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COMPARISON OF CATIONIC RHODIUM AND IRIDIUM COMPLEXES IN DIRECTED HOMOGENEOUS HYDROGENATION

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Abstract: The hydrogenation of endo-6-methylenebicyclo[2,2,2]octan-2-ol catalysed by a range of rhodium and iridium complexes has been investigated. Unlike the corresponding exo-alcohol, reduction is highly stereoselective leading to 95 - 99.7% of endo-exo-6-methylbicyclo[2,2,2]octan-2-ol. Selectivity is much less pronounced for the corresponding methyl ether. Rhodium catalysts promote a competitive isomerisation of the double bond to endo-6-methyl-bicyclo[2,2,2]oct-5-en-2-ol, of which an authentic sample was reduced in high yield to pure exo-endo product. Reduction of both endo-hydroxy substrates by iridium complexes is rapid and highly selective.

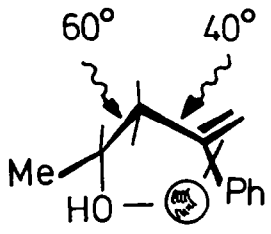
NMR studies employing europium shift reagents played a central part in defining the stereochemical interrelationships of 2,6-disubstituted bicyclo[2,2,2]octanes.

Hydroxyl-group coordination provides a means of exerting stereochemical control over the outcome of homogeneous hydrogenations. In the reduction of acyclic allylic and homoallylic alcohols in which the hydroxyl-group is attached to an asymmetric carbon atom, one diastereomeric product is strongly preferred,[1,2] and effective kinetic resolution may occur with optically active rhodium catalysts.[3] For related cyclic compounds,[4,5,6] hydrogenation is face selective, leading to a high preponderance of the product in which hydrogen has been delivered cis to the hydroxy-group. The cyclic examples tend to have trisubstituted double bonds and where this is the case iridium complexes cause more rapid reduction than rhodium complexes, the latter tending to require high-pressure[2] to be effective. Rhodium complexes may be superior in acyclic systems.[1,3]

For unsaturated cyclic alcohols the rationalisation is straightforward. If coordination of the hydroxyl-group to Rh^+ or Ir^+ is necessary to establish the catalytic cycle, then hydrogen must be delivered to one face of the olefin. In flexible acyclic molecules, the origin of diastereoselectivity is less obvious and we have previously explained the results through a model in which the hydroxyl- and olefin occupy cis-adjacent sites in the coordination sphere, with the double bond associated through the face which engenders less non-bonded interaction. With homoallylic alcohols, this suggests that the cisoid (1) rather than the transoid conformation (2) is involved with the alkyl substituent at the hydroxyl site in a pseudo-equatorial conformation[†] (Figure 1). Some constrained cyclic examples studied by Stork and Kahne,[4] particularly (3) must coordinate via a close approximation to the transoid-conformation, and are still reduced with high selectivity. To clarify the structural requirements, and compare Rh and Ir catalysts under standard conditions, we have carried out a series of hydrogenations of bicyclo[2,2,2]octan-2-ols.

[†] If the product-determining intermediate is square-planar, the cisoid-conformation would be preferred on energetic grounds because the olefin is more closely perpendicular to the coordination plane.

Figure 1



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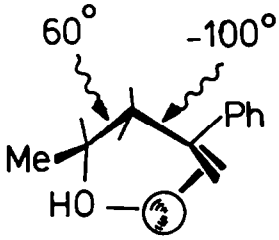
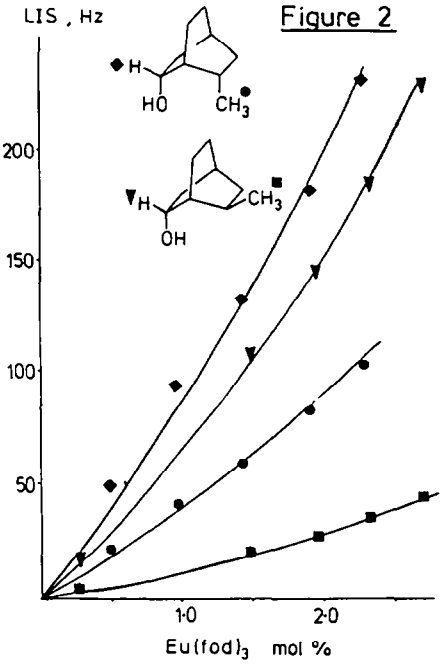


