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A STUDY OF A NOVEL DEGENERATE CARBOCATION REARRANGEMENT OF THE 4,9-DIMETHYL-9-BARBARALYL CATION BY DYNAMIC ^{13}C AND ^{1}H NMR SPECTROSCOPY IN SUPERACID

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The 4,9-dimethyltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl (4,9-dimethyl-9-barbaralyl) cation (3) was generated from 4,9-dimethyl-9-barbaralol (5) at −135 °C in two different superacid mixtures [FSO_3H–SO_2ClF–SO_2F_2(1:6:1) and FSO_3H–SO_2ClF–SO_2F_2–$CHCl_2$ (2:10:10:1 by volume)]). Its ^{1}H and ^{13}CNMR spectra show a strong temperature dependence in the range −150 to −125 °C. The changes in band shapes with temperature show that the following exchanges take place: 4-methyl with 9-methyl, C-4 with C-9, C-1 with C-3 and C-2 with C-8. C-5, C-6 and C-7 are found not to exchange rapidly either with each other or with the other carbons in 3. The mechanism of this novel rearrangement is suggested to involve the bicyclic 2,7-dimethylbicyclo[3.2.2]nona-3,6,8-trienyl cation and the secondary barbaralyl cation 4,6-dimethyltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl as intermediates rather than 7,8-dimethyl bicyclo[3.2.2]nona-3,6,8-trienyl cation, which does not have a methyl group on the allyl cation moiety. Comparisons with rearrangement mechanisms for other barbaralyl cations were also made. The rate constant for the degenerate rearrangement of 3 is 160 s^{-1} at −140 °C, which corresponds to $\Delta G^{\neq}s$ = 26 kJ mol^{-1} (6·3 kcal mol^{-1}). At −125 °C ion 3 rearranges non-degenerately to the 1,4-bishomotropylium cation 1,8-dimethylbicyclo[4·3·0]nona, 2,4,7-trienyl (4) with $k = 3 \times 10^{-4}$ s^{-1}. A mechanism for this rearrangement and the synthesis and purification of the ion precursor 4 are also reported.

INTRODUCTION

The parent barbaralyl cation (**1**) is the cationic counterpart of bullvalene but much more reactive.[1] It is composed of the structural elements cyclopropylcarbinyl cation and two homoallylic cations superimposed on each other. The stereoelectronic composition of these elements suggests a high reactivity. The parent ion **1** and substituted barbaralyl cations have been shown to make use of several interesting pathways that are either degenerate or non-degenerate in nature. For example, NMR studies have shown that ion **1** undergoes fast degenerate rearrangements at −125 °C and also rearranges rapidly non-degenerately at −125 °C to the 1,4-bishomotropylium ion **2**. Extensive mechanistic studies have been carried out which have revealed novel reaction mechanisms for the degenerate rearrangements.[1,2]

1

2

In this paper we report a novel partially degenerate rearrangement of 4,9-dimethyltricyclo[3·3·1·0^{2,8}]nona-3,6-dien-9-yl (4,9-dimethyl-9-barbaralyl)cation (**3**), which results in temperature-dependent band shapes of the NMR bands in the range −150 to −125 °C. It is shown that **3** favours structure **3a** over **3b**. At about −125 °C ion **3** rapidly and irreversibly transforms mainly to the 1,4-bishomotropylium cation 1,8-dimethylbicyclo[4·3·0]nona-2,4,7-trienyl (**4**).

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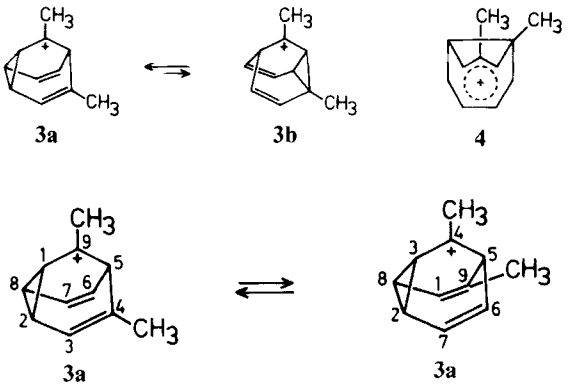


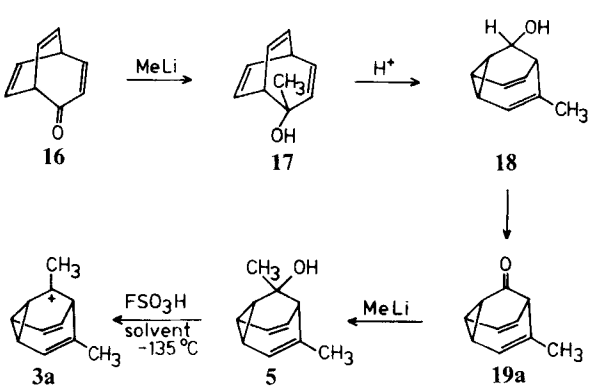
Scheme 1

The degenerate rearrangement of **3** has been shown to involve the atom exchange indicated in Scheme 1, i.e. the methyl groups exchange with each other and at the same time C-4 exchanges with C-9, C-2 with C-8 and C-1 with C-3. C-5, C-6 and C-7 have not been found to participate in any degenerate rearrangement. Possible mechanisms for the rearrangements are also discussed and the synthesis and purification of the precursor 4,9-dimethyltricyclo[3·3·1·$0^{2,8}$]nona-3,6-dien-9-ol (**5**) and the preparation of ion **3** from **5** are also reported.

RESULTS AND DISCUSSION

The ion precursor 4,9-dimethyltricyclo[3·3·1·$0^{2,8}$]nona-3,6-dien-9-ol (**5**) and the ion were prepared as outlined in Scheme 2 and the procedures are reported in detail under Experimental.

