Bicyclo[3.2.2]nonatrienyl-lithium and -potassium and their Degenerate Rearrangements studied by Multiple Labelling with ^{13}C and ^{2}H,^{13}C Nuclear Magnetic Resonance Spectroscopy, ^{13}C–^{13}C Coupling Constants, and Isotopic Perturbation

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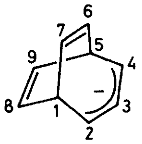
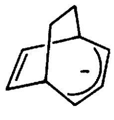
[^{13}C,^{2}H$_7$]Bicyclo[3.2.2]nonatrienyl-potassium (**8**) and -lithium (**9**) in [^{2}H$_{10}$]-1,2-dimethoxyethane have been investigated by ^{13}C nuclear magnetic resonance spectroscopy. The absence of an observable isotopic perturbation effect on ^{13}C chemical shifts indicates a symmetric structure of this $(CH)_9^-$ anion in solution, rather than rapidly equilibrating unsymmetrical homoaromatic ions. One-bond ^{13}C–^{13}C coupling constants obtained from the [^{13}C$_2$]-labelled ion (**10**), $^1J_{C1C2}$ 38, $^1J_{C1C7}$ 40.0, and $^1J_{C2C3}$ 62.5 Hz, were compared with those of the corresponding hydrocarbon [^{13}C$_2$]bicyclo[3.2.2]nona-2,6,8-triene (**11**). The couplings indicate no significant structural change in the bridgehead region and support a symmetrical delocalized structure for the bicyclo[3.2.2]nonatrienyl anion. It is proposed that the controversial stabilization of carbanions is not caused by delocalization and homoaromaticity but is rather due to a previously ignored important interaction with the metal ion. The observed scrambling of ^{13}C labels in (**8**) and (**9**), from C(3) to C(6)—C(9) and subsequently to C(2), C(4) and C(1), C(5), is consistent with a degenerate rearrangement *via* the 9-barbaralyl anion. Further support for this mechanism was obtained from the scrambling of two ^{13}C labels from C(3) and C(2), C(4) which is three times faster to C(6)—C(9) than to C(1), C(5) in ion (**10**).

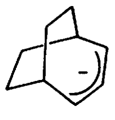
It was predicted that the bicyclo[3.2.2]nona-3,6,8-trien-2-yl anion (**1**) would be stabilized by longicyclic interactions involving the three unsaturated bridges.[1] Thus, this anion should be more stable than the bicyclo[3.2.2]nonadienyl anion (**2**), which is suggested to be bishomoaromatic.[2] Kinetic investigations supported increased stability of (**1**) and (**2**) relative to the bicyclo[3.2.2]nonenyl anion (**3**), but the stabilizing effect of the second double bond was smaller than that of the first.[2] N.m.r. spectroscopic studies of (**1**),[3,4] (**2**),[2a] and the related bicyclo[3.2.1]octadienyl anion (**4**)[5] indicated considerable delocalization of charge into vinyl bridges. Studies of monodeuterium-labelled ion (**1**) revealed a facile degenerate rearrangement, scrambling deuterium bonded to C(2) to all other positions (E_a 22.5 kcal mol^{-1}).[3] It was proposed that the rearrangement uses the 9-barbaralyl anion [tricyclo[3.3.1.0^{2,8}]-nona-3,6-dien-9-yl anion,† (**5**)] as an intermediate (*cf.* Scheme 5).[3]



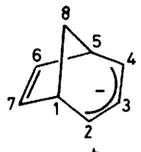
(**1**)†



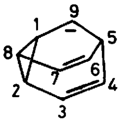
(**2**)



(**3**)



(**4**)†



(**5**)†

However, from *ab initio* STO-3G calculations it was not possible to identify the stabilizing HOMO–LUMO interactions proposed to account for the stability of (**1**) and (**4**), and homoaromaticity and bicycloaromaticity were ruled out as contributors to carbanion stability.[6] This conclusion has been questioned in a complementary MO study of interacting fragments.[7] Recent MO calculations gave an energy difference between (**1**) and (**5**) (*ca.* 17 kcal mol^{-1}) in agreement with the observed rearrangement barrier.[8] Support for homoaromaticity in carbanions was provided by pK_a measurements of the hydrocarbons corresponding to (**1**), (**2**), and (**4**), which indicated the stabilizing effect of the remote double bond in (**4**) to be >12.2 kcal mol^{-1}, exceeding the effect of a conjugated double bond or phenyl ring. The stabilization of (**2**) and (**1**) was found to be >8.7 and >11.4 kcal mol^{-1}, respectively, suggesting only a small stabilization by the second double bond in (**1**) (*i.e.*, 2.7 kcal mol^{-1}).[9]

The present study is aimed to resolve the controversy regarding the structure of (**1**) and to elucidate further the mechanism of its degenerate rearrangement. Isotopic labelling methods, isotopic perturbation, and one-bond ^{13}C–^{13}C coupling constants have been used for this purpose.[10]

