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PREPARATION, CHARACTERIZATION AND REARRANGEMENT PATHWAYS OF 10-ALKYL-9-DECALYL CARBOCATIONS

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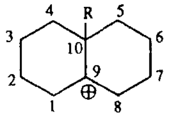
The preparation and characterization of 10-methyl- and 10-ethyl-9-decalyl cations is described. Both cations undergo a rapid, degenerate 10,9-alkyl shift, but the ethyl group migration is about 700 times slower at −120 °C than that of the methyl group. This preference is opposite to that usually found for alkyl migration rates and, on the basis of MO calculations, it is suggested that a conformational interchange may be the rate-determining step. Both cations irreversibly rearrange at about −100 °C, giving in the methyl case the rearrangement cascade 10-methyl-9-decalyl → *cis*-1-methyldecalyl → *trans*-1-methyldecalyl → *trans*-2-methyldecalyl. Each of these rearrangement ions was independently prepared and characterized by NMR spectroscopy. One can rationalize the initial formation of the less stable *cis* ring junction on the basis of suprafacial hydride and methyl shifts. Attempts to add molecular hydrogen to the 10-methyl-9-decalyl cation were unsuccessful.

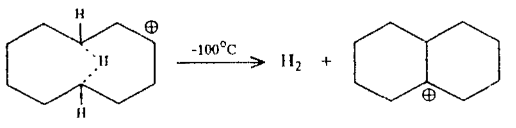
INTRODUCTION

There have been a number of solvolysis–acid catalysis studies of the 9-decalyl cation **1**,[1] but in the stable ion area only the parent cation **1a** has so far been reported.[2]



1a R=H
1b R=CH_3
1c R=CH_3CH_2

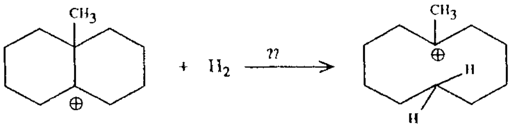
In addition to starting with 9-decalyl precursors, the parent 9-decalyl cation can also be produced[3] from the cyclodecyl cation **2** in a unique organic reaction involving the loss of molecular hydrogen at −100°C, as shown in equation 1. [The observable cyclodecyl cation is actually not structure **2**, but a 1,5-μ-hyrido-bridged species.[3] We believe that this 1,5-bridged species is in rapid equilibrium with a small concentration of **2**, the latter then undergoing the reaction shown in equation (1). Thus the actual rate of H_2 loss from **2** is even greater than that indicated by the overall reaction kinetics.]



(1)

2 **1a**

Although this particular reaction proceeds to the right, we considered that the corresponding 10-methyl-9-decalyl cation **1b** might add molecular hydrogen to form the tertiary 1-methyl-1-cyclodecyl cation **3**, a known species,[3b] the driving force being the formation of the tertiary cation in this case [equation (2)].



(2)

1b **3**

In order to study this possible reaction, it was necessary to prepare a long-lived cation **1** (R = alkyl). This paper reports on the preparation and characterization of two 10-alkyl-9-decalyl cations **1b** (R = CH_3) and **1c** (R = CH_3CH_2). There are several facets to this study, including the question of the actual structure of a presumed **1b** or **1c**, the question of degenerate rearrangements and the question of thermal stability, i.e. possible irreversible structural rearrangements. The last aspect is particularly importance since the H_2 addition reaction [equation (2)], could easily require temperatures higher than the −100 °C needed for the

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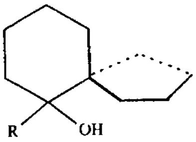
process shown in equation (1). [If the activation energy profile for equation (2) followed that for the reverse reaction in equation (1), i.e. a larger barrier in the backward direction due to the exothermicity of the reaction, then one would expect that a temperature higher than − 100 °C would be needed.]

RESULTS AND DISCUSSION

The organic starting materials for the cation preparations were the known spirodecanols **4b** or **4c**, both easily obtainable from the corresponding ketone. Addition of **4b** to 1 : 1 FSO_3H–SbF_5 in SO_2ClF solvent at *ca.* − 125 °C leads to a light yellow solution giving a ^1H NMR spectrum showing three peaks (8 : 8 : 3 ratio), the two larger peaks being broad. The corresponding ^{13}C NMR spectrum shows four peaks (Table 1) in a 2 : 4 : 1 : 4 area ratio. The lowest field ^{13}C peak (of area 2) is broad.