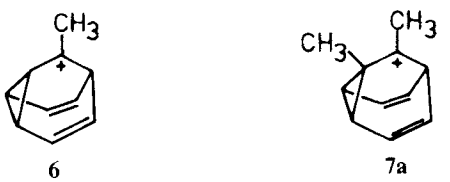
Ion **3** was synthesized directly from **5** in a 5 mm NMR tube at about $-135\,^{\circ}C$ using an ion-generation apparatus and a procedure which have previously been described in detail.[3] The ion was prepared in two different solvent mixtures, $FSO_3H-SO_2ClF-SO_2F_2$ (1:6:1) and $FSO_3H-SO_2ClF-SO_2F_2-CHCl_2F$ (2:10:10:1 by volume) and coloured the solutions pale yellow. With the latter solution it was possible to obtain NMR spectra at temperatures as low as ca $-15\,^{\circ}C$. The concentration of ion **3** was ca 0·35 M.



Scheme 2

Studies of cation 3 by ^1H NMR spectroscopy

The proton NMR spectra at 100 MHz of the 4,9-dimethyl-9-barbaralyl cation **3** show a reversible temperature dependence in the temperature range -125 to $-159\,^{\circ}C$, demonstrating the presence of degenerate rearrangements of cation **3**. However, only some of the signals display a temperature dependence, indicating that the rearrangement is only partially degenerate. At ca $-130\,^{\circ}C$ the spectrum shows only five separate bands. At $-146\,^{\circ}C$ the large band at ca 2·5 ppm has split into two new signals at 2·1 and 2·8 ppm, respectively. These signals derive from 4-CH_3 and 9-CH_3, respectively, which obviously exchange with each other. Also, the band at δ 5·1 undergoes changes on lowering the temperature to $-146\,^{\circ}C$. It splits into three signals. One (one proton) remains at about the shift of the original signal (δ 5·1) and the other two appear at δ 4·7 (one proton) and δ 5·6 (one proton), respectively. The last signal is superimposed on another two-proton band appearing at ca 5·7 ppm. This latter band and the remaining two one-proton bands at δ 6·0 and 6·2, respectively, remain essentially unchanged on varying the temperature. These results have been confirmed at 400 MHz. Assignments of the signals were made by comparison with the chemical shifts of 9-methyl-9-barbaralyl cation (**6**)[4] and 1,9-dimethyl-9-barbaralyl cation (**7a**)[4,5] (cf. Table 1).



From these results, it is clear that the degenerate rearrangements results in exchange of the methyl groups and exchange of H-1 with H-3, respectively. However, the spectra do not reveal any exchange of H-5, H-6 and H-7 either with each other or with any of the other protons. Whether H-2 and H-8 exchange or not could not be revealed, since they have closely similar resonance frequencies. Further insight into the dynamics of **3** is given by ^{13}C NMR studies.

Studies of 3 by ^{13}C NMR spectroscopy

The proton noise decoupled ^{13}C NMR spectrum at 25 MHz of **3** at $-144\,^{\circ}C$ in a Freon-containing solvent

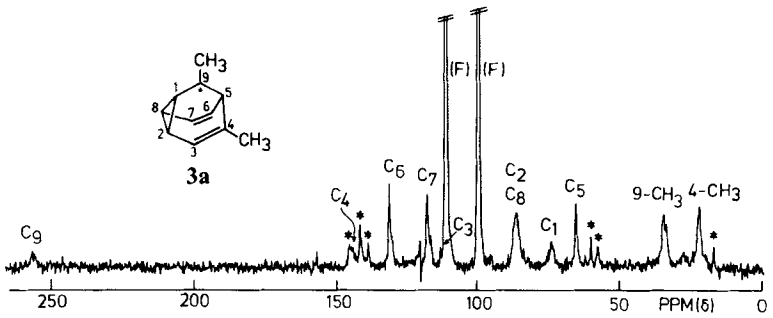
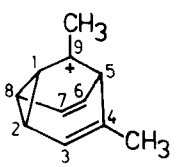
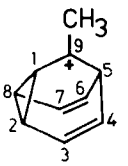
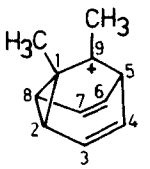


Figure 1. Proton noise decoupled ^{13}C NMR spectrum of **3** in the superacid medium FSO_3H–SO_2F_2–SO_2ClF–$CHCl_2F$ (2:10:10:1 by volume) obtained at 25 MHz at −144 °C. The peaks marked F are due to $CHCl_2F$ (δ_c 110·3, 98·6) used as the solvent and internal standard reference, and peaks marked with asterisks originate from 1,4-bishomotropylium ion **4**. Inserted is part of the spectrum obtained at −146 °C showing two separate signals from C-2 and C-8

Table 1. ^{13}C and (in parentheses) ^1H chemical shifts (ppm) of **3a**, **6**[4b,5a] and **7a**[4b,5a]

		 **3a**[a]		 **6**[b]		 **7a**[a,c]	
C-1	(H-1)	73·2	(4·71)	72·5	(4·77)	81·2	(—)
C-2	(H-2)	85·5 or 85·8	(5·69)	86·2	(5·80)	94·3	(5·75)
C-3	(H-3)	112·0	(5·69)	116·6	(5·93)	116·6	(5·93)
C-4	(H-4)	143·7	(—)	130·2	(6·18)	129·7	(6·15)
C-5	(H-5)	64·5	(5·09)	59·2	(5·21)	59·3	(5·25)
C-6	(H-6)	130·5	(6·18)	130·2	(6·18)	129·7	(6·15)
C-7	(H-7)	117·0	(5·99)	116·2	(5·93)	116·6	(5·93)
C-8	(H-8)	85·5 or 85·8	(5·69)	86·2	(5·80)	94·3	(5·75)
C-9	(—)	256·7	(—)	260·0	(—)	252·4	(—)
1-CH_3	(1-CH_3)	—	(—)	—	(—)	18·3	(1·89)
4-CH_3	(4-CH_3)	20·4	(2·10)	—	(—)	(—)	(—)
9-CH_3	(9-CH_3)	32·9	(2·79)	33·2	(2·94)	31·7	(2·77)