TRANSOID 2

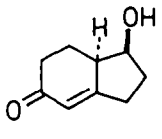
Synthesis of Substrates

Bicyclo[2,2,2]octan-2,6-dione[7] reacts with one equivalent of $Ph_3P{=}CH_2$ to effect selective methylenation of one double bond;[8] we followed this method after several less successful trials with zinc[9] and titanium methylenating agents.[10] The product (4) was subjected to hydride reduction to give a mixture of exo-6-methylene-bicyclo[2,2,2]octan-2-ol (5) and the endo-isomer (6) which were separated by preparative g.c. These epimers have recently been prepared by independent routes, one involving intramolecular allylsilane/aldehyde condensation.[11] A separate sample of keto olefin (4) was hydrogenated and the mixture of exo-6-methylbicyclo[2,2,2]octan-2-one (7) and the endo-isomer (8) likewise separated by preparative g.l.c.; the latter compound has previously been described,[12] and reduction products endo exo-6-methylbicyclo-[2,2,2]octan-2-ol (9) and endo endo-isomer (10) are likewise known.[12] The new compounds exo exo-6-methylbicyclo[2,2,2]octan-2-ol (11) and the exo-endo isomer (12) were prepared from ketone (7) by reduction and showed similar retention times on preparative g.l.c. The stereochemical assignments were confirmed by N.m.r. studies in the presence of $Eu(fod)_3$ (Figure 2). Samples of the two pure alcohols, and of compounds (11) and (12) in admixture, were made up as solutions in $CHCl_3$ (0.05M) and the chemical shifts of $\underline{CH}OH$ and $\underline{CH_3}$ monitored on addition of successive portions of $Eu(fod)_3$ (0.2M in $CHCl_3$). The plot of LIS versus $[Eu(fod)_3]$ confirms the identity of the endo-endo isomer and hence defines the stereochemistry of the remainder, when the information is coupled with the results of hydrogenation experiments (vide infra).

Figure 2



The methyl ether (13) of unsaturated endo-alcohol was prepared in conventional manner (KH/MeI, 20°) and purified by preparative g.l.c.



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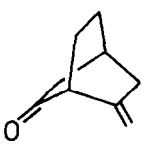

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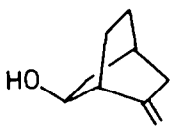

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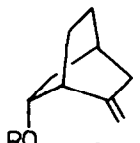
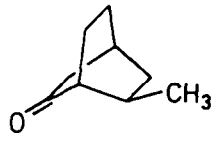


6 R = H
13 R = CH_3



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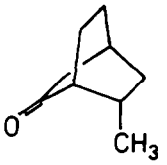

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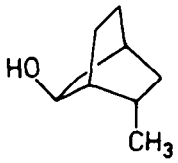

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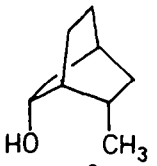

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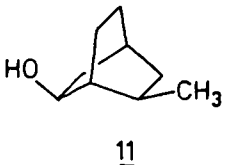

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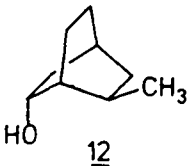

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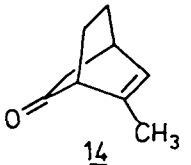

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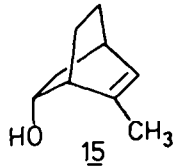