4b $R=CH_3$
4c $R=CH_3CH_2$

In principle, there are three easily formed [by facile Wagner–Meerwein (WM) shifts] tertiary carbocations deriveable from **4b**, cations **1b, 5** or **6** (or conceivably mixtures of these in rapid equilibrium). However, on ring strain arguments, one can confidently dismiss cation **6** from further consideration (for a discussion see Ref. 1e). There have been several studies[4] on the acid-catalysed rearrangement (dehydration) of **4b**, showing that under thermodynamic conditions alkene **7** is the sole product.

Clearly, a neutral alkene derivative of **1b** is therefore more stable than a neutral alkene derivative of **5**. Perhaps even more relevant is a study[5] on the superacid reaction of a benzyl spirodecanol **4** (R = benzyl), which also yields a product derivable from the rearranged 9-decalyl cation rather than a product derived from the initially formed spirodecalyl cation. We were therefore reasonably confident before starting this work that the cation which we would obtain from alcohol **4b** would

Table 1. ^{13}C NMR chemical shifts[a] for the cations

Cation	Position											
1b[b]	C-1	C-4	C-5	C-8	C-2	C-3	C-6	C-7	C-9	C-10		CH_3
	49·3				26·9				202·2			32·5
1c[c]	C-1	C-8	C-2	C-7	C-3	C-6	C-4	C-5	C-9	C-10	CH_2	CH_3
	53·3		28·5		19·2		35·5		337·8	69·5	41·4	8·8
8[d]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10		CH_3
	323·4	53·1	36·6	31·0	29·0	27·8	23·2	19·4	70·8	43·0		43·7
9[e]	317·7	59·8	48·9	36·2	33·6	25·6	24·8	23·2	78·2 or 76·7	76·7 or 78·2		38·1
10[f]	64·4	324·9	58·1	39·3	34·5	31·6	25·8	25·5	50·3	39·9		43·2

[a] δ Values in ppm relative to internal $CFCl_3$ at 117·9 ppm.

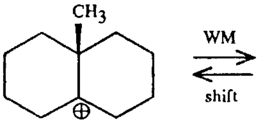
[b] Data reported are for a temperature of − 112 °C.

[c] Data are for a temperature of − 142 °C.

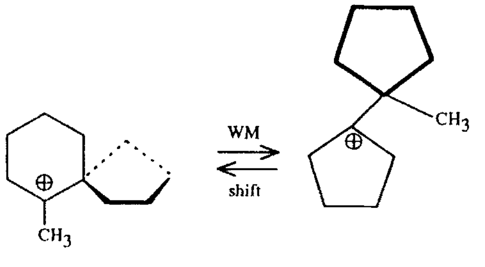
[d] Data for a temperature of − 120 °C. A set of minor peaks are also present, two of which are clear of the major peaks and which also have temperature-dependent chemical shifts. At − 120 °C, δ 287·4 and 100·6; at − 115 °C, 285·8 and 101·9; at − 110 °C, 284·4 and 103·1; and at − 105 °C, 282·6 and 104·4.

[e] Data are for a temperature of − 120 °C; the peaks at 317·7 and 78·2 are reasonably temperature dependent, C-1 gradually changes from 318·0 at − 131 °C to 313·5 at − 70·4 °C, while the other peak goes from 77·7 to 81·8 over the same range.

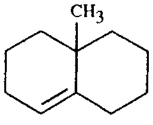
[f] Data are for a temperature of − 90 °C. The peaks for C-4 and C-10 are temperature dependent, C-4 moves from 38·0 to 40·6 on going from − 110 °C to − 60 °C, while C-10 moves from 48·7 to 52·1. This downfield shift of *both* carbons is indicative of an equilibrium between two carbocation conformers, one involving C–H hyperconjugation and one involving C–C hyperconjugation (see Ref. 14 for a detailed discussion involving the related cyclohexyl and 2-adamantyl carbocations).



1b



5 **6**



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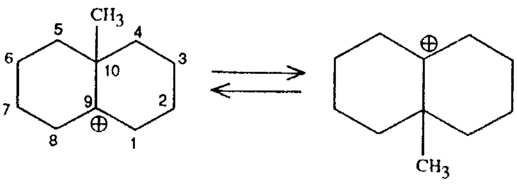
have the structure **1b**, and this was confirmed as discussed in the next section.

