The Energetics of a Readily Occurring Intramolecular Hydride Shift

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7-*exo*-Hydroxybicyclo[3.3.1]nonan-3-one (1a) and the 1-methyl homologue (1b) have been synthesised and found to undergo a rapid base-induced intramolecular 3,7-hydride shift. In the case of (1a), the associated activation energy ($\Delta G^\ddagger$ 19.4 ± 0.2 kcal mol^{-1} at 113 °C) has been determined by variable temperature ^{1}H n.m.r. spectroscopy.

INTRAMOLECULAR 1,*n*-hydride shifts of the general type shown in Figure 1 have been noted in a wide variety of hydroxy-ketones.[1] A knowledge of the energies associated with the actual hydride transfer process would be of considerable assistance in elucidating the detailed mechanisms of such reactions [2] but to date there has been a dearth of such information. We now report the results of an investigation of the degenerate rearrangements of the bicyclic ketols (1a and b).

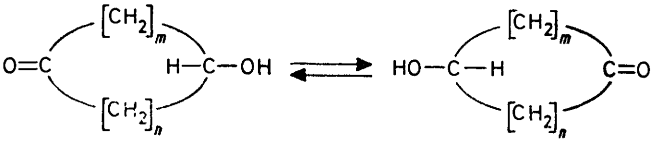
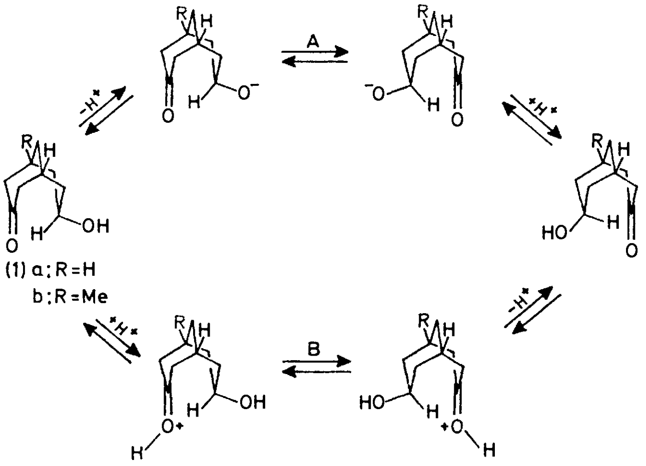


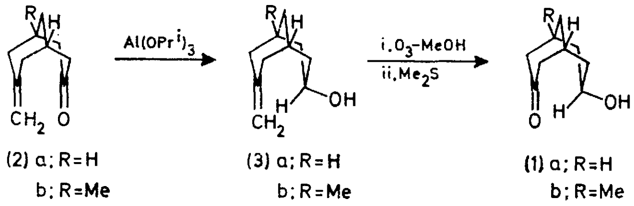
FIGURE 1

The 3,7-hydride transfer in these molecules could conceivably be either acid- (path B) or base- (path A) catalysed. This report deals with the base-catalysed pathway, which has intermolecular analogies in the Meerwein–Ponndorf–Verley[3] and Cannizzaro[4] reactions. In the case of either substrate, a 3,7-hydride transfer results in regeneration of the starting material. However, in (1b), the presence of a bridgehead methyl group renders the starting material chiral, and the overall reaction would be a racemisation process. It seemed to us that this offered a simple chiroptical method of monitoring the course of the reaction.



SCHEME 1

The substrates for the kinetic measurements were prepared by a standard series of functional group manipulations from the corresponding exocyclic methylene ketones, (2a) [5] and (2b).[6] As only limited quantities of the optically active ketone (2b) were available, the preparative sequence (Scheme 2) was first carried through on the achiral ketone (2a).