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Hydrogenation experiments

Suitable cationic Rh and Ir catalysts for directed hydrogenation have been described previously and were employed in the present work.[1,4] In addition, the iridium analogue of the now-standard rhodium catalyst, $(Ph_2P(CH_2)_4PPh_2)Ir(C_7H_8)BF_4$ was prepared; its application has recently been described by Evans and Morrissey.[13] Hydrogenations were carried out at ambient temperature and pressure according to the protocols of Table 1. A number of control experiments were conducted with the anticipated lack of selectivity. Thus keto-olefin (4) is hydrogenated slowly from both endo- and exo- directions with some competing isomerisation to the endocyclic unsaturated ketone (14).[14] Likewise exo- alcohol (5) is reduced rather slowly to produce a mixture of exo-exo- alcohol (11) and the endo-exo isomer (9). In methanol solution, where solvent coordination is anticipated to override the directing effect of the hydroxyl-group, endo-alcohol (6) gives a 50:50 mixture of the two possible reduction products (10) and (12).

The most selective reductions of endo-alcohol (6) were carried out in CH_2Cl_2 solution. With iridium catalyst B hydrogenation is particularly fast and fifty turnovers are completed in less than 30 s. at 0 . Selectivity to the exo-endo isomer is at least 99.7% and side products are completely absent. The related iridium chelate biphosphine catalyst C promotes a slower and less selective reaction but the preference for exo-methyl product is still 95:5. The high reactivity demonstrated by catalyst B indicates that it can be used effectively at low molar ratios rather than the 20 mol % (relative to substrate) suggested earlier. Indeed, high concentrations of catalyst can affect the stereochemical outcome adversely.[13]

Reduction of the endo-alcohol (6) by rhodium complex A was only moderately selective in thf and in CH_2Cl_2, addition of a small quantity of mercury was found to be necessary to obtain reproducibility. Under these optimised conditions, 98% selectivity to exo-endo alcohol (12) was observed. The course of reaction was monitored directly by g.l.c., and it was noted that a new compound appeared at short reaction times and decayed as hydrogenation proceeded. The new species was isolated and shown to be the endocyclic isomer (15) on the basis of the vinylic proton and methyl group observed in the ^1H N.m.r. spectrum. An authentic sample was prepared by base-catalysed equilibration of starting material ($KOBu^t$/DMSO/75°) and isolated by preparative g.l.c. Reduction of this product proceeded smoothly to exo-endo alcohol with all three catalysts. For the iridium complexes, reaction proceeded rather more slowly than had been observed for the exocyclic isomer (6). In contrast, rhodium catalyst A effected rather faster reaction with endocyclic isomer (15). This raised the possibility that reduction of the former might be subsequent to its metal-catalysed isomerisation, or that hydrogenation and isomerisation might at least be competitive.

To test this point both isomers were reduced with D_2 employing catalyst A, and the isolated products examined by ^1H, ^2H and ^{13}C N.m.r. The endocyclic olefin (15) gave a single product with two equal signals in the ^2H N.m.r. at 2.15 and 1.85 p.p.m, and the ^1H N.m.r. integrated for incorporation of two deuterium atoms into (12) within experimental error.

A 2D-COSY N.m.r. spectrum was recorded for the parent alcohol so that assignments could be made without ambiguity, aided by some long-range 'W'-couplings between protons on different bridges which are "exo-exo" related. Comparison of the ^{1}H and ^{2}H spectra then shows that addition of D_2 to (15) gives only the 5-endo, 6[^{2}H]$_2$-isomer of product (12). The result was confirmed by examination of the ^{13}C N.m.r. spectrum, which additionally revealed a $^{3}J_{C,D}$ coupling to C7 and C8 of ca. 1 Hz. Reduction of the exocyclic olefin (6) with D_2 and catalyst A gave a product with three signals in its ^{2}H N.m.r. spectrum at 2.15, 1.85 and 0.95 p.p.m. in ratio 0.76 : 1.00 : 0.24. The first two corresponded to H5-endo and H6, and the last to the CH_3-group. The ^{1}H spectrum again showed incorporation of two deuterium atoms, within experimental error. These results support the pathway of Figure 4 in which the endocyclic olefin (15) is reduced without competitive isomerisation, but exocyclic olefin (6) mainly isomerises prior to reduction. It is of interest to note that Rh, but not Ir catalysts, reduce compound (15) faster than compound (6).