Degenerate alkyl shift in 1b and 1c

The simplicity of the observed ^1H and ^{13}C NMR spectra indicate that at $-120\,^\circ C$, cation **1b** is undergoing a rapid, degenerate, 10,9-methyl shift. (A hypothetical cation **5** could also plausibly give such a spectrum via a very rapid $\mathbf{5} \rightleftharpoons [\mathbf{1b} \rightleftharpoons \mathbf{1b}'] \rightleftharpoons \mathbf{5}'$ sequence. Note that in the parent decalyl cation **1a**, the corresponding spirodecalyl species would be a secondary cation, so there is no possible ambiguity in the structure of **1a**). The parent 9-decalyl cation **1a** has been prepared previously[2] and shows a similar 'simplified' spectrum, due in this case to a very rapid 10,9-hydride shift. In contrast to **1a**, there is already NMR line broadening of the lowest field peak in the ^{13}C NMR spectrum of **1b** at $-120\,^\circ C$. This peak can be assigned to the averaged C-9–C-10 carbons and is broadened most because the 'frozen-out' positions for C-9 and C-10 are expected to differ by about 5500 Hz on our instrument, a much larger separation than one would expect for the other averaging positions. The methyl carbon should of course experience no NMR change since it occupies an identical position in both **1b** and **1b′**.



1b **1b′**

On cooling the sample below $-120\,^\circ C$, one sees a further broadening of the C-9–C-10 peak, and eventually this peak 'disappears' into the baseline noise ($-139\,^\circ C$). At the latter temperature, the averaged C-1, -8, -4, -5 and C-2, -3, -6, -7 peaks are also becoming broad. At $-150\,^\circ C$, the experimental lower limit, one can just begin to observe 'frozen-out' peaks as very broad resonances at δ *ca* 320–325 ppm (C-9) and δ 65–70 ppm (C-10). Unfortunately, the remaining high-field carbon peaks are very broad and overlapped, and it is impossible even to count the number involved (a 'frozen-out' structure **1b** should have seven peaks in total if one assumes that the cation has C_2 or C_s symmetry).

Fortunately, and surprisingly, the 10-ethyl cation **1c** was found to undergo a much slower 10,9-shift. At $-118\,^\circ C$, the averaged C-9–C-10 peak in the ^{13}C NMR spectrum of this ion is not even visible, and the C-1, -8, -4, -5 and C-2, -3, -6, -7 peaks are considerably broadened compared with the unchanged pair of ^{13}C peaks from the ethyl group. One begins to see the decoalesced spectrum at $-133\,^\circ C$ and by $-143\,^\circ C$ eight distinct resonances are observed (equivalent to seven for **1b**). This 'frozen-out' spectrum clearly fits structure **1c** since a 'frozen-out' spirodecyl cation would have shown ten peaks. We can conclude, therefore, that it is possible to prepare both the 10-methyl- and 10-ethyl-9-decalyl cation structures as observable long-lived species.

A standard NMR line-broadening analysis of the 10,9-degenerate shift in both **1b** and **1c** leads to activation free energy $\Delta G^{\ddagger}$ values of 4·2 and 6·2 kcals mol^{-1}, respectively (1 kcal = 4·184 kJ). At $-120\,^\circ C$, this corresponds to a rate difference of about 700 favouring the methyl migration. This observation is unusual because numerous other migratory aptitude measurements, under stable carbocation conditions, favour ethyl over methyl, and one might therefore suppose that the alkyl migration may not be the rate-determining step. [For an extensive review, see Ref. 6. As a referee has pointed out, there are also some published examples where methyl migration is faster than ethyl. Two points should be kept in mind in evaluating such results. (a) Some overall rearrangements, e.g. pinacol–pinacolone type, consist of several steps. Various protonation or conformational equilibria prior to the rate-determining step can obviously influence the measured methyl vs. ethyl migratory aptitude. (b) Most such studies involve irreversible processes and the transition state is not symmetrical. The methyl vs ethyl migrating preference depends on the geometric and electronic details of the originating site and the migrated site. Stable ion conditions are helpful in allowing one to have symmetrical transition states and in reducing the number of pre-rate-determining equilibria.]