SCHEME 2

Meerwein–Ponndorf–Verley reduction[3] of the ketone (2a) gave, in good yield, a single alcohol which was identical with that isolated by Eakin *et al.*[7] as the minor product of reduction of (2a) by lithium aluminium hydride. The assignment of *exo*-stereochemistry rests (*a*) on the method of synthesis (the Meerwein–Pondorf–Verley reduction is expected[3] to give the thermodynamically more stable alcohol) and (*b*) on the ^{1}H n.m.r. spectrum (the C*H*OH signal appears as a septet centred at δ 4.55, partially obscured by the signal from the exocyclic methylene protons). The apparent magnitudes of the couplings are consistent with the C*H*OH signal being the X portion of an A_2B_2X system with J_{AX} *ca.* 11 and J_{BX} *ca.* 5 Hz and these values, in turn, are

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[1] For examples, see (*a*) W. Acklin and V. Prelog, *Helv. Chim. Acta.*, 1959, **42**, 1239; (*b*) J. M. Shepherd, D. Singh, and P. Wilder, jun., *Tetrahedron Letters*, 1974, 2743; (*c*) D. Dvornink and J. E. Edwards, *Proc. Chem. Soc.*, 1958, 280; (*d*) J. Wicha and E. Caspi, *J. Org. Chem.*, 1973, **38**, 1280; (*e*) P. T. Lansbury and F. D. Saeva, *J. Amer. Chem. Soc.*, 1967, **89**, 1890; (*f*) W. Parker and J. R. Stevenson, *Chem. Comm.*, 1969, 1289.

[2] (*a*) M. A. Eakin, J. Martin and W. Parker, *Chem. Comm.*, 1968, 298; (*b*) M. A. Eakin, J. Martin, W. Parker, Sister C. Egan, and S. H. Graham, *Chem. Comm.*, 1968, 337; (*c*) W. Parker and C. I. F. Watt, *J.C.S. Perkin II*, 1975, 1647; (*d*) E. N. Marvell, J. Seubert, D. Sturman, and W. Frederici, *J. Org. Chem.*, 1970, **35**, 396.

[3] A. L. Wilds, *Org. Reactions*, 1944, **2**, 178.

[4] For a review see T. A. Geissman, *Org. Reactions*, 1944, **2**, 94.

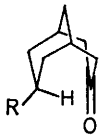
[5] (*a*) G. L. Baughman, *J. Org. Chem.*, 1964, **29**, 238; (*b*) H. Stetter and P. Tacke, *Chem. Ber.*, 1963, **96**, 694; (*c*) A. R. Gagneux and R. Meier, *Tetrahedron Letters*, 1969, 1365; (*d*) H. Hamill, A. Karim, and M. A. McKervey, *Tetrahedron*, 1971, **27**, 4317.

[6] H. Hamill and M. A. McKervey, *Chem. Comm.*, 1969, 864.

[7] M. A. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1967, 955.

consistent with the proton being axially oriented in a chair cyclohexane.[8]

Cleavage of the exocyclic methylene residue with ozone in methanol at low temperature, followed by treatment of the mixture with dimethyl sulphide [9] yielded the ketol * (1a), whose structural assignment follows from analytical and spectroscopic data. The high resolution mass spectrum showed the molecular ion at *m/e* 154.099 3 ($C_9H_{14}O_2$). The i.r. spectrum indicated the presence of the hydroxy (bands at 3 610 and 3 450 cm^{-1}) and ketone (band at 1 710 cm^{-1}, split) functionalities. The split $\nu_{C=O}$ band also appears in the i.r. spectra of the *exo*-7-methylbicyclo[3.3.1]nonan-3-one (5; R = Me) [10,11] and is possibly due to the proximity of C-3 and C-7 in the double chair conformation. In the ^1H n.m.r. spectrum of (1a) the C*H*OH signal appears at δ 3.82, again as a seven-line multiplet, very similar to that in the exocyclic methylene alcohol (3a).