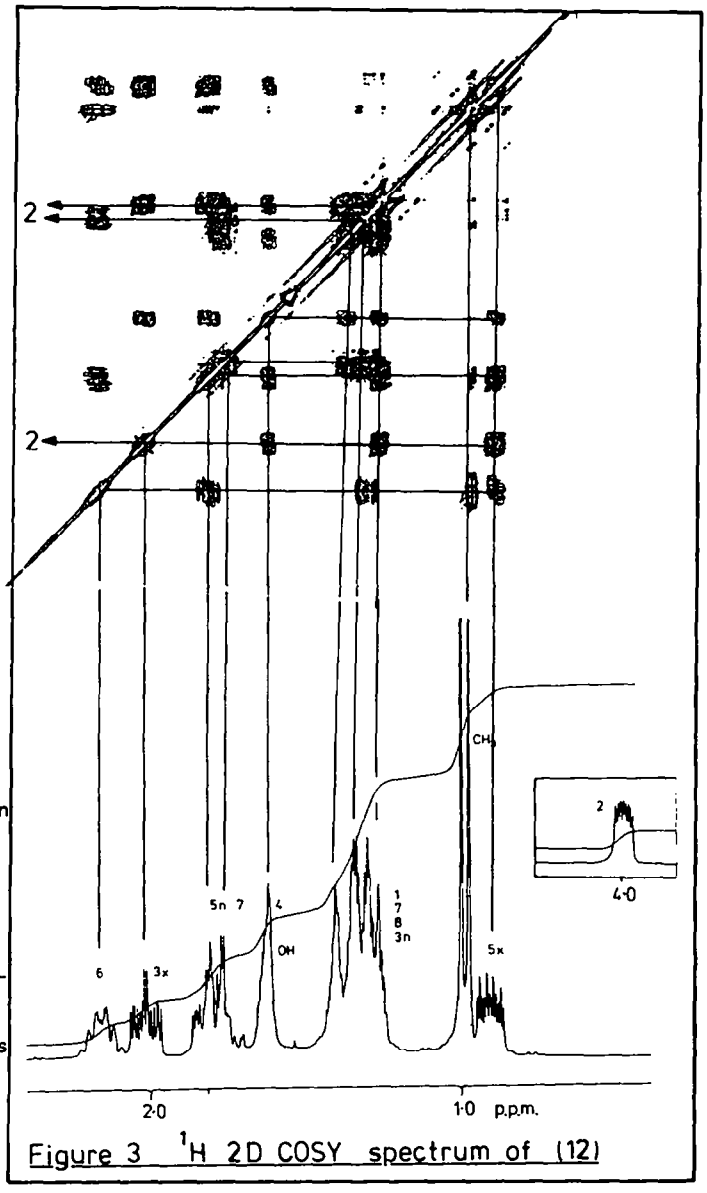

Figure 3 ^{1}H 2D COSY spectrum of (12)

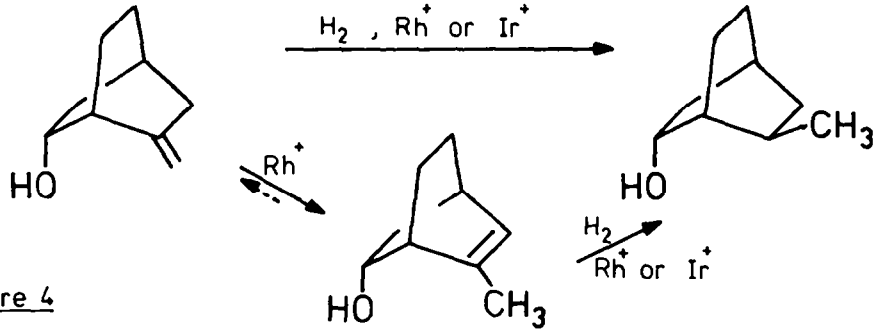

Figure 4

Methyl ether (13) is hydrogenated with less pronounced selectivity than the parent alcohol, following a similar ordering to the latter on catalyst variation. The results suggest that ethers are poorer than alcohols in coordination to rhodium or iridium, in line with other observations.[15] In earlier work,[1] allylic and homoallylic acetates were found to be unselective substrates for directed hydrogenation, so that the methoxyl-group occupies an intermediate position, between -OH and OCOR in effectiveness.