There are several discussions in the solvolysis–acid catalysis literature which postulate that one might have *cis*-like and *trans*-like conformations for a 9-decalyl cation intermediate,[1] and similar discussions also apply to the 9-decalyl radical.[7] Conceivably, in one of these conformations, the 10,9-alkyl shift would not be favourable and one might then have to have a rate-determining conformational change prior to the actual shift. We have therefore carried out geometry optimized MO calculations to see if these might provide some insight into the matter. Eight input conformations of **1a** were initially considered for optimization at the semi-empirical MINDO/3, MNDO and AM1 levels,[8] including a *trans*-like geometry, a *cis*-like geometry (four versions) and diboat geometry (three versions). The results can be summarized as follows: (1) the *trans*-like geometry was the most stable conformer in all cases; (2) the *cis*-like geometries all optimize to structures with one nearly undistorted chair and one half-chair (half-boat) ring; one can optimize structures with this half-chair in various conformations and we have used the lowest energy of these forms as input for the subsequent *ab initio* STO-3G calculations (see later); (3) all diboat structures optimize normally, but the W-shaped conformation, viewing trough the C-9–C-10 bond, is the lowest in energy of these three (compared with the corresponding ‘U’ and ‘sickle’ conformers), as would be expected.

The *trans*-like, *cis*-like and W-diboat (twist-boat) conformers were then optimized at the *ab initio* STO-3G level[9] and the energies of these are listed in Table 2. The resulting conformational structures are depicted in Figure 1.

Returning to the original question of why a 10-methyl shift in **1b** is faster than the 10-ethyl shift in **1c**, one can propose the possibility shown in equation (3).

$$C_1 \underset{\text{determining}}{\overset{\text{rate}}{\rightleftharpoons}} \left[C_2 \underset{\text{shift}}{\overset{\text{alkyl}}{\rightleftharpoons}} C_2' \right] \rightleftharpoons C_1' \qquad (3)$$

Such a scenario requires that the 10,9-alkyl shift would not take place in the most stable conformer C_1, a proposal which actually agrees fairly well with the MO calculations. The *trans*-like structure shown in

Table 2. Energies of STO-3G-optimized 9-decalyl cation conformers

Conformer	STO-3G energy (hartree)	Relative energy (kcal mole^{-1})
trans-Like	−383·846676	0
cis-Like	−383·846579	0·061
Diboat	−383·839118	4·74

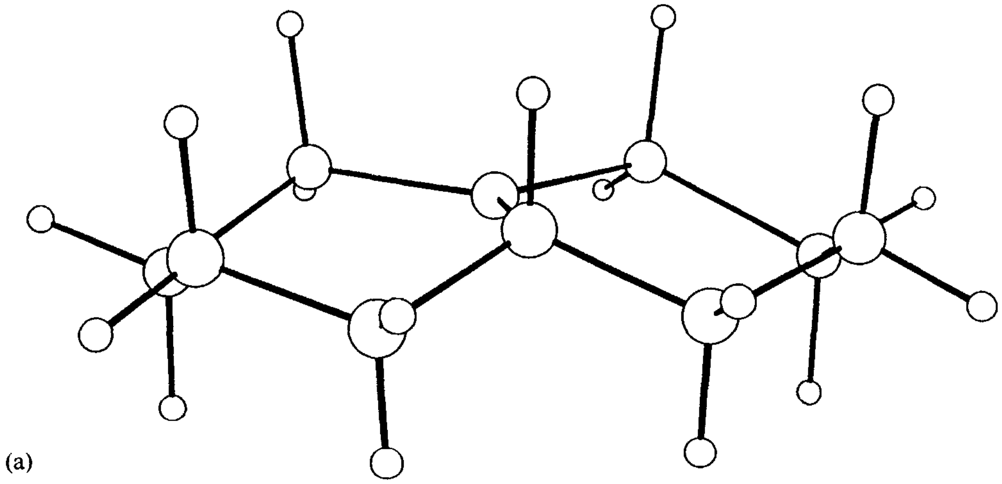


Figure 1. STO-3G-optimized conformations of the 9-decalyl cation. (a) *trans*-like conformation; (b) *cis*-like conformation; note the near-normal cyclohexane ring on the left; (c) ditwist-boat conformation