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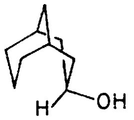
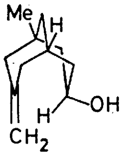


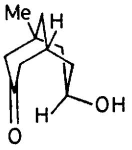
(6)

The relative chemical shifts of the C*H*OH signals in the exocyclic methylene alcohol (3a) (δ 4.55) and the ketol (1a) (δ 3.82) are worthy of comment. These shifts should be compared with those of axial C*H*OH in cyclohexanols [12] (δ 3.3—4.0) and in the simple bicyclic alcohol (6) (δ 4.3).[2a,11] Dreiding models show that replacement of the protons of the 7-methylene group in *exo*-bicyclo[3.3.1]nonan-3-ol by either an exocyclic methylene group [to yield (3a)] or an oxygen atom [to give(1a)] places the axial proton of the alcohol above the plane of the π-bond of the olefin or carbonyl group, always assuming that both these molecules exist in the depicted double chair conformation. The simple picture of the magnetic anisotropies around such bonds suggests that both should exert a shielding influence on the C*H*OH proton, and indeed the signal for the ketol (1a) is shifted to higher field by 0.47 p.p.m. However, in the exocyclic methylene alcohol (3a) the corresponding signal is shifted to lower field by 0.25 p.p.m. It may well be that the anisotropic regions around carbonyl and exocyclic methylene groups are sufficiently different to account for the observed difference in chemical shifts.[13] The alternative and much less plausible possibility that the conformations of the two molecules are subtly different awaits further study.

The optically active ketone (2b) was converted into the *exo*-alcohol (3b) and thence into the ketol (1b) by application of the same series of reactions, and the spectroscopic and analytical data were in all cases consistent with the structure. The ketone (2b) [5] as received (a gift from Dr. M. A. McKervey, Queen's University, Belfast) had $[\alpha]_D$ +4.1° and the derived exocyclic methylene alcohol (3b) and ketol (1b) had rotations as shown in the Table. The observed change in sign of the optical rotation on conversion of the chromophore from exocyclic methylene to ketone functionality is in accord with the Octant Rules for olefins and ketones.[14] The optical purity of the material has not yet been determined.

Potassium t-butoxide–t-butyl alcohol was chosen as the base–solvent combination for the polarimetric studies on (1b). The relative pK_a values associated with the various acidic protons in this system (*e.g.* $R_2CH\cdot OH$ pK_a *ca.* 18; $Me_3C\cdot OH$ *ca.* 19; $RCH_2\cdot COR$ *ca.* 20) [15] were expected to be such that a high concentration of the substrate alkoxide would be ensured. In the event, treatment of a solution of (1b) with 1 equiv. potassium t-butoxide in t-butyl alcohol at 35 °C led to almost complete loss of optical activity in the time required for mixing of solutions and placing in the polarimeter. The half-life for the racemization process must be *ca.* 1—2 min; hence a lower limit for the rate constant may be placed at *ca.* 10^{-2} s^{-1} at 35 °C. The material recovered from the experiment was completely inactive but other-





λ/nm	[α](°) (*c* 0.08 5 g ml^{-1} in MeOH)	[α]° (*c* 0.1 g ml^{-1} in Bu^{t}OH)
582	+ 2.0	− 0.5
579	+ 2.4	− 0.6
547	+ 2.9	− 0.6
436	+ 4.5	− 1.9
365	+ 4.8	− 3.4

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* Application of the conditions described by J. M. Conia and P. Lerwerend (*Compt. rend.*, 1960, **250**, 1078) to the ozonolysis of (3a) (*viz.* use of pyridine as the reaction medium) led to a 1 : 1 mixture of (1a) and spiro[bicyclo[3.3.1]nonane-7,2′-oxiran]-3-*exo*-ol. Small amounts of spiro[bicyclo[3.3.1]nonane-7,2′-oxiran]-3-one were also formed. Epoxidation of methylene groups by ozone has been noted, particularly when one side of the methylene functionality is hindered; see P. S. Bailey, *Chem. Rev.*, 1958, **58**, 925, and R. Criegee, 'Products of Ozonation of some Olefins,' A.C.S. Advances in Chemistry Series No. 21, 1959, p. 133.

[8] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.

[9] J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Letters*, 1966, 4263.

[10] M. A. Eakin, Ph.D. Thesis, Glasgow, 1967.

[11] C. I. F. Watt, Stirling, unpublished results.

[12] E. L. Eliel, M. H. Gianni, T. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 1972, 741.