Stereochemical considerations

The conformation of bicyclo[2,2,2]octane and its derivatives has been studied by X-ray and electron diffraction, and been the subject of several MO and molecular mechanics calculations.[16] The consensus of opinion is that the D_{3h} conformation is a shallow energy minimum, but the twisted C_{3v} enantiomers are readily accessible. For efficient directed hydrogenation of compound (6) the 2-hydroxyl-group must occupy a ψ-axial site in the twisted conformation of bicyclo[2,2,2] octane. Molecular models constructed on that basis (with the assistance of X-ray structural data on related compounds[17]) suggest that the reacting conformation is as indicated in Figure 5. Similar reasoning leads to the illustrated conformation for directed hydrogenation of compound (13). In the former case the torsion angles are related to those in the transoid-isomer of Figure 1 and in the latter they are related to the cisoid-form. It is not immediately obvious why there should be any preference for coordination of one or other to iridium except that the cisoid form is closer to the ideal[18] olefin geometry in a square-planar four-coordinate complex with the double-bond perpendicular to the coordinate plane. Nevertheless, the endocyclic olefin is more readily reduced by Rh^+ catalysts (as is clearly demonstrated by the D_2 additions) and the results provide a useful correlation with the acyclic series.

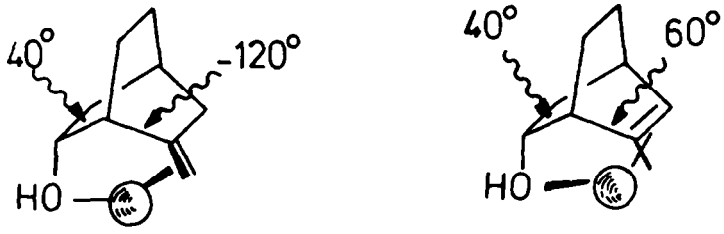

Figure 5

Acknowledgment We thank SERC and B.P. Research Centre for a CASE award, and Dr. D.J.H. Smith for many useful discussions. Johnson-Matthey generously provided a loan of Rh salts. Dr. A.E. Derome recorded the 2D-COSY spectrum of compound (6) at 500 MHz.

Experimental

N.m.r. spectra were normally recorded on a Bruker WH-300 spectrometer, in $CDCl_3$ unless otherwise indicated, with accumulation of ^2H spectra carried out on the deuterium lock channel. Mass spectra were recorded on a VG-Micromass instrument as described for individual compounds. Analytical g.l.c. was carried out on a Pye-Unicam series 204 chromatograph (10% PEG 20M, on 100 - 120 mesh Chromosorb G, 1.5M., 30 ml. min^{-1}, column A; 3% OV-225, idem, column B) or series 104 Chromatograph (10% OV 17 on 100 - 120 mesh Gas-Chrom Q, 3m., 40 ml. min^{-1}, column C). Preparative g.l.c. was carried out on a Pye series 105 Automatic Preparative Chromatograph (15% PEG-20M, 20 p.s.i. N_2, 2.2 m. (column D) or 4.5 m. (column E). Analyses were carried out by Dr. Strauss in the Dyson Perrins Laboratory, or by the University of Manchester Microanalytical Service.