Results

Ions were prepared by sodium–potassium alloy cleavage of methyl ether precursors in [^{2}H$_{10}$]dimethoxyethane ([^{2}H$_{10}$]-DME) under vacuum line conditions, using a modified procedure described by Grutzner and Winstein.[3] Specifically labelled precursors, 4-methoxy[3-^{13}C, 1,2,5,6,7,8,9-^{2}H$_7$]bicyclo-[3.2.2]nona-2,6,8-triene (**6**) and 4-methoxy[3,4-^{13}C$_2$]bicyclo-[3.2.2]nona-2,6,8-triene (**7**) with 90% ^{13}C and *ca.* 97% ^{2}H in each of the labelled positions, respectively, were prepared by methylation of the corresponding alcohols.[3] Degenerate rearrangements were studied at 25 °C in a thermostat, while n.m.r. spectra were recorded at −27 °C, rearrangement being slow at this temperature.

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† The numbering of the carbons in the structure is according to IUPAC conventions.

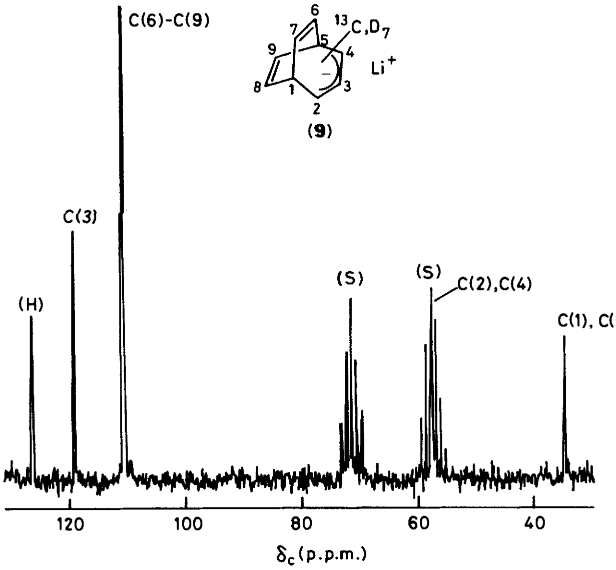
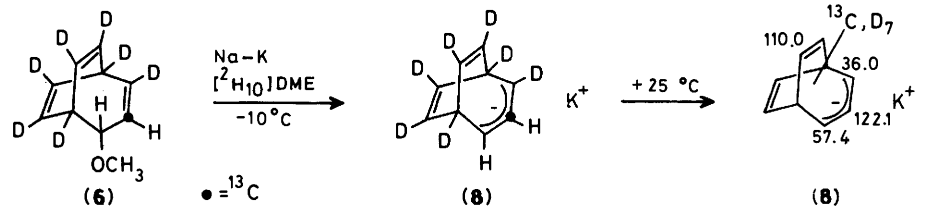


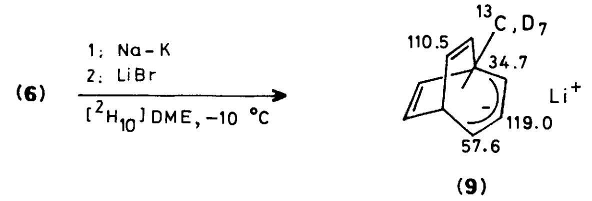
Figure 1. Proton noise decoupled ^{13}C n.m.r. spectrum for [^{13}C,^{2}H$_7$]-bicyclo[3.2.2]nonatrienyl-lithium (**9**) in [^{2}H$_{10}$]DME (internal reference δ 57.8 p.p.m.) at −27 °C. The spectrum was obtained after 1 min rearrangement at 25 °C. The peak marked (H) is due to [3-^{13}C,^{2}H$_7$]-bicyclo[3.2.2]nona-2,6,8-triene and the multiplets marked (S) originate from solvent

[^{13}C,^{2}H$_7$]*Bicyclo*[3.2.2]*nonatrienylpotassium* (**8**).—Na–K alloy cleavage of (**6**) gave an ion with its ^{13}C label exclusively at C(3). Warming at 25 °C gave a rapid scrambling of ^{13}C to C(6)–C(9), with an observed rate constant of 1.6 × 10^{-3} s^{-1}. The label was also slowly scrambled to C(2), C(4) and even more slowly to C(1), C(5). Each ^{13}C resonance was a singlet and chemical-shift changes from deuteriation were small (*cf.* Schemes 1 and 3).



Scheme 1.

[^{13}C,^{2}H$_7$]*Bicyclo*[3.2.2]*nonatrienyl-lithium* (**9**).—Cleavage of (**6**) under the same conditions which provided (**8**), followed by LiBr metathesis,[4] gave (**9**) with a considerable scrambling of labels. Only 40% ^{13}C remained at C(3), while 48% was found at C(6)–C(9) and 6 and 5% were scrambled to C(2), C(4) and C(1), C(5), respectively. On warming very rapid scrambling was observed by ^{13}C n.m.r. (Figure 1) and was complete within 10 min at 25 °C. The rate constant for scrambling of ^{13}C from C(3) to C(2), C(4) and C(1), C(5) was 4.6 × 10^{-2} s^{-1}. All ^{13}C resonances were sharp singlets and chemical shifts were close to those of (**8**) (Scheme 2). The most significant difference (−3.1 p.p.m.) was observed at C(3).