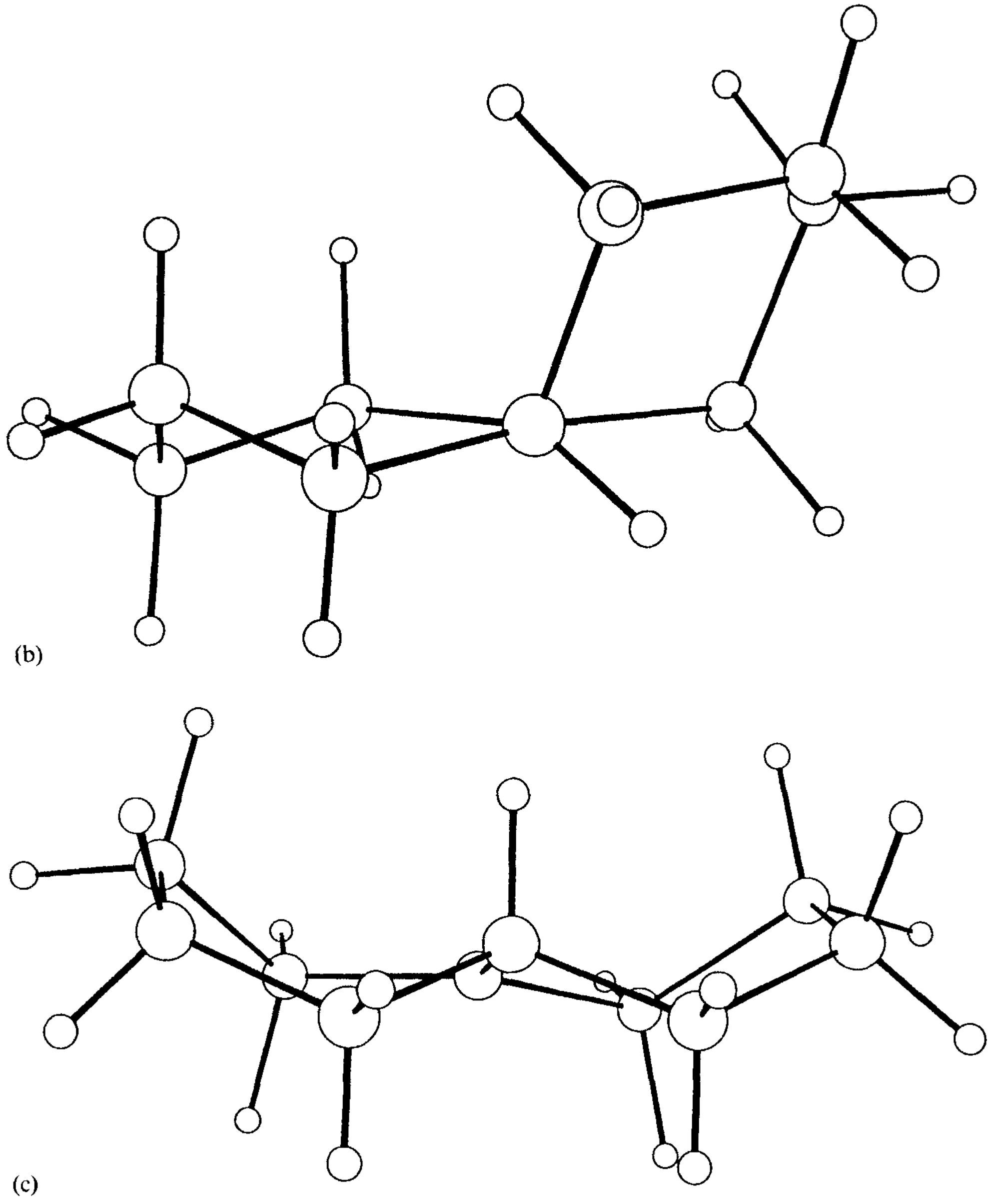


Figure 1. (*Continued*)

Figure 1 (the most stable) is not an appropriate conformation for the 10,9-alkyl shift because one would require an improbable simultaneous double chair–chair inversion to accompany the alkyl shift. The *cis*-like geometry (Figure 1) has a poor overlap angle between the C^+ centre and the migration group (47·7°) and one still requires one chair–chair inversion to accompany the migration. The diboat conformation is ideal from the overlap angle viewpoint and requires no significant ring conformational changes during the shift. However, the calculated energy of this conformation is relatively high, as might have been expected. In our view, either of these latter conformations could represent C_2 in equation (3) but neither is a completely satisfactory choice based on our computational results.

The *ab initio* computations involve only cation **1a** but we have computed **1b** and **1c** in various conformations (and dihedral angles for the ethyl group) at the

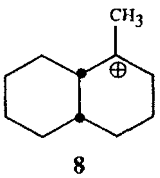
MNDO and MINDO/3 levels, and generally the *trans*-like geometry is the most stable, with *cis*-like next and the diboat form the least stable. Further, there are no particularly noticeable differences in the conformational preferences of **1b** and **1c**. Our actual experimental results would require, of course, that an ethyl group would increase the conformational interchange barrier compared with a methyl substituent, a situation which does not seem inherently unreasonable.