Exo- and endo-6-methylenebicyclo[2,2,2]octan-2-ol

To a solution of 6-methylenebicyclo[2,2,2]octan-2-one (1.7 g., 12.5 mmol.) in EtOH (25 ml.) was added $NaBH_4$ (0.475 g., 12.5 mmol.) and the mixture stirred at 20° for 30 m. when g.l.c. (column B, 125°) showed no trace of starting material. Work-up with rigorous Et_2O extraction and preparative g.l.c. (column D, 150°) gave first endo-6-methylenebicyclo[2,2,2]octan-2-ol, m.p. 70° (0.359 g., 21%) I.r. ($CDCl_3$): ν3615 (m) 3072 (w) 1640, 1630 (m) 1061 (m) 1010 (br,m) cm^{-1}. N.m.r.: δ4.86 (1H,m,=CH) 4.74 (1H,dd,=CH) 4.00 (1H,dt,H2,J=4,10 Hz) 2.3 = 1.9 (5H,m) 1.85 (1H,spt,H4,J=3 Hz) 1.7 = 1.3 (5H,m) p.p.m. M.s.(in beam EI), m/z 138 (18,M^+) 105 (20) 94 (99) 79 (100), and then endo-6-methylenebicyclo[2,2,2]octan-2-ol, m.p. 53° (0.309 g. 18%); Found: C 78.19, H 10.34; $C_9H_{14}O$ requires C 78.21, H 10.22%. I.r. ($CHCl_3$) ν3530 (br m) 3425 (br m) 1640 (m) 1125 (m) 1080 (m) cm^{-1} N.m.r.: δ4.89 (2H,t,J=2.5 Hz=CH_2) 3.89 (1H,m,H2) 2.30 (2H,br m) 2.23 (1H,q,H1,J=3 Hz) 2.08 (1H,m) 1.85 (1H,spt,H4,J=3 Hz) 1.8 = 1.2 (6H,brm).

Compound		Catalyst	Solvent	Selectivity exo : endo	Time[a]	Comments
	(4)	A	thf	68 : 32	~24 h.	c. 5% olefin isomerisation[b]
		A	CH_2Cl_2	55 : 45	~24 h.	c. 20% isom.
	(5)	A[c]	thf	51 : 49	<24 h.	
		B	CH_2Cl_2	55 : 45	3 h.	competing isom.
		B	CH_3OH	55 : 45	3 h.	~ 50 % isom.
		C	CH_3OH	54 : 46	5 h.	clean product
	(6)	A	thf	15 : 85	24 h.	reaction 85 % complete.
		A	CH_3OH	49.5 : 50.5	5 h.	reaction 75 % complete.
		A[c]	CH_2Cl_2	2 : 98	5 h.	
		B	CH_2Cl_2	0.3 : 99.7	30s. 0°	
		C	CH_2Cl_2	5 : 95	45 m.	
	(15)	A[c]	CH_2Cl_2	0.3 : 99.7	50 m	
		B	CH_2Cl_2	0.3 : 99.7	3 m., 0°	
		C	CH_2Cl_2	0.5 : 99.5	4 h.	
	(13)	A[c]		14.5 : 86.5	5 m.	faster than (6)
		B		2.6 : 97.4	3 m.	
		C		41.9 : 58.1	4 h.	

Table 1 Hydrogenation reactions of bicyclo[2.2.2]octane derivatives. Reactions were normally carried out at 20° and 1 atm. H_2, and progress of the reaction monitored by g.l.c. (PEG 20M, 6', 120° - 155°) and products identified mainly on the basis of their ^1H N.m.r. spectra (see Experimental Section).
Catalysts A $(Ph_2P(CH_2)_4PPh_2)(C_7H_8)Rh^+BF_4^-$; B $((C_6H_{11})_3P)(C_8H_{12})(C_5H_5N)Ir^+PF_6^-$; C $(PH_2P(CH_2)_4PPh_2)(C_7H_8)Ir^+BF_4^-$.
Footnotes [a] Time taken for complete reaction, with catalyst : substrate of 1:50; [b] The resulting endocyclic isomer is stable to hydrogen; [c] Reaction carried out in the presence of Hg (30μL, dispersed by stirring).