[13] (*a*) L. M. Jackson, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon, Oxford, 1962, p. 129; (*b*) J. W. ApSimon, W. G. Craig, P. V. De Marco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, 1967, **23**, 2339, 2375; (*c*) J. W. ApSimon, P. V. De Marco, D. W. Mathieson, W. G. Craig, A. Karim, L. Saunders, and W. B. Whalley, *Tetrahedron*, 1970, **26**, 119.

[14] (*a*) For a review see G. Snatzke, 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry,' Heydon, London, 1967; (*b*) A. I. Scott and A. D. Wrixon, *Chem. Comm.*, 1969, 1182; (*c*) A. I. Scott and A. D. Wrixon, *Tetrahedron*, 1971, **27**, 4787.

[15] H. O. House, 'Modern Synthetic Reactions,' 2nd edn., Benjamin, New York, 1972.

wise unchanged. These polarimetric experiments were not pursued further and were only of use in that they suggested the reaction might be fast enough to be observed on the ^{1}H n.m.r. time-scale at elevated temperature.

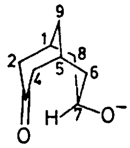

FIGURE 2 H-1 and -5 δ 2.33; H-2, -4, -6, and -8 δ 2.55; H-7 δ 3.3; H-9 δ 1.48

Accordingly, the ^{1}H n.m.r. spectrum of the ketol (1a) in deuteriochloroform was examined in more detail. Besides the one-proton signal at δ 3.83 (C*H*·OH), it shows a broadened singlet (4 H) at δ 2.49 and a complex unresolved signal between δ 1.3 and 2.3 (*ca.* 8 protons). This spectrum is substantially unchanged when $(CD_3)_2SO$ is used as solvent. On addition of $NaCD_2{\cdot}SO{\cdot}CD_3$ (1 equiv.), a base strong enough to generate the alkoxide from the alcohol functionality (pK_a of $Me_2SO = 23$),[15] the spectrum changes dramatically to show a featureless signal at δ 3.3 (1 H), a fine-structured signal at δ 2.55 (8 H), a broad signal at δ 2.33 (2 H), and a quartet of triplets centred at δ 1.48 (2 H). These signals were tentatively assigned to C*H*·OH (δ 3.3), C*H*$_2$·CO·C*H*$_2$ and C*H*$_2$·CHOH·C*H*$_2$ (δ 2.55), the bridgehead protons (δ 2.33), and the methylene bridge-protons (δ 1.48). The quartet of triplets centred at δ 1.48 is consistent with the signal expected for the non-equivalent pair of protons on the 9-position methylene bridge with a geminal coupling (J_{AB}) of 11.4 Hz and a chemical shift difference of 18.0 Hz. The smaller triplet splitting (*J* 3 Hz) is consistent with that expected from the bridgehead protons at δ 2.33. The coupling from the bridgehead protons to the α-proton of the alcohol in adamantan-2-ol[16] and bicyclo-[3.3.1]nonan-9-ol[17] (2.6 Hz) is very similar. Decoupling experiments support these assignments, *e.g.* irradiation at δ 2.33 leads to collapse of the triplet coupling, leaving only the AB quartet. Similarly irradiation at δ 1.48 leads to sharpening of the signal at δ 2.33.

Further support for the assignment is provided by deuterium exchange experiments. Treatment of the ketol with NaOD–D_2O gives material which contains up to 8 deuterium atoms per molecule, consistent with exchange of deuterium at sites adjacent to carbonyl groups at both ends of the molecule. The ^{1}H n.m.r. spectrum of the anion of the deuteriated material in $(CD_3)_2SO$ shows a substantial decrease in intensity of the signal at δ 2.55, a sharpening of the signals at δ 3.3 and 2.33, and no change in the signal at δ 1.48.

As hoped, the ^{1}H n.m.r. spectrum of the anion was temperature-dependent. The C*H*·OH signal at δ 3.3 becomes much sharper as the temperature is raised, and the signal at δ 2.55 first loses its fine structure at *ca.* 100 °C then regains detail as the temperature is further raised. The bridgehead signal at δ 2.33 becomes a triplet, showing *J* 3 Hz. Most instructive is the behaviour of the signal at δ 1.48 (Figure 3). The quartet of triplets collapses with a coalescence temperature of 113 °C. As the temperature is further raised, the signal sharpens to a triplet (*J* 3 Hz). On cooling, the spectrum reverts to its original form. The coalescence temperature is independent of the concentration of the sample, supporting the fact that the observed process is intramolecular.