[a]At −144·4 °C in $CHCl_2F$ and FSO_3H–SO_2ClF–SO_2F_2.
[b]At −132 °C in CD_2Cl_2 and FSO_3H–SO_2ClF–SO_2F_2.
[c]At −130 °C in CD_2Cl_2 and FSO_3H–SO_2ClF–SO_2F_2.

is displayed in Figure 1. Nine separate signals originating from **3** are clearly distinguished. Another carbon signal is hidden in the base of the low-field Freon-carbon signal, which was shown using Freon-free solvent. Assignments of all ten peaks were made using comparison with ^{13}C NMR data for other barbaralyl cations (**6** and **7a**) (cf. Table 1). The comparison also shows that structure **3a** is the favoured isomer over **3b**, i.e. a methyl group appears to stabilize more on the ethylene moiety than on cyclopropane. This is similar to what was found for **19**[12a] and **5**. The signals in Figure 1 that do not belong to **3** originate almost exclusively from the non-degenerate rearrangement product **4** (cf. Table 1).

Of the nine clearly visible signals from **3**, six are broader than the other three, which indicates that these carbons participate in exchange reactions. The broad signal from C-2 and C-8 splits into two new signals at δ 85·3 and 85·8 on lowering the temperature to −146 °C. In contrast, an increase in temperature

sharpens the C-2/C-8 signal. These results clearly show that the C-2 and C-8 are exchanging with each other. This has important mechanistic implications, as discussed below.

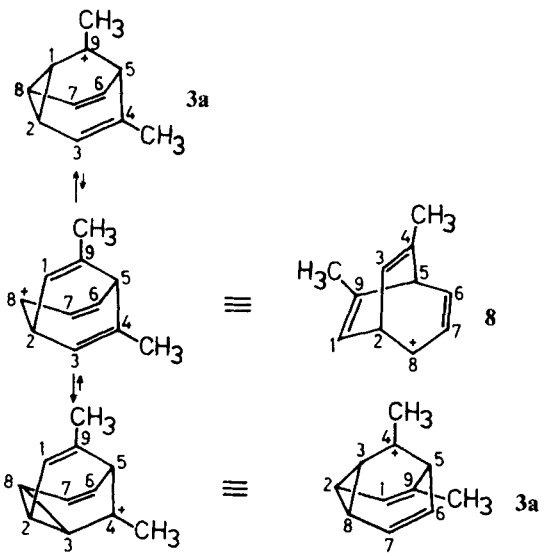
The other five broad signals sharpen on lowering the temperature. On the other hand, an increase in temperature results in further broadening of these signals. At $-130\,^{\circ}C$ only four sharp signals from ion **3** are visible in the spectrum. Hence at this temperature the signals from C-4/C-9 and C-1/C-3 disappear in the baseline noise owing to medium fast exchange. The broad complex signal from 4- and 9-CH_3 indicate that these groups now are also exchanging rapidly.

An attempt was made to use ^{13}C spin-transfer saturation to study quantitatively the carbon exchange. Unfortunately, the rate of exchange appears to be much slower than the relaxation rate of exchanging carbons. Instead, the rate constant of exchange (k) was estimated at $-140\,^{\circ}C$ from the bandwidth $\Delta\nu_{1/2}$ of one of the methyl signals and the equation $k = \pi(\Delta\nu_{1/2} - \Delta\nu_0)$. The natural bandwidths $\Delta\nu_0$ was taken as the average value of the bandwidths of signals from C-5, C-6 and C-7. The k value obtained was $160\ s^{-1}$, which corresponds to $\Delta G^{\neq} = 26\ kJ\,mol^{-1}$ ($6{\cdot}3\ kcal\,mol^{-1}$).

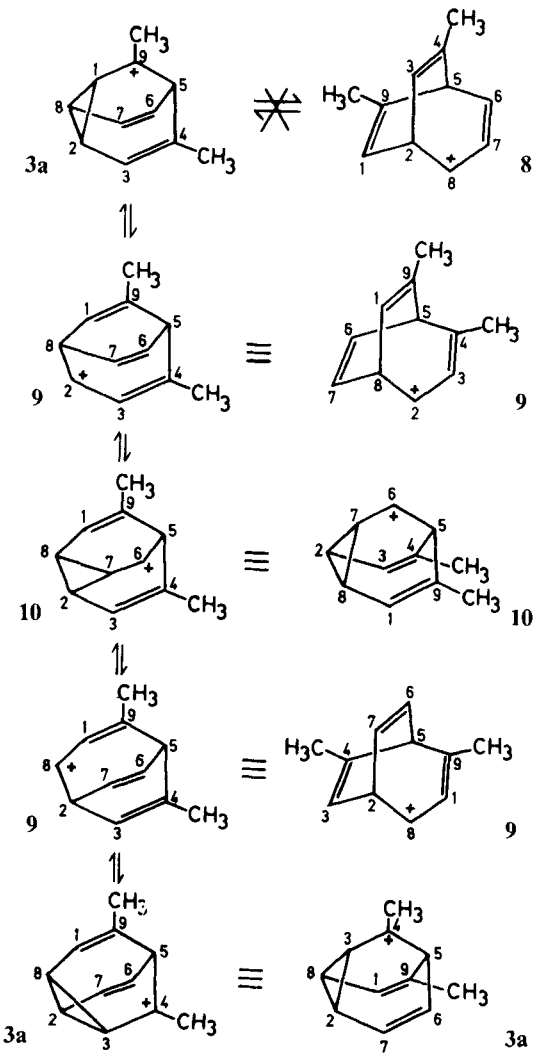
Mechanisms of degenerate rearrangement of 3

Let us first consider the mechanism shown in Scheme 3, which involves the bicyclic ion **8** as an intermediate. Ion **8** has a plane of symmetry and therefore the methyl groups, C-1 and C-3, and C-4 and C-9 are made equivalent. Formation of a bond between C-3 and C-8 yields the mirror image of **3**, which is indistinguishable from **3** by the present NMR experiments. Since they are indistinguishable by our experiments, we use the same label for the two enantiomers. As a result, the methyl groups, C-1 and C-3, and C-4 and C-9 have exchanged positions. So far this mechanism is consistent with the observations. However, C-2 and C-8 are left unexchanged and therefore some other mechanism must be in operation. The mechanism in Scheme 3 is therefore concluded to be a high-barrier process.