Scheme 2.

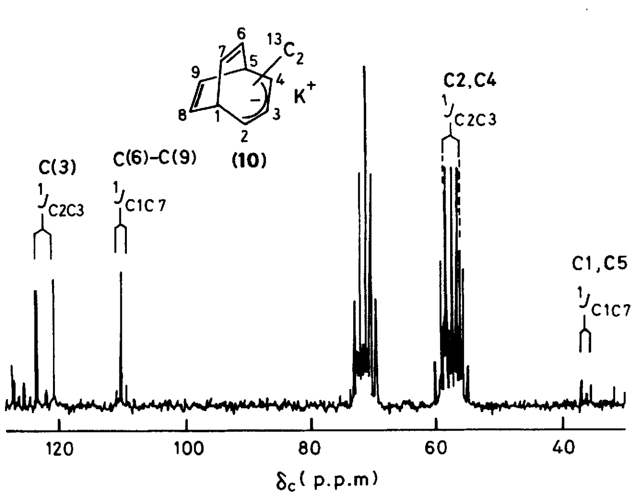
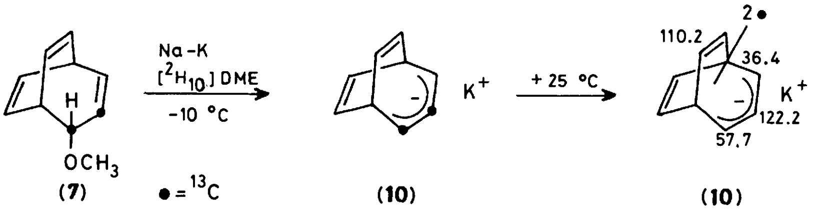


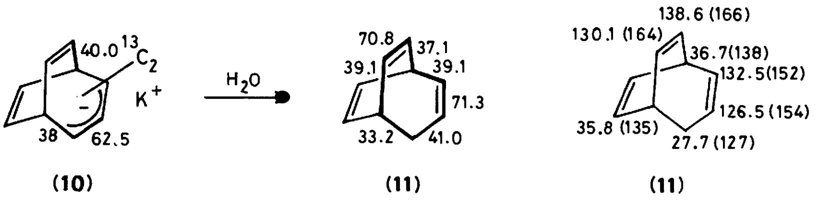
Figure 2. Proton noise decoupled ^{13}C n.m.r. spectrum for [^{13}C$_2$]-bicyclo[3.2.2]nonatrienylpotassium (**10**) in [^{2}H$_{10}$]DME (internal reference δ 57.8 p.p.m.) at −27 °C. The spectrum was obtained after 10 min rearrangement at 25 °C. The multiplets originate from solvent and other small peaks from hydrocarbon formed slowly at 25 °C

[^{13}C$_2$]*Bicyclo*[3.2.2]*nonatrienylpotassium* (**10**).—Treatment of (**7**) with Na–K alloy gave ion (**10**), with its labels almost exclusively at C(2), C(4), and C(3) ($^{1}J_{\mathrm{C2C3}}$ 62.5 Hz), with only 4% ^{13}C at C(6)–C(9). On warming, the ion rearranged, scrambling ^{13}C to C(6)—C(9) three times faster than to C(1), C(5). The vinyl resonance [C(6)—C(9)] emerged as a singlet (75%) with ^{13}C satellites (25%, $^{1}J_{\mathrm{C1C7}}$ 40.0 Hz, Figure 2). The observed rate constant for scrambling from C(3) to C(6)—C(9) was estimated to be 1.1 × 10^{-3} s^{-1} at 25 °C.

Other isomers were formed by further rearrangement, as seen by the changing relationship between central resonances and ^{13}C satellites, but no further C–C coupling could be observed [C(2), C(4) is partly hidden by solvent]. Irradiation of C(6)—C(9) in a triple resonance experiment revealed a second coupling at C(1), C(5) assigned to $^{1}J_{\mathrm{C1C2}}$ 38 Hz. The degenerate rearrangement was accompanied by some formation of the corresponding hydrocarbon [^{13}C$_2$]bicyclo[3.2.2]nona-2,6,8-triene (**11**). The ion (**10**) was quenched by the addition of H$_2$O (50 μl) under nitrogen gas which gave (**11**), identified by ^{13}C n.m.r. The one-bond ^{13}C–^{13}C coupling constants in (**11**) were used as a suitable reference system (Scheme 4). However, the signal intensity was higher by a factor of 10 in hydrocarbon (**11**) as compared with (**10**), indicating that a considerable



Scheme 3.