This observed temperature dependence of the ^{1}H n.m.r. spectrum of the anion of (1a) is exactly that expected from a rapid reversible 3,7-hydride shift. As the temperature is raised and the migration becomes rapid, both ends of the molecule become equivalent on the n.m.r. time-scale; hence the protons on the methylene bridge become equivalent, resulting in collapse of the AB quartet.[18] The observed chemical shift difference and coupling constant between these protons at the low temperature limit allow calculation[19] of the energy barrier for the ^{1}H n.m.r. exchange process, which we identify with the activation energy for the hydride shift in the anion at the coalescence temperature. The coalescence experiment was performed with decoupling

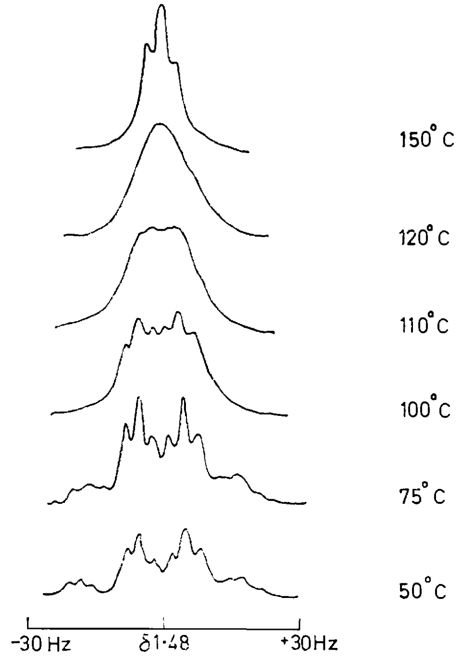

FIGURE 3 Temperature dependence of the δ 1.48 signal in the ^{1}H n.m.r. spectrum of the anion of the hydroxy-ketone (1a)

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[16] F. W. Van Deursen and P. K. Korver, *Tetrahedron Letters*, 1967, 3923.

[17] C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.

[18] For discussion of effects of exchange processes see E. D. Becker, 'High resolution NMR,' Academic Press, New York, 1972, ch. 10.

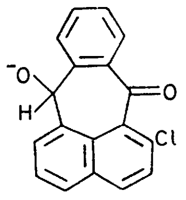
[19] (*a*) F. G. Riddell and J. M. Lehn, *Chem. Comm.*, 1966, 376. (*b*) J. E. Anderson and J. C. D. Brand, *Trans. Faraday. Soc.*, 1966, **62**, 517.

of the bridgehead hydrogens, thus removing the triplet coupling, and provided an activation energy of 19.4 $\pm$ 0.2 kcal mol^{-1} at a coalescence temperature of 113 $\pm$ 3 °C. The apparent coalescence in the absence of decoupling was *ca.* 10 °C higher.*

DISCUSSION

Intermolecular transfer of hydride from the α-carbon atom of an alkoxide to the carbon atom of a carbonyl group has long been known.[20] Where the metal involved is aluminium, the reaction is the synthetically valuable Meerwein–Ponndorf–Verley reduction,[6] which can take place extremely readily, *e.g.* the reduction of cyclohexanone in propan-2-ol with aluminium isopropoxide at 83 °C is estimated to have a half-life of *ca.* 3 min,[21] and the activation energy for the exchange of tetrameric aluminium isopropoxide with deuteriated acetone is 17.1 kcal mol^{-1}.[22] Activation energies are not available for cases where the metal is other than aluminium, but since a similar mode of bifunctional catalysis by the metal ion does not appear to be possible in the case of simple alkali metal ions, it seems reasonable to expect activation energies to be higher in these cases.

As already noted, examples of base-catalysed intramolecular hydride shifts in ketols are well documented,[1] but to our knowledge rates have been determined in only one other case. 6-Chloro-7-hydroxypleiaden-12(7*H*)-one (7) is reported to rearrange to the 1-chloro-analogue (8) with an activation energy [$\Delta G^{\ddagger}$ (48 °C)] of 24 kcal mol^{-1} [1e] for the 1,4-(or 1,5-)shift, a value substantially higher than that observed with the ketol (1a).