Instead of opening the cyclopropane ring of **3** between C-1 and C-8, which yields ion **8**, cleavage of the bond between C-1 and C-2 may take place. Such a process results in another bicyclic ion, **9**, having methyl substitution on the allylic ion part (cf. Scheme 4).



Scheme 3

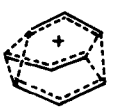


Scheme 4

Ring closure of **9** by formation of a bond between C-2 and C-7 yields another intermediate, the secondary 4,6-dimethyl-9-barbaralyl cation (**10**), which has a plane of symmetry making not only the methyl groups, C-1 and C-3, and C-4 and C-9, equivalent, but also C-2 and C-8.

Ring opening by breaking the bond between C-7 and C-8 to yield **9** followed by ring closure through formation of a bond between C-3 and C-8 results in ion **3**. As a result, the experimentally observed exchanges have taken place, i.e. C-2 and C-8, the methyl groups, C-1 and C-3, and C-4 and C-9 have exchanged with each other. Further, C-5, C-6 and C-7 neither exchange with each other nor with other carbons in **3** by this mechanism. This is also consistent with the mechanism in Scheme 4.

It is interesting to compare the mechanisms in schemes 3 and 4 with those found to be consistent with the behaviour of other barbaralyl cations. The parent barbaralyl cation has been shown by a combination of dynamic NMR and isotopic perturbation to have the 9-barbaralyl cation structure **1** rather than D_{3h} structure **11**, or the bicyclic ion **12.**



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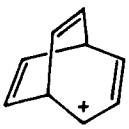

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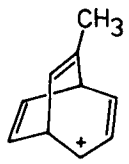
Ion **1** is extremely reactive and is observed in ^1H NMR as a sharp singlet at $-125\,^{\circ}C$. The total degeneracy of **11** ($\Delta G = 21\ kJ\,mol^{-1}$) is suggested to be achieved through the intermediacy of the bicyclic cation **12**, but a faster six-fold degenerate process ($\Delta G < 16\ kJ\,mol^{-1}$) has also been detected, i.e. a disvinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cationic rearrangement shown in Scheme 5 and /or ion **11** is an intermediate.[2] Cope rearrangements in barbaralyl cations have been concluded to be high-energy processes.[6]

The 9-methyl-9-barbaralyl cation **6** also shows degenerate rearrangements but only partial degeneracy ($\Delta G^{\neq} = 32\ kJ\,mol^{-1}$). The mechanism shown in Scheme 6 has been suggested. However, ^{13}C labelling experiments have also revealed a much slower, more extensive degenerate process, in which C-2, -3, -4, -6, -7 and -8 exchange with each other and with C-1 and C-5. The rearrangement has been suggested to make use of the bicyclic ion **13.**[7] Structure–reactivity studies have



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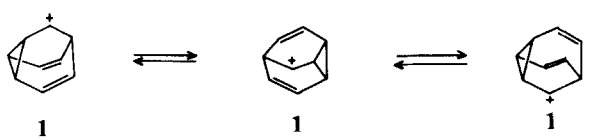
favoured the mechanism in Scheme 6 over the intermediacy of structure **13.**[6]

The 1,9-dimethyl-9-barbaralyl cation (**7a**) has been shown to be favoured over **7b** in the equilibrium shown in Scheme 7. Nevertheless, **7a** shows extensive degeneracy. C-2, -3, -4, -6, -7 and -8 exchange with each other but none of the other carbons have been shown to participate in any rapid exchange. The phenomenological mechanism shown in Scheme 8 is in operation. Each step in this mechanism has been proposed to make use of the microscopic mechanism shown in Scheme 9.

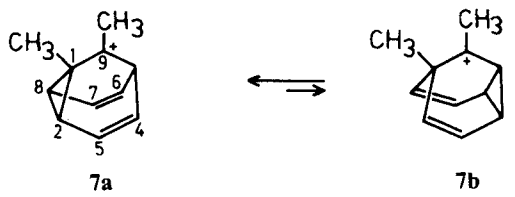
Mechanism of non-degenerate rearrangement of ion 3

The product of the non-degenerate rearrangement of **3**, i.e. the 1,4-bishomotropylium ion **4**, cannot be a direct



1 **1** **1**

Scheme 5

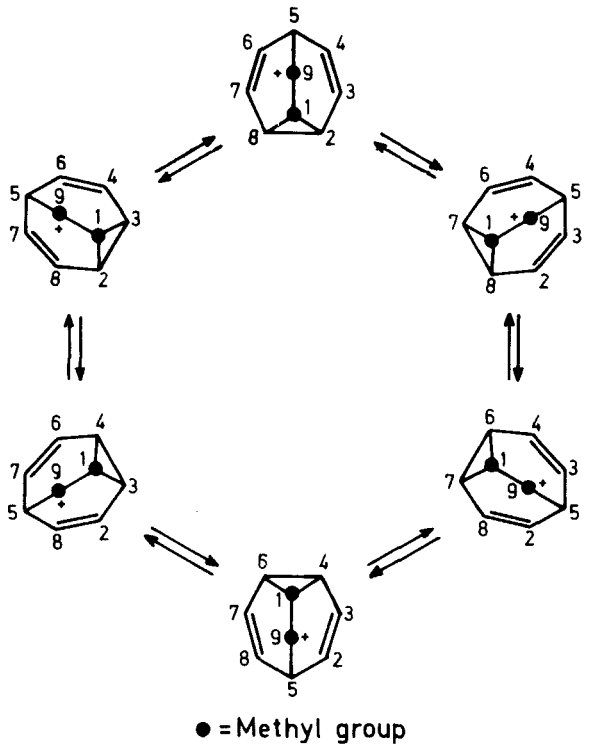


7a **7b**

Scheme 7

6 **6**

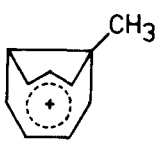
Scheme 6



Scheme 8

homoallylic rearrangement product of either **3a** or **3b**, since other dimethyl-substituted 1,4-bishomotropylium ions would have been formed. Instead, ion **4** is suggested to be formed from an unstable secondary barbaralyl cation in equilibrium with **3a**, as shown in Scheme 10. The 1,3-relationship between the methyl groups has been retained in **4**.

