z=4, F(000)=520, Rigaku AFC6S, Mo-Kα radiation (graphite monochromator), λ=0.71073Å, μ(Mo-Kα)=0.278 mm^{-1}, D_c=1.326 g/cm^3, 3789 independent reflections, 1894 with $I \geq 4\sigma(I)$ used, direct method, SHELXTL PLUS,[23] R=0.047, R_w=0.048. Non-hydrogen atoms refined anisotropically, all hydrogen atoms refined isotropically, 203 parameters refined. Selected bond lengths, angles and torsion angles are given in Tables 3, 4 and 5. Full atomic coordinates, bond lengths and angles, thermal parameters and list of structure factors have been deposited at the Cambridge Crystallographic Data Centre.

Table 3. Selected Bond Lengths (Å) for Compound **15**.

Cl-C(7)	1.821(2)	C(1)-C(2)	1.558(4)
C(1)-C(8)	1.536(3)	C(1)-C(12)	1.517(3)
C(3)-C(9)	1.544(4)	C(2)-C(3)	1.521(4)
C(4)-C(9)	1.544(3)	C(4)-C(5)	1.520(5)
C(6)-C(7)	1.514(3)	C(5)-C(6)	1.518(4)
C(7)-C(8)	1.522(4)	C(8)-C(9)	1.546(3)
C(9)-C(10)	1.525(3)	C(10)-C(11)	1.499(4)
C(10)-O(1)	1.215(3)	C(12)-C(13)	1.490(4)
C(12)-O(2)	1.208(3)		

Table 4. Selected Bond Angles (°) for Compound **15**.

C(2)-C(1)-C(8)	105.0(2)	C(2)-C(1)-C(12)	109.2(2)
C(8)-C(1)-C(12)	115.2(2)	C(1)-C(2)-C(3)	107.0(3)
C(2)-C(3)-C(9)	105.3(2)	C(5)-C(4)-C(9)	112.2(2)
C(4)-C(5)-C(6)	110.7(2)	C(5)-C(6)-C(7)	109.6(2)
Cl-C(7)-C(6)	109.0(2)	Cl-C(7)-C(8)	110.8(2)
C(6)-C(7)-C(8)	114.7(2)	Cl-C(7)-H(7)	105.7(16)
C(1)-C(8)-C(7)	116.3(2)	C(1)-C(8)-C(9)	104.9(2)
C(7)-C(8)-C(9)	111.8(2)	C(3)-C(9)-C(4)	110.2(2)
C(3)-C(9)-C(8)	102.1(2)	C(4)-C(9)-C(8)	110.8(2)
C(3)-C(9)-C(10)	110.3(2)	C(4)-C(9)-C(10)	110.8(2)
C(8)-C(9)-C(10)	112.4(2)	C(9)-C(10)-C(11)	118.1(2)
C(9)-C(10)-O(1)	121.5(2)	C(11)-C(10)-O(1)	120.4(3)
C(1)-C(12)-C(13)	116.3(2)	C(1)-C(12)-O(2)	121.8(2)
C(13)-C(12)-O(2)	121.9(2)		

Table 5. Selected Torsion Angles (°) of Ring Carbon Atoms for Compound **15**.

Five-ring		Six-ring	
C8-C1-C2-C3	3.6(0.2)	C9-C4-C5-C6	58.7(0.3)
C2-C1-C8-C9	-26.6(0.2)	C5-C4-C9-C8	-53.5(0.3)
C1-C2-C3-C9	20.7(0.3)	C4-C5-C6-C7	-57.6(0.3)
C2-C3-C9-C8	-36.7(0.2)	C6-C7-C8-C9	-51.1(0.3)
C1-C8-C9-C3	39.1(0.2)	C5-C6-C7-C8	55.0(0.3)
		C7-C8-C9-C4	48.7(0.3)

Acknowledgements. We thank Dr. M. Jones and Miss L.M. Turner for mass-spectroscopic analyses.

REFERENCES

1. Baddeley, G.; Wrench, E. *J. Chem. Soc.* **1959**, 1324-1327.
2. Baddeley, G.; Heaton, B.G.; Rasburn, J.W. *J. Chem. Soc.* **1960**, 4713-4719.
3. Baddeley, G.; Heaton, B.G.; Rasburn, J.W. *J. Chem. Soc.* **1961**, 3828-3835.
4. Baddeley, G.; Heaton, B.G.; Rasburn, J.W. *J. Chem. Soc.* **1961**, 3835-3838.
5. Raphael, R.A. in *Chemistry of Carbon Compounds* Vol. 2; Rodd, E.H. Ed.; Elsevier: Amsterdam, **1953**, 308-321.
6. Clark, R. Ph.D. thesis, C.N.A.A. (Newcastle Polytechnic), England, **1975**, 50-52.
7. Tardella, P.A.; Campana, F. *Gazz. Chim. Ital.* **1971**, 101, 990-993.
8. Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, 44, 542-561.
9. Bodenhausen, G.; Kogler, H.; Ernst, R.R. *J. Magn. Reson.* **1984**, 58, 370-388.
10. Ahmad, M.S.; Baddeley, G.; Heaton, B.G.; Rasburn, J.W. *Proc. Chem. Soc.* **1959**, 395.
11. Criegee, R.; Zogel, H. *Chem. Ber.* **1951**, 84, 215-219.
12. Allinger, N.L.; Coke, J.L. *J. Amer. Chem. Soc.* **1960**, 82, 2553-2556, and references therein.
13. Emarton, R.J.L. M.Sc. thesis, University of Leicester, England, **1966**, 56-60.
14. Blanchard, K.R.; Schleyer, P.v.R. *J. Org. Chem.* **1963**, 28, 247-248.
15. Fields, R.; Holt, G.; Orabi, M.O.A.; Naseeri-Noori, B. *J. Chem. Soc., Perkin Trans. 1* **1979**, 233-236.
16. Baddeley, G. *Quart. Rev.* **1954**, 8, 355-379.
17. Augustine, R.L. in *Reduction Techniques and Applications in Organic Synthesis*, Augustine, R.L Ed.; Dekker: New York, **1968**, 34.
18. Hendrickson, J.B. *J. Amer. Chem. Soc* **1961**, 83, 4537-4547.
19. Pitzer, K.S.; Donath, W.E. *J. Amer. Chem. Soc.* **1959**, 81, 3213-3218.
20. Kolossváry, I.; Guida, W.C. *J. Amer Chem. Soc.* **1993**, 115, 2107-2119.
21. Morris, G.A.; Freeman, R. *J. Amer. Chem. Soc.* **1979**, 101, 760-762.
22. Adamczyk, M.; Watt, D.S. *J. Org. Chem.* **1984**, 49, 4226-4237.
23. Sheldrick, G.M. SHELXTL PLUS, University of Göttingen, Germany, **1991**.