Exo- and endo-6-methylbicyclo[2,2,2]octan-2-one

A solution of 6-methylenebicyclo[2,2,2]octan-2-one (0.19 g., 1.4 mMol.) in CH_2Cl_2 (4 ml.) containing bicyclo[2,2,1]hepta-2,5-diene bis (1,4-diphenylphosphino)butanerhodium(I)tetrafluoroborate (0.02 g, 30 μMol) was equilibrated under H_2 at -78° and allowed to come to room temperature. Stirring was commenced and the reaction followed by g.l.c. (column B, 125°). After 24 h. reaction was seen to be complete and three components were present in ratio 20:44:36. They were separated by preparative g.l.c. after removal of catalyst by passage through a short column of silica gel (column E, 120°) and identified by comparison of their N.m.r. spectra with literature data. In order of elution they were 6-methylbicyclo[2,2,2]oct-5-ene-2-one, endo-6-methylbicyclo[2,2,2]octan-2-one and exo-6-methylbicyclo[2,2,2]octan-2-one.

Endo-6-methyl-exo (and endo) bicyclo[2,2,2]octan-2-ol

The sample of endo-ketone isolated as described above was dissolved in Et_2O (2 ml.) and small quantities of $LiAlH_4$ added by spatula until the reduction was adjudged to be complete (g.l.c., column A, 160°). After workup by the usual method,[19] the product was purified by preparative g.l.c. (column E, 180°). The major component was endo-6-methyl-endo-bicyclo[2,2,2]octan-2-ol, m.p. (sealed tube) 94.5-95° [Lit. 59.5 - 61.5° subl.] Found C, 76.8, H, 11.5, $C_9H_{16}O$ requires C, 77.08, H 11.51% I.r. ($CDCl_3$) ν3625 (m) 1240 (m) 1030 (s) cm^{-1}. N.m.r.: 4.03 (1H,br,H2) 1.99 (1H,ddt) 1.9-1.1 (11H,m) including 1.19 (3H,d,CH , J=7.5 Hz) p.p.m. M.s. (CI,NH_3) m/z 140 (54,M^+) 122 (100). The minor component was endo-6-methyl-exo-bicyclo[2,2,2]octan-2-ol, N.m.r.: δ4.13 (1H,m) 2.1 - 1.5 (11H,m) 1.00 (3H,d,CH , J=7 Hz) 0.87 (1H,m) p.p.m.

Exo-6-methyl-exo (and endo) bicyclo[2,2,2]octan-2-ol

In similar manner $LiAlH_4$ reduction of exo-6-methylbicyclo[2,2,2]octan-2-ol yielded a mixture of exo exo and exo endo alcohols which were eluted together as an approximately 1:1 mixture on attempted preparative g.l.c. Configurational assignments of the four alcohols were confirmed by N.m.r. spectra in the presence of $Eu(fod)_3$, see Figure 2.

Exo-6-methyl-endo-bicyclo[2,2,2]octan-2-ol

[Vide infra for a more general discussion of hydrogenation procedures]. A solution of endo-6-methylenebicyclo[2,2,2]octan-2-ol[0.015 g., 110 μMol] and cycloocta-1,5-dienepyridinetricyclohexylphosphineiridium (I) hexafluorophosphate (0.002 g., 2.2 μMol) in CH_2Cl_2 was freeze-thaw degassed under H_2 and allowed to warm to ca. 0°. Vigorous agitation ('Whirlimix', Fisons) was carried out for 1 minute, when g.l.c. analysis (column C, 160°) indicated complete reaction. Solvent was removed in vacuo and catalyst removed by passing the residue in $CHCl_3$ through a short column of silica gel (3 cm. x 6 mm.). After solvent removal and sublimation in vacuo exo-6-methyl-endo-bicyclo[2,2,2]octan-2-ol was obtained as white needles, m.p. 92° (sealed tube). Found C 76.9, H 11.7; $C_9H_{16}O$ requires C, 77.08, H 11.51%. I.r. ($CDCl_3$) ν3610 (m) 1630 (m) cm^{-1}. N.m.r, see Figure 3. M.s. (CI,NH_3) m/z 158 (18,M^++18) 140 (25,M^+) 122 (100).