The rate of formation of **4** from **3** at $-125\,^{\circ}C$ is $3 \times 10^{-4}\ s^{-1}$. The corresponding rate constants for formation of **2** and **14** from **1** and **6** are $1{\cdot}4 \times 10^{-3}$ and $4{\cdot}8 \times 10^{-5}\ s^{-1}$, respectively.[7,8] The products **2**, **14** and **15** are direct rearrangement products of ions **1**, **6** and **7**. Obviously, the second methyl group in **3** compared with **6** lowers the barrier towards non-degenerate rearrangement.



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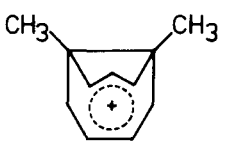

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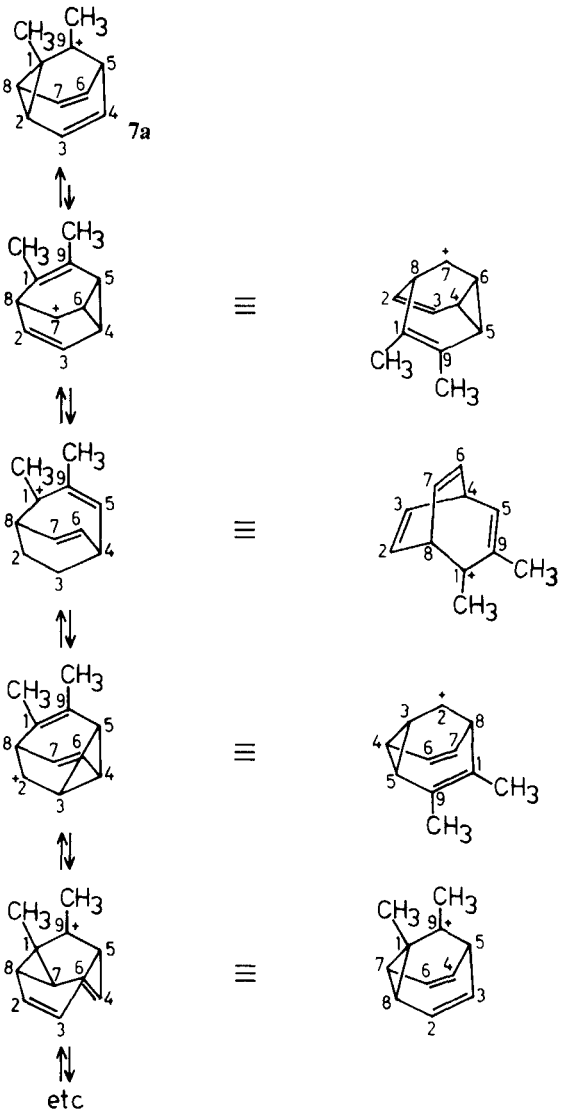
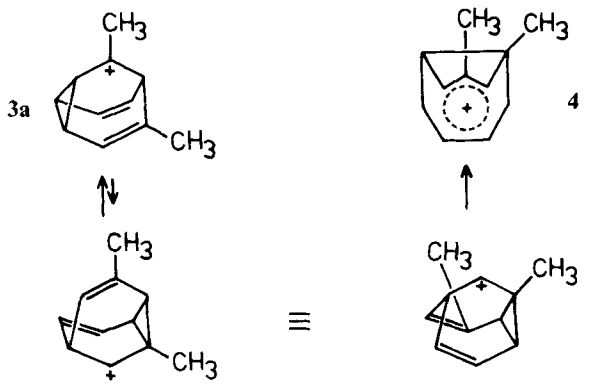


Scheme 9

EXPERIMENTAL

The ^1H NMR and the proton noise decoupled ^{13}C NMR spectra were obtained with a JEOL-FX 100 pulse spectrometer equipped with a 5 mm variable-temperature $^1H/^{13}C$ dual probe, external ^7Li lock, quadrature phase detector and a multi-irradiation unit. Data autostacking programs FAFT 20/21/22 were used. As internal standards CD_2Cl_2 (δ_C 53·8 [δ_H 5·35]), $CHCl_2F$ (δ_C 98·6, 110·3), $CDCl_3$ (δ_C 77·0 [δ_H 7·2]), C_6D_6 (δ_C 128·0 [δ_H 7·20]) and $(CD_3)_2CO$ (δ_C 29·8, 206·0, δ_H 2·05]) were used (figures in square brackets represent ^1H NMR shifts from ^1H-containing species.



Scheme 10

The temperature in the NMR probe was determined with a precalibrated chemical shift thermometer [CH_3OH in $CHCl_2F$–$CDClF_2$ (1 : 1, v/v)][4b]

Regarding the carbon NMR spectra at the lowest temperatures, experiments to supress the solvent signals using a double-pulse sequence (180°, τ, 90°)^2, in which τ was taken as ca $T_1 \times \ln 2$ for the $CHCl_2F$ signal, were unsuccessful. The large signal from the solvent was sufficiently suppressed, but there were no traces of C-4 or C-9 in **3** visible, probably owing to the large T_1 values of these quaternary carbons, comparable in magnitude to the T_1 value of $CHCl_2F$. The final spectra were recorded with single-pulse technique allowing 'overflow' of the solvent signals.