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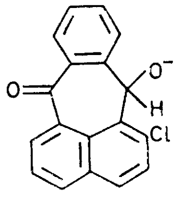

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This difference in activation energies must be due, in part at least, to the fact that the ground state conformation of (1a) is more favourably disposed for the 3,7-hydride shift. The ^{1}H n.m.r. evidence (*i.e.* the coupling constants and chemical shift associated with the C*H*OH at the 3-position), points to the depicted double chair being the ground state conformation of (1a). It seems reasonable to suppose that the derived alkoxide anion maintains this preferred conformation and the geometry around the reaction centres (see Figure 4) is then such that the migrating hydride is *ca.* 1.9 Å (from Dreiding models) from the carbon atom of the receptor carbonyl group.

The 'least motion' changes[23] in nuclear geometry around the reaction centres as the reaction proceeds can be visualised as follows: the C–O$^-$ bond shortens and rotates towards the C(6)C(7)C(8) plane. The H–C(O$^-$) bond lengthens and the C–H bond axis rotates upwards away from the C(6)C(7)C(8) plane. Such motion places the migrating hydride over the *p*-orbital on the carbonyl carbon atom. As the migrating hydride now approaches the carbonyl carbon atom, the C=O bond lengthens and rotates out from the C(2)C(3)C(4) plane. Such motion appears to be possible without any gross conformational changes in the bulk of the bicyclic molecule. It is, however, a matter of conjecture whether or not all these motions are synchronous, *i.e.* the energy profile for the course of the reaction could present either one or two maxima, but must be symmetrical.

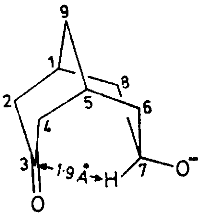

FIGURE 4

By *ab initio* procedures, Burgi, Lehn, and Wipff[24] have calculated the minimum energy path for the approach of a hydride ion to the carbonyl function of a formaldehyde molecule and have shown it to be in agreement with the preferred path of nucleophilic attack on a carbonyl group as deduced from crystallographic evidence. The least energy position for hydride at a distance of *ca.* 1.9 Å as it approaches (or leaves) the carbonyl group is calculated to be behind the orthogonal to the plane of the carbonyl group running through the carbonyl carbon atom. Such motion in the ketol (1a) would tend to force the migrating hydride upwards into the bulk of the bicyclic molecule, where it would suffer non-bonded repulsions, thus tending to raise the energy barrier of the hydride migration process.

The role of the alkali metal in these processes is not clear. To date we have employed only Na$^+$, but Lansbury [1e] used a variety of alkali metal ions and found small but significant differences in activation energy, with the lithum alkoxide being least and caesium alkoxide the most effective.

We note that activation energies for the hydroxyketone rearrangements are much higher than those observed for 1,4- and 1,5-H$^-$ shifts in carbocations,[25]

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* For a discussion of the effect of small poorly resolved couplings on n.m.r. rate measurements, see T. Drakenburg and R. E. Carter, *Org. Magnetic Resonance*, 1975, **7**, 307.

[20] A. Verley, *Bull. Soc. chim. France*, 1925, **37**, 537, 871; 1929, **41**, 788.

[21] J. Hach, *J. Org. Chem.*, 1973, **38**, 293.

[22] V. J. Shiner and D. Whittaker, *J. Amer. Chem. Soc.*, 1970, **91**, 394.

[23] (*a*) 'Those elementary reactions will be favoured which involve least change in atomic position and electronic configuration': F. O. Rice and E. Teller, *J. Chem. Phys.*, 1938, **6**, 489; 1939, **7**, 199; (*b*) J. Hine, *J. Org. Chem.*, 1966, **31**, 1236.

[24] (*a*) H. B. Burgi, J. M. Lehn, and G. Wipff, *J. Amer. Chem. Soc.*, 1974, **96**, 1956; (*b*) H. B. Burgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, 1974, **30**, 1563; (*c*) H. B. Burgi, J. D. Dunitz, and E. Shefter, *J. Amer. Chem. Soc.*, 1973, **95**, 252.