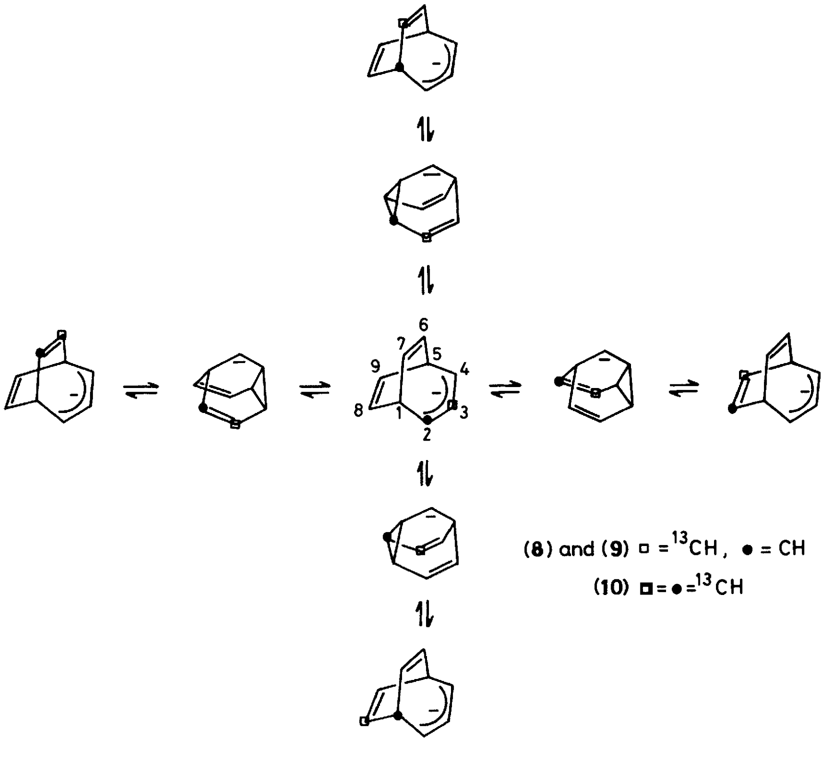
Scheme 4.

fraction of the potassium salt (**10**) was present in the solid state. The ^{13}C chemical shifts (and $^1J_{CH}$) for (**11**) are summarized above. An attempt to increase the solubility of (**1**)–K^+ in tetrahydrofuran by the addition of Kryptofix^R 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) to the anion solution gave the hydrocarbon bicyclo[3.2.2]nona-2,6,8-triene as the only observable product.

Discussion

The scrambling of a label to all positions in (**1**) was discovered in a ^1H n.m.r. study of a monodeuteriated anion. The coupling pattern of the remaining eight protons was used to follow the rearrangement, which was suggested to use (**5**) as an intermediate. However, the reported data could hardly have ruled out another mechanism if an alternative had been proposed.[3] The rearrangement *via* (**5**) was later supported by a similar 7-carbon scrambling in the 6,7-benzobicyclo[3.2.2]-nonatrienyl anion[11] and the exclusive formation of (**1**) on cleavage of 9-halogen-substituted barbaralanes.[12] Recently, ^2H n.m.r. was used to study a deuterium-labelled anion (**1**) with caesium as metal ion, which rearranged at a rate comparable with that of the potassium salt and decomposed to form barbaralane.[9]

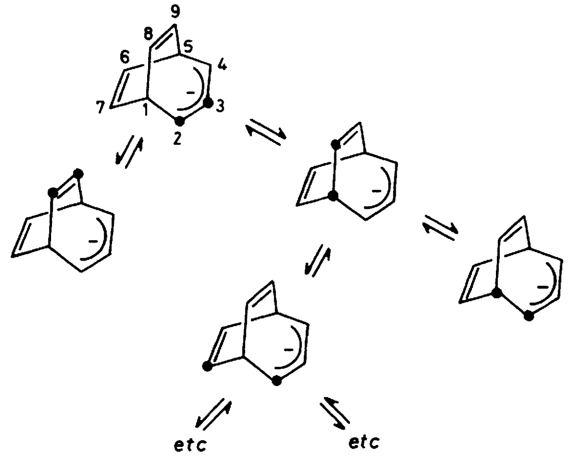
The redistribution of labels in ions (**8**)—**10**) upon a degenerate rearrangement using (**5**) as an intermediate was analysed in detail (*cf.* Scheme 5). The expected scrambling of one ^{13}C label from C(3), and two ^{13}C labels from C(2), are summarized in Schemes 6 and 7, respectively. Scheme 6 includes



Scheme 5.

$$\begin{tikzcd}
{}^{13}\mathrm{C}(3) \arrow[d, shift left, "k"] \\
{}^{13}\mathrm{C}6\text{-}\mathrm{C}9 \arrow[u, shift left, "k/4"] \arrow[d, shift left, "k/4"] \\
{}^{13}\mathrm{C}2,\mathrm{C}4 \arrow[u, shift left, "k/2"] \arrow[d, shift left, "k/2"] \\
{}^{13}\mathrm{C}1,\mathrm{C}5 \arrow[u, shift left, "k/2"]
\end{tikzcd}$$

Scheme 6.