The one bond carbon–proton coupling constants, J_{CH}, were obtained from non-decoupled ^{13}C NMR spectra with NOE.

^1H NMR spectra at 400 MHz and ^{13}C NMR spectra at 100 HMz were obtained with a Varian XL 400 spectrometer.

All reactions were carried out under dry nitrogen in glassware dried at 120 °C overnight. All the purified solvents used were stored over molecular sieves (4 Å). Analytical GLC was performed using a Perkin-Elmer 990 gas chromatograph equipped with a 2·0 m × 1·8 in i.d. copper column with 5% Reoplex 400 on Chromosorb W (100–200 mesh) at a column temperature of 150 °C.

For distillation a Spaltrohr distillation apparatus with an HMS 300 column (Fischer) was used.

Materials. Pyridine (purum) was refluxed with CaH_2 for 2 h and then distilled. The fraction collected for use boiled at 92–94 °C. Triethylamine (TEA) (Mercks, purum) was distilled through a Vigreux column. The fraction collected for use boiled at 88–89 °C. Methylene chloride (Mercks) (p.a.) was dried over molecular sieves for 2 days before being distilled. The fraction used boiled at 40 °C. *n*-Heptane (Mercks, pract.) was dried over molecular sieves and distilled. The fraction used boiled at 92–94 °C.

Tropylium tetrafluoroborate. Prepared by the method of Conrow.[9]

Cyclohepta-2,4,6-trien-1-yl acetic acid (20). Prepared by the method of Jurch and Taylor.[10] The purified white crystalline acid **20**, melted at 35–36 °C. IR (KBr) showed a carbonyl peak at 5·85 μm.

^1H NMR (C_6D_6), δ 2·37 (m, 3H; H-1 and CH_2), 5·03 (d,d $J_{H\text{-}1H\text{-}2} = J_{H\text{-}1H\text{-}7} = 5{\cdot}37$ Hz, $J_{H\text{-}2H\text{-}7} = J_{H3\text{-}H6} = 9{\cdot}10$ Hz, $J_{H\text{-}2H\text{-}4} = J_{H\text{-}5H\text{-}7} = 0{\cdot}9$ Hz; 2H; H-2 and H-7), 6·04 (d,t $J_{H\text{-}3H\text{-}4} = J_{H\text{-}5H\text{-}6} = 3{\cdot}41$ Hz, $J_{H\text{-}4H\text{-}6} = J_{H\text{-}3H\text{-}5} = 2{\cdot}93$ Hz; 2H; H-3 and H-6), 6·49 (m, 2H; H-4 and H-5), 12·57 (s, 1H; acidic proton). ^{13}C NMR (C_6D_6), δ 35·5 ($J_{CH} = 135{\cdot}5$ Hz; C-1), 37·4 ($J_{CH} = 129{\cdot}5$ Hz; CH_2), 124·6 ($J_{CH} = 160$ Hz; C-2 and C-7), 125·5 ($J_{CH} = 153{\cdot}8$ Hz; C-3 and C-6), 131·2 ($J_{CH} = 156{\cdot}3$ Hz; C-4 and C-5) and 179·6 (C=0).

Cyclohepta-2,4,6-trien-1-yl acetyl chloride (21). Prepared by the method of Grutzner and Winstein.[11] The acid chloride was used without any purification. IR (neat) showed a carbonyl peak at 5·54 μm.

Bicyclo[3.2.2]nona-3,6,8-trien-2-one (16). Prepared by the method of Grutzner and Winstein[11] with some modification. Instead of *n*-hexane we used *n*-heptane as the solvent to speed up the reaction (higher reflux temperature); thus the acid chloride **21** was dropped slowly into the stirred refluxing solution over 15 h instead of 3 days. The crude product contained 54% [3.2.2]ketone **16** and 46% 1-indanone **22** (analytical GLC). The crude product, a brown oil, was first flash-distilled and a fraction boiling at about 72 °C at 0·5 mmHg was collected. This pinkish yellow viscous liquid was carefully redistilled on a Spaltrohr system. The first fraction, b.p. b.p. 93 °C/3 mmHg, was pure [3.2.2]ketone **16**, and the next faction, b.p. 94 °C/3 mmHg, was a mixture of [3.2.2]ketone **16** (80%) and 1-indanone **22** (20%). The overall yield of **16** based on starting substrate acid **20** was 27% with m.p. 40–41 °C.

^1H NMR (C_6D_6, TMS), δ 3.60 (1H; H-5), 4·10 (1H; H-1), 5·00 (1H; H-3), 6·26 (2H; H-7 and H-8), 6·56 (2H; H-6 and H-9) and 6·82 (1H; H-4). ^{13}C NMR ($CDCl_3$), δ 40·9 (C-5), 58·8 (C-1), 124·0 (C-3), 128·0 (C-7 and C-8), 137·9 (C-6 and C-9), 152·7 (C-4), 188·6 (C-2).

Data for 1-indanone **22**: ^1H NMR [$(CD_3)_2CO$], δ 2·60 (m, 2H; H-2), 3·16 (m, 2H; H-3), 7·42 (m, 1H) and 7·63 (m, 3H), olefinic protons. ^{13}C NMR [$(CD_3)_2CO$], δ 26·2 (C-3), 36·5 (C-2) 123·7, 127·7 (C-4 and C-7), 127·9, 135·1 (C-5 and C-6), 136·7 (C-8), 156·0 (C-9) and 206·3 (C-1).

2-Methylbicyclo[3.3.2]nona-3,6,8-trien-2-ol (17). Prepared by the method of Ahlberg[5b] from 4·27 g ($3{\cdot}23 \times 10^{-2}$ mol) of ketone **16** and diethyl ether solution of methyllithium (0·15 mol). Evaporation of the

ether from the product solution yielded 4·09 g of a white crystalline residue of alcohol **17** ($2{\cdot}76 \times 10^{-2}$ mol, 85%, analysed by ^{1}H NMR), which was not further purified. The mass spectrum showed a parent peak at m/z 148 ($C_{10}H_{12}O$).