[25] M. Saunders and J. J. Stofko, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 252.

presumably owing to the higher ground state energy of the cations. It is possible that, although *absolute* values may differ for the two classes of reaction, a proportionality would be maintained between the activation energies, and hence relative ease of hydride migration in hydroxy-ketones could give useful information on relative ease of hydride shifts in the corresponding carbocations.

Finally, it remains to be seen whether it would be possible to construct a system which on ionisation would give a symmetrical (or nearly symmetrical) resonance-stabilised hydride-bridged alkoxide. Such a system would be predicted to exhibit low pK_a.

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 157G and 457G spectrophotometers. Ambient temperature n.m.r. spectra were determined for solutions in carbon tetrachloride with a Perkin-Elmer R32 spectrometer (90 MHz; tetramethylsilane as internal standard). The mass spectra were determined with an A.E.I. MS902 (P.C.M.U., Harwell) and a Perkin-Elmer RMU-7 instrument (Glenochil). Optical rotations were determined with a Perkin-Elmer 141 digital polarimeter. Analytical g.l.c. was performed with a Perkin-Elmer F11 instrument employing either a 2 m × $\frac{1}{8}$ in stainless steel column [packings 5% FFAP and $2\frac{1}{2}$% OV-1 Silicone on Chromosorb-G (80—100 mesh) at 150 °C; carrier gas, nitrogen; inlet pressure, 20 lb in^{-2}] or a 50 m capillary with TCEP as stationary phase. Light petroleum refers to the fraction of b.p. 40—60 °C. For t.l.c. Silica GF_{254} was used for both analytical and preparative separations.

7-Methylenebicyclo[3.3.1]nonan-3-one (2a) was prepared by published methods.[4] 1-Methyl-7-methylenebicyclo-[3.3.1]nonan-3-one (2b) was a gift from Dr. M. A. McKervey (Queen's University, Belfast).[5]

7-*Methylenebicyclo*[3.3.1]*nonan*-3-exo-*ol* (3a).—A solution of the methylene ketone (2a) (0.98 g) and aluminium isopropoxide (3.0 g) in toluene (25 ml) was heated under reflux for 15 h. The mixture was then cooled, aqueous 10% sodium hydroxide (10 ml) was added, and the mixture was stirred for 2 h at room temperature. The layers were then separated and the aqueous layer was further extracted with ether (10 ml). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure to leave an oily residue, which was adsorbed on a short column of silica gel from light petroleum. Elution with the same solvent first removed toluene and non-planar material; further elution with ether, evaporation of the eluate, and sublimation of the waxy residue under reduced pressure yielded the *alcohol* (3a) as a white crystalline solid (0.62 g), m.p. 88—90° (sealed tube); $\nu_{max.}$ (CCl_4) 3 624, 3 071, 1 663, 1 645, 1 467, 1 448, and 1 175 cm^{-1}; M^+ 152; δ_H (CCl_4) 1.1—2.5 (14 H, unresolved), 4.55 (1 H, t of t, J 11 and 4.5 Hz), and 4.65br (2 H, s).

1-*Methyl*-7-*methylenebicyclo*[3.3.1]*nonan*-3-exo-*ol* (3b). This *alcohol* (3b) (0.57 g) was prepared from the ketone (2b) (1.0 g) by the above route; m.p. 36.5° (Found: *m/e*, 166.135 8. $C_{11}H_{18}O$ requires *M*, 166.135 8); $\nu_{max.}$ (CCl_4) 3 615, 3 540, 2 910, 1 645, 1 480, 1 241, 1 010, 862, and 851 cm^{-1}; δ_H (CCl_4) 0.9 (3 H, s); 1.0—2.5 (11 H, complex unresolved m), 3.35br (1 H, s), 4.39 (1 H, t of t, J 11 and 4.5 Hz), and 4.6br (2 H, s).