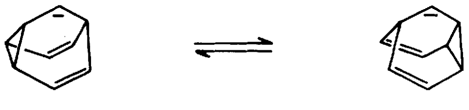


Scheme 7.

the fractional rate constants obtained from the number of effective rearrangement paths in each direction.

The observed redistribution of one ^{13}C label in (**8**) and (**9**) from C(3) to C(6)—C(9), subsequently to C(2), C(4), and finally to C(1), C(5) is consistent with Scheme 6. The initial rate of scrambling from C(3) to C(6)—C(9) in the potassium salt (**8**) shows satisfactory reversible first-order behaviour, but the scrambling rate to C(2), C(4) and C(1), C(5) is slower than expected.* Thus, when (**8**) was allowed to stand in the freezer at −20 °C for 9 days, the rearrangement apparently reversed. The fraction of ^{13}C(3) labelled ions in solution increased from 26 to 40%.

Together with the scrambling pattern of (**10**) forming the ^{13}C(1)—^{13}C(7)- and ^{13}C(6)—^{13}C(7)-labelled isomers with equal rates (Scheme 7), our results are quite decisive. The bicyclo[3.2.2]nonatrienyl anion (**1**) rearranges *via* the 9-barbaralyl anion (**5**) as an intermediate (Scheme 5). Ion (**5**) was found to be represented by a potential energy minimum in MINDO/3 and MNDO calculations.[8] These results favour (**5**) as an intermediate rather than as a transition state in Scheme 5. The present labelling patterns do not provide information about the possible degenerate Cope rearrangement of the intermediate (**5**) (Scheme 8). This process is expected to be facile from extrapolation of experimental results[13] and some theoretical work.[14] However, recent semiempirical and *ab initio* (STO-3G) calculations indicate a high barrier for such a rearrangement.[8]



(5) **(5)**

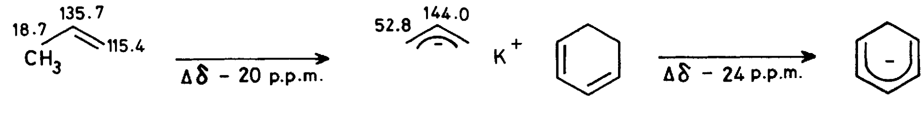
Scheme 8.

When the mechanistic rate constants in Scheme 5 were corrected for 50% return from (**5**) (assumed to be an intermediate) to the reacting isomer without scrambling of labels, we obtained: k_8 3 × 10^{-3}, k_9 9 × 10^{-2}, and k_{10} 2 × 10^{-3} s^{-1}. The barriers for the formation of (**5**) from (**1**) are estimated at 21 kcal mol^{-1} with K$^+$ and 19 kcal mol^{-1} with Li$^+$. The higher rearrangement rate observed for the lithium salt can be an effect of different fractions of contact–solvent-separated ion pairs, different states of aggregation,[15] or just reflect better ability of lithium to stabilize a rather localized carbanion, like the intermediate (**5**).

^{13}C *Chemical Shifts and Isotopic Perturbation.*—The ^{13}C chemical shifts obtained for ions (**8**) and (**9**) differ only slightly, in agreement with previously reported small effects of solvent, metal ion, and temperature on n.m.r. data for (**1**).[4] This indicates that ion pairs of one type are predominant in the solutions of ions (**8**)—(**10**). These are most probably contact ion pairs.

The most prominent feature of the ^{13}C chemical shifts of (**8**)—(**10**) is the considerable upfield shift of the C(6), C(9) and C(7), C(8) signals, by 20 and 28 p.p.m., respectively, relative to the hydrocarbon (**11**). This indicates appreciable delocalization of negative charge into the vinyl bridges and/or considerable rehybridization of these carbons, previously suggested to explain similar effects in (**4**).[5c] Rehybridization is supported by the accompanying decrease of C–H coupling constants in vinyl CH groups on going from (**11**) to (**1**)[4] (Δ^1J_H 25 Hz).

Carbocations have been subdivided into two classes (classical and non-classical) by using the ^{13}C chemical shift sum of all carbons in the cation compared with that of the corresponding hydrocarbon.[16] A similar approach to carbanion chemical shifts yields some interesting results as shown below. The ^{13}C chemical shift sum of allylpotassium (**13**) is 250 p.p.m.,[17] which is 20 p.p.m. less than for (**12**),[18] an effect of two counteracting components. Rehybridization of the methyl carbon to an sp^2-carbon is expected to increase the total ^{13}C chemical shift by *ca.* 100 p.p.m., while the added electron contributes a net shielding of *ca.* 160 p.p.m.[17] Approximately the same change in total ^{13}C chemical shifts (Δδ) is observed on formation of other simple conjugated carbanions, *e.g.*, (**14**)-(**15**).[19]



(12)[18] **(13)**[17] **(14)**[19] **(15)**[19]