We have no way of interpreting the cation NMR spectra in terms of a particular conformation, other than the experimental observation that one has at least an averaged C_2 or C_s symmetry even at $-150\,^{\circ}$C, implying that even if the cation conformations are unsymmetrical, then very low barriers are involved in these symmetrization processes. From the computations, the *trans*-like conformer shown in Figure 1 has virtual C_s symmetry (the *trans*-like conformer was originally optimized under a C_s symmetry constraint, and later with C_1 symmetry; virtually no difference in geometry or energy was found), so the idea that this conformation could be the stable ground state is in excellent agreement with the $-150\,^{\circ}$C NMR results.

Thermal stability of cations 1b and 1c

At about $-105\,^{\circ}$C, the ^{13}C NMR spectrum of cation **1b** starts to show a number of small rearrangement ion peaks. The first-formed cation, which we shall call A, is itself further rearranged to B. The rates of **1b** → A and A → B are competitive so that a solution of pure A is never observed. At about $-70\,^{\circ}$C, cation B is transformed to C, although there is some indication from the spectra that this reaction does not go fully to completion. At about $-50\,^{\circ}$C, the ^{13}C NMR peaks for C begin to disappear, indicating that a general decomposition is underway.

The identities of A, B and C were established by preparing the pure cations from their corresponding alcohols (see Table 1 for the NMR data). Cation A is the 1-methyl-*cis*-decalyl cation **8**, B is the corresponding *trans* isomer **9** and C is the 2-methyl-*trans*-decalyl cation **10**.



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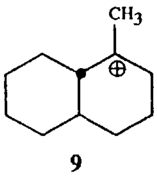

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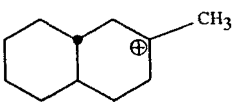

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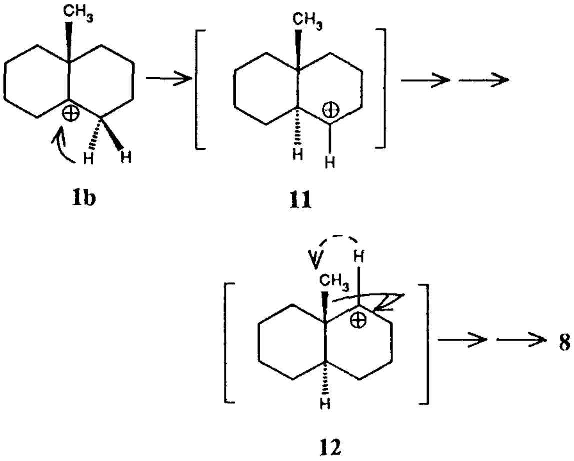
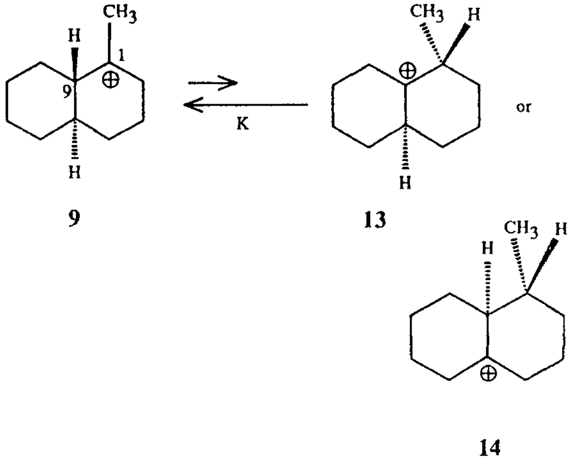
The initial formation of **8** from **1b** is of interest, and is consistent with the following mechanism, in which one would expect, on energetic grounds, a preferential *trans* ring junction in an intermediate secondary cation **11**. The more immediate precursor to **8** is secondary cation **12**, from which the suprafacial migration of the methyl group and back migration of the hydride ultimately reforms the cis ring junction of **8**.

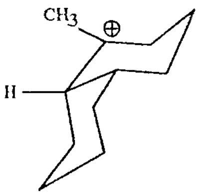


The ^{13}C NMR data listed for cations **8** and **9** (Table 1) show several interesting features. The *trans* structure **9** appears to be in very rapid equilibration (i.e. average NMR peaks) with a small amount of a 9-decalyl cation (presumably **13** or **14**). This conclusion is based on a noticeable temperature dependence for the C$^+$ carbon and *one* of the CH carbons. As one goes to higher temperatures in the ^{13}C NMR spectrum, the C$^+$ peak moves to higher field, while the CH peak moves a similar amount to lower field, an expected result if the Boltzmann population of **13** or **14** increases. One can