7-exo-*Hydroxybicyclo*[3.3.1]*nonan*-3-*one* (1a).—The methylene alcohol (3a) was oxidised by the method of Pappas *et al.*[9] Ozone was passed into a cooled (−80 °C) solution of (3a) (0.5 g) in methanol (10 ml) and methylene chloride (10 ml) until the blue colour persisted. The excess of ozone was then flushed from the mixture with dry nitrogen. Dimethyl sulphide (2 ml) was then added and the solution was allowed to come to room temperature and set aside overnight. Removal of the solvent under reduced pressure gave an oil which was adsorbed on a short silica gel column from chloroform. Subsequent elution with chloroform–methanol (99 : 1 v/v) gave the *ketol* (1a), which crystallised from light petroleum in needles (0.32 g), m.p. 157—158° (sealed tube) (Found: *m/e*, 154.099 3. $C_9H_{14}O_2$ requires *M*, 154.099 4); $\nu_{max.}$ (CCl_4) 3 610, 3 450, 2 915, 1 710 (split) 1 465, 1 445, 1 410, 1 349, 1 230, 1 110, 1 057, 960, and 930 cm^{-1}; δ_H ($CDCl_3$) 1.2—2.4 (8 H, complex m), 2.49br (4 H, s), and 3.83 (1 H, t of t, J 11 and 4.5 Hz).

7-exo-*Hydroxy*-1-*methylbicyclo*[3.3.1]*nonan*-3-*one* (1b).—The ketol (1b) (0.22 g) was prepared from the methylene alcohol (3b) (0.5 g), by application of the above ozonolysis conditions, as needles (from ether–petroleum), m.p. 95—96° (sealed tube) (Found: *m/e*, 168.115 1. $C_{10}H_{16}O_2$ requires *M*, 168.115 0); $\nu_{max.}$ (CCl_4) 3 615, 3 450, 2 915, 1 710, 1 450, 1 410, 1 355, 1 225, 1 115, 1 025, and 905 cm^{-1}; δ_H ($CDCl_3$) 1.05 (3 H, s), 1.05—2.7 (11 H, unresolved m), 3.2br (1 H, s), and 3.62 (1 H, t of t, J 11 and 4.5 Hz).

Deuteriation of the Ketol (1a).—The ketol (1a) was dissolved in dioxan–D_2O (50% v/v) in which sodium (100 mg) had been dissolved. The solution was degassed with nitrogen then sealed in an ampoule and heated at 100—110 °C for 72 h. The cooled mixture was extracted with ether, and the extracts dried (Na_2SO_4) and evaporated to give the deuteriated ketol. Mass spectral analyses showed $^2H_6$ 2.1%, $^2H_7$ 12.3%, $^2H_8$ 85.6%, all other ^2H_n <0.2%.

Polarimetric Experiments.—Stock solutions of the ketol (1b) (56 mg ml^{-1}) and potassium t-butoxide [1.71M in t-butyl alcohol (freshly distilled from calcium hydride)] were prepared and stored under nitrogen. Solutions for polarimetry were prepared by mixing equivalent amounts of the stock solutions and making up the total volume to 2 ml with t-butyl alcohol, before transferring the solution by syringe to a thermostatted (35 °C) polarimeter cell (10 cm length; 2 ml volume). Times of mixing and transference varied from 2 to 5 min. No optical activity was detected at 365, 436, or 578 nm. A small rotation was observed at 546 nm.

Recovery of the ketol (1b) by dilution of the solutions with water and extraction with chloroform gave material which was optically inactive, but otherwise unchanged from the starting material.

N.m.r. Experiments.—Solutions were prepared under nitrogen by dissolving weighed amounts of the ketol (1a) in $(CD_3)_2SO$ (0.15 ml). An equivalent amount of a solution of sodium hydride (1.21M) in $(CD_3)_2SO$ was added, and the total volume of solution was made up to 0.5 ml with $(CD_3)_2SO$. The solutions for the variable temperature studies contained 80 and 120 mg ml^{-1} of (1a), respectively. A capillary of benzene was used as external reference standard and lock signal.

We thank the S.R.C. and NATO for support of this work, and W. T. Moodie for technical assistance.

[6/184 *Received*, 28*th January*, 1976]