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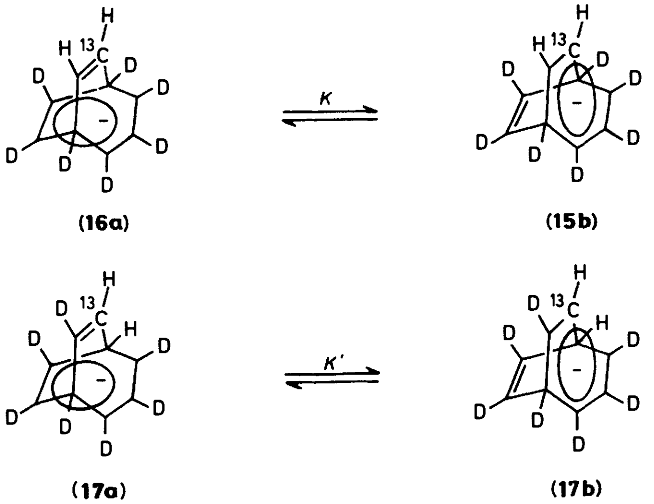
* However, kinetic evaluation is complicated by slow molecular exchange with a pool of unrearranged solid anion salt, which is present despite filtration through the fritted disc. The use of a finer fritted disc would make the preparation of the ions unduly slow due to slow filtration.

The deprotonation of (**11**) forming (**10**), on the other hand, gives a total shielding of ^{13}C chemical shifts ($\Delta\delta$) as large as -145.5 p.p.m. This is mainly an effect of the considerable shielding of C(6)—C(9), while the carbons of the allyl fragment [C(2)—C(4)] changed by -48.9 p.p.m., totally. The corresponding $\Delta\delta$ between bicyclo[3.2.1]octadiene and (**4**) was -141 p.p.m., also from a large shielding of the vinyl bridge carbons.[5c] The shielding per carbon atom [C(6), C(7)] is twice as large in (**4**), resulting in remarkably similar net shielding effects.

The net charge is the same in all these anions (**1**), (**4**), (**13**), and (**15**) and the shielding effect of an electron is probably less in homoaromatic ions (117 p.p.m./e^-) than in planar conjugated systems (160 p.p.m./e^-).[20] Thus, the additional shielding effect (*ca.* 120 p.p.m.) observed in anions (**1**) and (**4**) relative to (**13**) and (**15**) supports an increased co-ordination of the olefinic carbons.

Ion (**1**) has been reported to be symmetric (C_{2v}) on the n.m.r. time scale down to -141 °C[4] and MO calculations favour a symmetrical structure.[6a] The considerable upfield shift of the vinyl bridge carbons [C(6)–C(9)] could be an observed average of rapidly rearranging unsymmetrical isomers. If so, deuterium substitution is expected to perturb such equilibria and thereby change average ^{13}C chemical shifts.[21]

The labelling pattern of (**6**) was designed to give two different isomers after one rearrangement step (in Scheme 5) of the corresponding anions (**8**) and (**9**). One isomer, (**16**), has the ^{13}CH and CH groups in one vinyl bridge while the other vinyl bridge is occupied by two CD groups. The other isomer, (**17**), has ^{13}CH and CD groups in one vinyl bridge and two CD groups in the other bridge (Scheme 9).



Scheme 9.

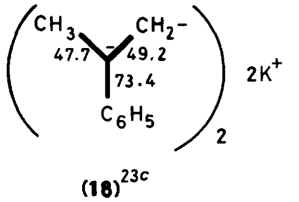
If the shielding of C(6)—C(9) had been an effect of preferential interaction between the allyl bridge and one of the vinyl bridges at a time, leaving the third bridge unaffected, a perturbation of the equilibria in Scheme 9 would have resulted. CH and CD groups are distributed so as to minimize the total zero-point energy in the system, *i.e.*, a deuterium atom prefers to occupy saturated carbons > cyclopropane carbons > olefinic carbons.[22] In (**16**) the carbons in the homointeracting vinyl bridge are expected to be rehybridized and thereby to have acquired some cyclopropane character by interaction with the allylic bridge. Thus, the vinyl bridge containing the two CD groups will preferentially occupy the intereacting position ($K < 1$). The perturbing effect of one deuterium is about half that of two deuteriums, thus $K < K'$. Since the average shielding of C(6)–C(9) is *ca.* 25 p.p.m., the frozen ^{13}C chemical shift difference (Δ) in a slow exchange between (**16a** and **b**) is estimated to be at least 40 p.p.m. [*cf.* (**4**)] with (**16a**) to be observed at the lower field. Therefore, a more downfield average ^{13}C chemical shift is expected for C(6)—C(9) in (**16**) than in (**17**), due to the greater preference for (**16a**) than for (**16b**), compared with the case of (**17a** and **b**).