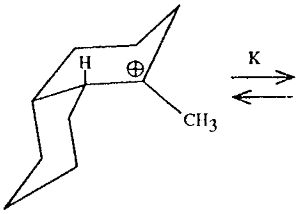


estimate that K for **9**/**13** or **14** is in the range 50–200 at $-100\,^{\circ}$C, $\Delta G = 1{\cdot}3$–$1{\cdot}8$ kcal mol^{-1} (obtained from a van't Hoff plot; the large uncertainty arises because the 'frozen-out' ^{13}C chemical shifts for **9** and **13** or **14** have to be estimated). One is not surprised that the transformation **9** $\rightleftharpoons$ **13** or **14** is very fast because molecular model studies indicate that there is a favourable orientation of the axial hydrogen at C-9 in **9** with the C^{+} orbital at C-1.

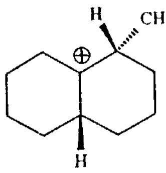
The *cis* ion **8** is also interesting because the major isomer of this does not show a behaviour similar to **9**, i.e. there are no corresponding temperature-dependent chemical shifts for the C^{+} or CH carbons. However, in the ^{13}C NMR spectrum of **8**, one sees an additional set of small peaks ($K = 7 \pm 2$) which we assign to the other chair–chair conformer of this *cis*-decalyl carbocation structure, and these small peaks do show the same NMR dynamic equilibrium behaviour as in **9**, but to an even greater extent. Based on the known activation energy barrier for a *cis*-decalin chair–chair inversion (perhaps the best model compound for this estimation would be *cis*-1-decalone, measured by Blunt *et al.*[10]), one would expect to freeze out this conformational process on the NMR time scale at $-100\,^{\circ}$C. From the NMR results observed, the major conformer of **8** must correspond to the configuration where the hydrogen at C-9 is equatorial, i.e. structure **8a**. In this structure, this hydrogen is not well aligned for a 1,2-hydride shift. However, the other chair–chair isomer **8b** has this hydrogen in an axial orientation (as in **9**), where a very rapid 1,2-hydride shift is possible. The observed equilibrium constant for **8b** $\rightleftharpoons$ **15** or **16** is *ca* 7 at $-115\,^{\circ}$C, $\Delta G \approx 700$ kcal mol^{-1} (obtained from a van't Hoff plot using estimated ^{13}C shifts for the 'frozen out' structures **8b** and **15** or **16**; we assume that **8b** is the dominant species but the spectral observations themselves could equally well be interpreted in the opposite sense). The smaller K value for **8b** $\rightleftharpoons$ **15** or **16** compared with **9** $\rightleftharpoons$ **13** or **14** is expected because a *cis*-decalin ring structure is obviously less stable than the trans isomer (i.e. **8** → **9**), whereas the 9-decalyl cation structures **15** or **16** and **13** or **14** are probably comparable in energy.



8a



8b



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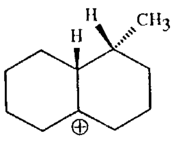

15 **16**

The existence of these equilibria shows that a 9-decalyl cation structure, in spite of the apparent bridgehead ring strain, is only of the order of $0{\cdot}5$–2 kcals mol^{-1} less stable than the unstrained *cis* or *trans* 1-yl cation isomers.

The ethyl-substituted cation **1c** also rearranges rapidly at $-100\,^{\circ}$C and the ^{13}C NMR pattern observed is similar to that seen for **1b**, i.e. *cis*-1-ethyl is formed first, followed closely by the *tans*-1-ethyl isomer. The spectra at higher temperatures are not as clean as for the **1b** rearrangement.

Having shown that cation **1b** could be prepared, we attempted to add H_2(g) to this species at $-125\,^{\circ}$C, with totally negative results. At slightly higher temperatures in the presence of H_2(g), the only observed products were the rearrangement ions **8** and **9**. Therefore, although cation **1b** is indeed observable, the facile internal rearrangements to **8** and **9** are obviously faster than the rate of any possible H_2 addition reaction [using very high pressures of H_2(g), one might hope in future to increase markedly the rate of the H_2 addition reaction].

EXPERIMENTAL

Spirodecanol **4b** was prepared as reported[11] and spirodecanol **4c** was obtained from Dr J. M. Coxon, Canterbury University, Christchurch, New Zealand. *trans*-1-Methyl-1-decalol was prepared as described.[12] NMR spectra of neutral compounds were obtained on a Bruker WH-90 or Varian XL-200 spectrometer. Only ^{13}C data are reported (s = singlet; d = doublet; t = triplet).

cis-*1-Methyl-1-decalol.* This alcohol was prepared from *cis*-1-decalone and methyllithium. The crude alcohol product always contained some ketone (enolization), so purification by chromatography on neutral alumina was required (elution with pentane–diethyl ether). The chromatographic residue was then microdistilled to yield a clear oil.