A small sample of the product was oxidised by CrO_3;py in CH_2Cl_2 and it was confirmed that exo-6-methylbicyclo[2,2,2]octanone was produced. Likewise the endo,endo-alcohol was oxidised to endo-6-methylbicyclo[2,2,2]octanone.

Endo-6-methylbicyclo[2,2,2]oct-5-ene-2-ol

A solution containing endo-6-methylenebicyclo[2,2,2]octan-2-ol (0.12 g., 0.87 mMol) and KoBu^t (0.45 g, 4 mMol) in DMSO (4 ml., dried over CaH_2 and distilled) was held at 70° under Ar for 2.5 d., monitoring by g.l.c. (column C). Water (5 ml) was added and the mixture extracted with Et_2O (5 x 5 ml.) washed with water (1 ml.) dried and the product isolated by preparative g.l.c. (column E). There was thus obtained endo-6-methylbicyclo[2,2,2]oct-5-ene-2-ol mp 56.7° (0.052 g., 43%). Found C, 78.0, H, 10.38; $C_9H_{14}O$ requires C 78.2, H, 10.25%. I.r. (CCl_4) ν3375 (m) 3030 (w) N.m.r. δ6.01 (1H,brd,H5,J=6.5 Hz) 3.96 (1H,brd,H2,J=8.5 Hz) 2.5 (2H,m) 1.94 (1H,ddd,J=14,10,3 Hz) 1.86 (3H,s,CH) 1.5 - 1.0 (6H,m) p.p.m. M.s. (EI) 138 (8,M^+) 94 (93) 79 (100).

endo-2-Methoxy-6-methylenebicyclo[2,2,2]octane

KH (0.04 g., 1 mMol) was added in small portions to a solution of endo-6-methylenebicyclo-[2,2,2]octan-2-ol (0.095 g., 0.7 mMol.) in CH_3I (1 ml.) under Ar at 20°. The evolution of gas was allowed to subside after each addition and after the last one t.l.c. (Et_2O, silica gel) showed the absence of starting material at R_f 0.4 and a single new spot at R_f 0.6. Solid KI was removed by filtration and rinsed with Et_2O, then preparative g.l.c. on the solution (column D, 120°) gave product (0.062 g., 59%) N.m.r.: δ4.77 (1H,dd,2.5 Hz,=CH) 4.73 (1H,dd,=CH) 3.45 (1H,dt,H2,J=10, 3 Hz) 3.24 (3H,s,OCH_3) 2.43 (1H,brq) 2.24 (2H,m) 1.93 (1H,m) 1.81 (1H,spt, H4,J=3 Hz) 1.7 - 1.3 (5H,m) p.p.m. M.s. (CI,NH_3): m/z 152 (24 M^+) 137 (12) 120 (92) 41 (100).

Hydrogenation prodedures

Reactions were carried out in septum-stoppered Schlenk tubes (20 cm. x 12 mm) equipped with greaseless vacuum tap (Young's, 6 mm bore) and containing a magnetic follower. Catalyst precursors were prepared by previously described procedures.[4,20] The solution of substrate (typically 0.020 g.) and catalyst (typically 0.002 g) was made up in solvent under Ar and attached to a specially adapted vacuum line. The sample was frozen and degassed several times, with the atmosphere being replaced by H_2 (or D_2) during the procedure. It was allowed to warm to ambient temperature and stirring commenced. Samples were removed at intervals by microsyringe and the progress of reaction followed by g.l.c., as described. For very rapid Ir^+ reductions the reaction was deemed to be complete when the colourless solution became a pale straw colour. On completion solvent was removed in vacuo and the sample redissolved in a small quantity of $CHCl_3$, and passed through a silica gel column (3 cm. x 6 mm.). Purification was effected by preparative g.l.c. following analysis of the isomer ratio by g.l.c. and ^1H N.m.r.

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