However, in ions (**8**) and (**9**) all ^{13}C resonances were observed as sharp singlets and the splitting (δ) of the C(6)—C(9) peak is less than 2 Hz. Moreover, the ^{13}C chemical shift differences between (**8**) and (**10**) are very small (<0.4 p.p.m.). The fraction of observed relative to maximal splitting (δ/Δ) is <0.002. Such small δ/Δ values have been found to be indicative of symmetrical structures in similar studies of carbocations.[21b] Reasoning similar to that presented above also rules out other conceivable rearrangements as significant contributors to the observed ^{13}C chemical shifts of ion (**1**).[5c]

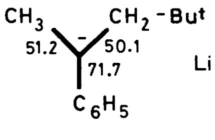
Two factors could reduce the observed splitting (δ) even if the equilibria outlined in Scheme 9 are present. The value of Δ (40 p.p.m.) can be overestimated and/or the rehybridization of C–H bonds in the interacting vinyl bridge can be small, giving a small isotopic perturbation effect. However, both factors would indicate a very small interaction between vinyl and allyl bridges. This is in conflict with the observed ^{13}C shielding and C–H coupling constants.[4]

One-bond ^{13}C–^{13}C Coupling Constants.—In recent studies of 1,4-bishomotropylium ions, the C–C coupling constants ($^{1}J_{CC}$) revealed considerable structural changes, with rehybridization of bridgehead and adjacent carbons and delocalization of bonds.[10c] However, the observed C(1)–C(2) and C(1)–C(7) coupling constants to the bridghead carbons in ion (**10**) were 38 and 40.0 Hz, respectively. These $^{1}J_{CC}$ were close to the corresponding values in the hydrocarbon (**11**), $^{1}J_{C1C2}$ 39.1, $^{1}J_{C1C7}$ 37.1 Hz. The C(2)–C(3) coupling in (**10**) (62.5 Hz) is smaller than the couplings to a conjugated phenyl ring in benzylic anions (**18**) and (**19**),[23c] but is in the expected range for a partial double bond. These results are in agreement with a symmetrical structure for ion (**10**) with no significant structural change in the bridgehead parts of the carbon skeleton between (**10**) and (**11**). The important C(6)–C(7) coupling unfortunately disappears by symmetry.

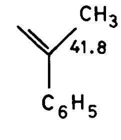
The Role of the Metal Ion.—All experimental results including ^{13}C n.m.r. chemical shifts, isotopic perturbation, and C–C coupling constants are in favour of a symmetric ion (**1**), in which the negative charge has been considerably delocalized into the vinyl bridges. But it has not been possible by theoretical calculations to find either the delocalization of the negative charge or the stabilizing HOMO–LUMO interactions which are proposed to mediate this delocalization.[6] This contradiction



(**18**)[23c]



(**19**)[23c]



(**20**)[23c]

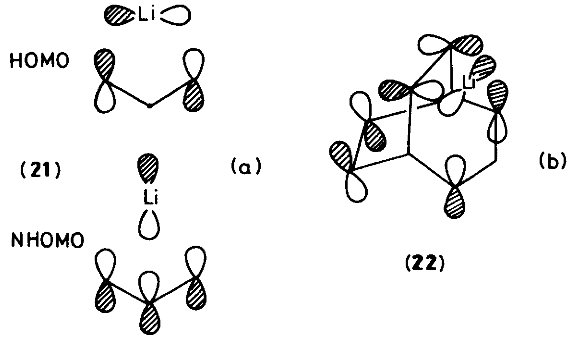


Figure 3. (a) Bonding interactions in the highest occupied MOs of the allyl-lithium ion pair (**21**).[24] (b) Possible HOMO of the bicyclo-[3.2.2]nonatrienyl-lithium ion pair (**22**)

of experimental and theoretical findings is possibly due to the presence of the metal ion in the experiments, while the MO calculations have been performed on isolated anions in the gas phase. The importance of the metal ion is illustrated by the following experiment. An attempt to increase the solubility of (**1**)-K^+ in THF by the addition of Kryptofix^R 222 resulted in immediate quenching of the anion by proton abstraction from solvent and only hydrocarbon could be observed.

Ab initio STO-31G calculations on the allyl-lithium ion pair (**21**) have shown lithium to prefer a symmetric position above the allyl anion, interacting with all three carbons. An orbital interaction analysis indicated large stabilizing interactions between Li^+ *p*-orbitals and the allyl anion χ_1 and χ_2 orbitals (Figure 3a).[24] The position of lithium in (**21**) does suggest that in the presence of favourably oriented vinyl groups, as in (**1**), (**2**), and (**4**), participation of the vinyl bridge orbitals will be geometrically favourable (Figure 3b). Even if orbitals of the allyl-lithium fragment and those of the vinyl bridges[6a] are still far apart in energy, a considerable interaction is possible (Figure 3b).

If such a complex will also be energetically favourable, what will its structure be? How can we account for C_{2v} symmetry? Will it be monomeric at all? These are questions which will have to be answered. *Ab initio* calculations above the minimal basis level could give valuable insights in these delicate systems.

Such computations are now being performed on the related anion (**4**) and its lithium salt.[25] Results have so far confirmed the suggested position of Li^+ and its considerable interaction with the vinyl bridge, even if the nature of this interaction seems to be largely electrostatic in nature.