Calculated for $C_{11}H_{20}O$: C, 78·5; H, 12·0%. Found: C, 78·5; H, 12·3%. ^{3}NMR: 72·93 (s); 47·82 (d); 34·97 (t); 34·13 (d); 32·01 (t); 27·49 (CH_3); 26·53 (t); 24·89 (t); 23·51 (t); 20·93 (t); 20·87 (t). Based on the ^{13}C NMR spectrum, this material is a single stereoisomer and can be assigned the 1α-ol,9β,10β stereochemistry. The other alcohol epimer has been reported.[13]

trans-*2-Methyl-2-decalol.* From the ketone (1·2 g, 7·9 mmol) in 30 ml of diethyl ether and 1·3 M methyllithium (6·2 ml, 8·1 mmol) there was obtained, after work-up, 1·2 g of a colourless oil which solidified on standing. This solid was distilled (bulb-to-bulb), chromatographed (neutral alumina, pentane–diethyl ether) and recrystallized from pentane to a constant m.p. 83–85 °C.

Calculated for $C_{11}H_{20}O$: C, 78·5; H, 12·0%. Found: C, 78·8; H, 12·4%. ^{13}C NMR: 70·00 (2); 46·32 (t); 42·62 (d); 38·80 (t); 38·15 (d); 33·76 (t); 33·46 (t); 31·54 (CH_3); 29·31 (t); 26·63 (t); 26·33 (t). These data (CH_3 at δ 31·54) are indicative of the 2α-ol,9β,10α stereochemistry.

Carbocation preparations. These preparations were carried out as described previously[14a] using the alcohol in 1 : 1 FSO_3H–SbF_5 in SO_2ClF solvent, or the *in situ* prepared chloride using SbF_5 in SO_2ClF or SO_2ClF–SO_2F_2 solvent. Because of the thermal instability of the cations, most preparations were conducted at *ca* −130 °C. ^{13}C NMR spectra were obtained at a number of different temperatures on a Bruker WH-90 spectrometer, employing a ^{19}F lock, and employing the same temperature calibration and referencing as described previously. Attempted hydrogen 'addition' experiments involving cation **1b** were carried out at pre-set low temperatures (slush baths) by bubbling precooled H_2 gas into the carbocation solution for set periods of time. ^{13}C NMR spectroscopy was used to monitor this reaction (non-reaction). The NMR line broadening observed in the ^{13}C NMR spectra of **1b** and **1c** was analysed using a standard two-site exchange (C-9 and C-10) computer program to generate spectra which matched the experimental ones. Van't Hoff plots were made using the relationship $\partial(\ln K)/\partial(1/T) = -\Delta H/R$, where K was obtained by estimating chemical shifts for the 'frozen-out' structures concerned and comparing these with the position of the averaged chemical shift, the latter obtained at a number of different temperatures.

Computations. The parent 9-decalyl cation **1a**, the 10-methyl **1b** and 10-ethyl **1c** ions were initially computed at the semi-empirical level, as described in the text. All geometries were optimized at the PRECISE level for MINDO/3 and MNDO, while AM1 used the default gradient optimization of the Gaussian protocol,[9] assuming in all cases no symmetry (C_1) for the cations. The *trans*-like and diboat (twist-boat) conformers optimized fairly well in most cases, but the *cis*-like conformer presented problems in that different input geometries resulted in slightly different final geometries. However, in all cases one ring is a fairly normal 'chair' and the other ring is very distorted, the latter distortion varying significantly with the input geometry used. After a number of different inputs, we used the lowest energy optimized structure as an input for the STO-3G *ab initio* computations, but we cannot be entirely certain that this corresponds to the global minimum for the *cis*-like structure. For the 10-ethyl cation **1c**, the dihedral angle of the ethyl group was also varied in the inputs. The results of these calculations are qualitatively summarized in the text. Any specific computational result (energy, geometry, etc.) is available from the authors. The STO-3G computations (complete gradient optimization) were carried out with starting geometries based on the semi-empirical structures using the Gaussian 86 package.[9] Only the parent 9-decalyl cation **1a** was computed, using the three conformers described above. The structures are shown in Figure 1 and the energies are listed in Table 2. Any further results are available from the authors.

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