^{1}H NMR ($CDCl_3$ and with a Varian XL 300, COSY-45 and HETCOR), δ 1·24 (s, 3H; CH_3), 1·86 (s, 1H; OH), 3·19 (m, J_{HH} = 7·8, 0·73 Hz; H-5) and 3·24 (m, J_{HH} = 6·3, 2·32 Hz; H-1) together, relative area of 2H, 4·75 (d,d,d J_{HH} = 10·7, 2·29, 0·73 Hz, 1H; H-3), 6·07 (d,d J_{HH} = 10·8 Hz, 1H; H-4), 6·17 (1H; H-7), 6·19 (1H; H-8), 6·55 (1H; H-9) and 6·65 (1H; H-6); H-6 and H-9 may be exchanged but in such case H-8 and H-7 must also be exchanged. ^{13}C NMR ($CDCl_3$), δ 27·1 (CH_3), 36·8 (C-5), 49·1 (C-1), 68·3 (C-2), 129·7, 130·4 (C-7 and C-8), 133·4 (C-4), 133·9 (C-3), 139·1 (C-9), 141·4 (C-6); C-6 and C-9 must be exchanged if the proton H-6 and H-9 shifts are exchanged.

4-Methylcyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-ol (18). 2-Methylbicyclo[3.2.2]nona-3,6,8-trien-2-ol (**17**) (4·09 g, $2{\cdot}76 \times 10^{-3}$ mol) was dissolved in 40 ml of acetone–water 7:3, v/v). A 10-mol volume of 1 M H_2SO_4 was added and the mixture was stirred at room temperature for 5 h. The reaction was followed by ^{1}H NMR spectroscopy. The methyl signal of **17** at δ 1·24 disappeared and a new signal at δ 1·83 increased. Then 15 ml of water were added to the reaction mixture. After extraction with 3 × 50 ml of diethyl ether, the collected ether portions were washed with 2 × 25 ml of 5% $KHCO_3$ and 25 ml of saturated sodium chloride solution and dried over potassium carbonate. After evaporation a bright oil remained, which on ^{1}H NMR showed **18** and only a trace of alcohol **17**. The crude product was used without further purification. Yield 3·5 g ($2{\cdot}36 \times 10^{-2}$ mol), 86% alcohol **18** (cf. ref. 12).

^{1}H NMR (CCl_4, TMS), δ 1·60 (s, 1H; OH), 1·83 (t, 3H; CH_3), 1·95–2·70 (m, 4H; H-1, H-2, H-5, H-8), 3·52 (m, 1H; H-9), 5·00–5·93 (m, 3H; H-3, H-6, H-7).

4-Methyltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-one (19). Prepared by the procedure of Ratcliffe and Rodehorst[13] with the exception of stirring the product solution for a longer time, 45 min instead of 15 min, at room temperature before decanting from the residue. The yield of crude product was 96%. Analysis by GLC revealed that the crude product contained 92% of the desired ketone **19**. This crude ketone was used without further purification in the next step of the syntheses. A small amount of the crude product was purified by GLC using a 0·75 m × 1/4 in i.d. copper column with 10% Carbowax 20M and 10% KOH on Chromosorb W (60–80 mesh) at a column temperature of 120 °C.

^{1}H NMR [$(CD_3)_2CO$] at room temperature, δ 1·83 (d, J_{HH} = 1·3 Hz, 3H; CH_3), 2·26 (1H; H-1), 2·86 (1H; H-5), 2·92 (m, 2H; H-2, H-8), 5·48 (m, J_{HH} = 1·3 Hz, 1H), 5·29 (m, 1H) and 5·78 (m, 1H) (H-3, H-6, H-7). ^{13}C NMR [$(CD_3)_2CO$] at room temperature, δ 22·0 (CH_3), 27·5 (C-1), 38·8 (broad; C-2, C-8), 54·1 (C-5), 116·5 (C-3), 122·1 (broad; C-6), 123·1 (C-7), 131·8 (broad; C-4), 210·2 (C-9). ^{13}C NMR at −80 °C, δ 21·8 (J_{CH} = 127 Hz; CH_3), 25·4 (J_{CH} = 182 Hz; C-1), 30·5 (J_{CH} = 170 Hz; C-2 or C-8), 31·3 (J_{CH} = 170 Hz; C-8 or C-2), 55·0 (J_{CH} = 143 Hz; C-5), 115·0 (J_{CH} = 161 Hz; C-3), 122·7 (J_{CH} = 163 Hz; C-7), 128·8 (J_{CH} = 170 Hz; C-6), 139·3 (C-4), 211·4 (C-9). Carbon chemical shifts of the 9-barbaralone in the same solvent at room temperature, δ 38·5 (C-1, C-5), 80·8 (broad; C-2, C-8, C-4, C-6), 121·7 (C-3, C-7), 209·5 (C-9); and at −100 °C, δ 26·1 (J_{CH} = 182 Hz; C-1), 32·4 (J_{CH} = 174 Hz; C-2, C-8), 49·7 (J_{CH} = 143 Hz; C-5), 121·7 (J_{CH} = 162 Hz; C-3, C-7), 128·1 (J_{CH} = 168 Hz; C-4, C-6), 210·9 (C-9).

4,9-Dimethyltricylo[3.3.1.0^{2,8}]nona-3,6-dien-9-ol (5). Prepared according to Ahlberg[5b] from 1·65 g of the crude product of the methylbarbaralone **19**. The crude product **5** was not distilled but purified by preparative GLC. A Varian 920 gas chromatograph was used, equipped with a 0·7 m × 1/4 in i.d. copper column with 10% Carbowax 20M and 10% KOH on Chromosorb W (60–80 mesh) at a column temperature of 115 °C. The yield was 74%.

^{1}H NMR [$(CD_3)_2CO$] at room temperature, δ 1·02 (d, 3H; 9-CH_3), 1·78–1·92 (4H; 4-CH_3, OH), 2·12–2·56 (4H; H-1, H-2, H-5, H-8), 5·12–5·78 (3H; H-3, H-6, H-7). ^{13}C NMR [$(CD_3)_2CO$] at room temperature,
δ 23·1 and 23·6 (J_{CH} = 126 Hz; 4-CH_3 or 9-CH_3), 24·4 and 24·6 (J_{CH} = 126 Hz; 9-CH_3 or 4-CH_3), 31·2 (broad, J_{CH} = 166 Hz; C-1), 32·1 and 32·3 (J_{CH} = 166 Hz; C-2 or C-8), 34·7 and 35·0 (J_{CH} = 166 Hz; C-8 or C-2), 49·8 (J_{CH} = 140 Hz; C-5), 66·1 and 66·3 (C-9), 114·8 and 116·4 (J_{CH} = 157 Hz; C-3*), 117·4 and 119·6 (J_{CH} = 163 Hz; C-7*), 121·3 and 123·3 (J_{CH} = 163 Hz; C-6*), 126·4 and 128·7 (C-4).

The complexity of the NMR data is due to **5** being a mixture of diastereoisomers. The carbon atoms marked with asterisks may exchange. The ^{13}C NMR spectra at a lower temperature (−80 °C) show the same chemical shifts as those at room temperature. The methyl groups prefer attachment on the olefinic carbons rather than the cyclopropane carbons.[2,12]

A smaller amount of **5**, used for running a spectrum of cation **3** at the 400 MHz was analysed and purified as follows. The HPLC analyses and purification of **5** were performed with a Varian 5000 or Varian Vista 5500 instrument equipped with a Varian RI-3 refractive index detector. Data sampling and peak-area integration were effected with a Varian DS 654. Organic solvents used for elution were Fisons HPLC grade. Water was distilled and filtered through a Millipore 0·45-μm HA filter. The eluent was degassed in an ultrasonic bath

before use. The samples were filtered through 100 mg of C_{18} or Bond-Elut silica disposable columns before injection.

GC analyses were performed on a Varian 3500 gas chromatograph equipped with a flame ionization detector. A J. & W. fused-silica capillary column (30 m × 0·251 mm i.d.) coated with DB-5 (0·25 μm) as the liquid stationary phase was used with hydrogen as the carrier gas. The injections were made on-column. Chromatographic data were sampled and analysed with a Varian DS 654 instrument.

For the purification of **5**, a Varian MikroPak MCH-10 (10 μm) column 300 mm × 8 mm i.d.) was used with 60% methanol in 0·1% potassium phosphate buffer (pH 7·5) as the mobile phase. The flow-rate was 3 cm^3 min^{-1} with a pressure of 104 atm at ambient temperature. About 50 μl of a 0·8 M solution of **5** in methanol was injected using a 2-ml loop. The fraction between 10·2 and 13·0 min was collected and extracted with methylene chloride, dried over anhydrous sodium sulphate, filtered and evaporated.

4,9-Dimethyltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl cation (3). Synthesized directly in a 5 mm NMR tube using the ion generation apparatus described previously in detail.[3a,4b] One preparation was done from 28·5 mg (0·18 mmol) of 4,9-dimethylbarbaralol (**5**) dissolved in CD_2Cl_2 and added at −133 °C to ca 0·4 ml of a solution of FSO_3H–SO_2ClF–SO_2F_2 (1:6:1, v/v/v). Another preparation was done from 26·8 mg (0·17 mmol) of precursor **5** dissolved in ca 0·1 ml of $CHCl_2F$ and added at −135 °C to ca 0·4 ml of a solution of FSO_3H–SO_2ClF–SO_2F_2 (2:7:7:1 by volume). ^1H NMR (CD_2Cl_2, ref. **4** δ_{CH_3} 1·88) at ca −129 °C, δ 2·5 (broad, 6H; 4-CH_3, 9-CH_3, 5·14 (broad, 3H; H-1, H-3, H-5), 5·73 (2H; H-2, H-8), 6·03 (1H; H-7), 6·22 (1H; H-6). ^1H NMR ($CHCl_2F$ δ 7·15 and 6·67) at ca −146 °C, δ 2·10 (4-CH_3), 2·78 (9-CH_3), 4·71 (H-1), 5·04 (H-5), 5·69 (H-3 and H-2, H-8), 5·94 (H-7), 6·12 (H-6). ^{13}C NMR (CD_2Cl_2) at ca −135 °C, δ 26 (very broad; 4-CH_3, 9-CH_3), 64·4 (C-5), 85·5 (C-2, C-8), 117·3 (C-7), 130·8 (C-6), ca 140 (C-4) (a hump in the noise line). ^{13}C NMR ($CHCl_2F$) at −144 °C, δ 20·4 (4-CH_3), 32·9 (9-CH_3), 64·5 (C-5), 73·2 (C-1), 85·5 and 85·8 (C-2, C-8), 112 (C-3), 117·0 (C-7), 130·5 (C-6), 143·7 (C-4), 256·7 (C-9) (cf. Figure 1).

1,8-Dimethylbicyclo[4.3.0]nona-2,4,7-trienyl cation (4). This 1,4-bishomotropylium ion is the non-degenerately rearranged product of the 4,9-dimethylbarbaralyl cation **3** when the temperature rises above −130 °C.[14]

^{13}C NMR (CD_2Cl_2) at −110 °C, δ 15·5 (J_{CH} = 129 Hz; 8-CH_3), 20·2 (J_{CH} = 128 Hz; 1-CH_3), 57·0 (J_{CH} = 160 Hz; C-6), 59·7 (C-1), 115·7 (J_{CH} = 172 Hz; C-2), 117·3 (J_{CH} = 175 Hz; C-5), 138·3 (J_{CH} = 170 Hz) and 140·8 (J_{CH} = 169 Hz) (C-3 and C-4), 141·3 (J_{CH} = 182 Hz) and 145·2 (J_{CH} = 175 Hz) (C-7 and C-9), 156·6 (C-8).

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