Experimental

The proton noise decoupled ^{13}C n.m.r. spectra were recorded with a JEOL-FX100 spectrometer equipped with a variable temperature 5 mm ^1H-^{13}C dual probe, ^2H lock, and quadrature phase detector. Ions were studied at −27 °C, using the FAFT 70-791221 program. As internal standards [$^2H_{10}$]-1,2-dimethoxyethane (δ_C 57.8 p.p.m.) and CD_2Cl_2 (δ_C 53.8 p.p.m. and residual protons at δ_H 5.35) were used.

The following parameters were used in the study of (**8**)—(**10**): pulse width 45°, spectral width 4 kHz, 8 192 data points when accumulating the spectra, acquisition time 1.0 s, pulse delay 1.0 s, and *ca.* 5 000 scans were accumulated. The measured C–C coupling constants are accurate within 1.0 Hz.

Analytical g.l.c. was carried out with an HP 5880 A instrument, using a 1.5 m × 2.5 mm glass column with 10% Carbowax 20M + 1% KOH on Chromosorb W at 100 °C. The kinetics were performed in a HETO O2 PT 623 thermostat at 25.0 °C. Lithium aluminium hydride (Merck, 'zur Synthese', 90%), sodium hydride (Merck, 'zur Synthese', with 20% paraffin liquid), sodium–potassium alloy (ALFA, 78:22, 99.95%), and Kryptofix^R 222 (Merck, 99%) were used as purchased. Tetrahydrofuran (THF) (Fisons; HPLC grade) and 1,2-dimethoxyethane (DME) (Fluka; purum, 99%) were dried over molecular sieves and distilled over lithium aluminium hydride. Methyl iodide (Riedel) was dried over molecular sieves (4 Å) and distilled. Diethyl ether (May and Baker; anhydrous) and n-pentane were dried over molecular sieves (4 Å). [$^2H_{10}$]-1,2-Dimethoxyethane (MSD) (> 99% ^2H) was dried over molecular sieves (4 Å) with indicator and degassed. Lithium bromide (Merck; extra pure) was dried at 150 °C and in a vacuum oven at 50 °C at 0.01 mmHg.

All reactions were carried out under dry nitrogen in glassware dried in a vacuum oven at 50 °C and 0.01 mmHg overnight.

[3-^{13}C, 1,4,5,6,7,8,9-$^2H_7$]*Bicyclo*[3.2.2]*nona*-3,6,8-*trien*-2-*ol*.[26]—[3-^{13}C, 1,4,5,6,7,8,9-$^2H_7$]Bicyclo[3.2.2]nona-3,6,8-trien-2-one[26] (55.4 mg, 0.394 mmol) was dissolved in diethyl ether and added dropwise to lithium aluminium hydride (30.3 mg, 0.80 mmol) in diethyl ether at −80 °C and stirred for 3 h. Work-up by the normal procedure gave the alcohol (47.1 mg, 0.332 mmol) (96% pure by g.l.c.) (yield 84%), $\delta_H(CD_2Cl_2)$ 4.98 (d, m, $^1J_{CH}$ 157.7 Hz, 0.9 H and m, 0.1 H, 3-H), 4.01 (br, 1 H, 2-H), and 1.92 (1 H), residual protons at δ 6.80, 6.69, 6.32, 6.13, and 3.3. C(3) Contained 90% ^{13}C and deuteriated positions held *ca.* 3% ^1H.

4-*Methoxy*[3-^{13}C, 1,2,5,6,7,8,9-$^2H_7$]*bicyclo*[3.2.2]*nona*-2,6,8-*triene* (**6**).[3]—Sodium hydride (16.7 mg, 0.556 mmol) was washed three times with dry pentane in a 2 ml flask, dried at oil-pump vacuum, and dissolved in 1,2-dimethoxyethane (DME) (0.5 ml). Methyl iodide (31 µl, 0.49 mmol) was added and the mixture was cooled on an ice-bath with magnetic stirring. A solution of the above alcohol (47.1 mg, 0.332 mmol) in DME (0.4 ml) was added dropwise with a syringe, followed by methyl iodide (8 µl, 0.13 mmol), and the solution was stirred for 4 h. The mixture was poured on ice–saturated NaCl and extracted with diethyl ether. The extract was dried over $CaCl_2$, filtered, and evaporated to give (**6**) (37.6 mg, 0.241 mmol, 73%). G.l.c. analysis showed that (**6**) was >95% pure and that all starting material had been consumed, $\delta_H(CD_2Cl_2)$ 5.02 (d, m, $^1J_{CH}$ 158.0 Hz, 0.9 H and m, 0.1 H, 3-H), 3.60 (d, d, *J* 5.0 Hz and 3.3 Hz, 4-H), and 3.39 (s, 3 H, CH_3) and residual protons at δ 6.70, 6.29, and 6.06 (*ca.* 3% ^1H in each deuteriated position).

4-*Methoxy*[3,4-$^{13}C_2$]*bicyclo*[3.2.2]*nona*-2,6,8-*triene* (**7**).[3]—[2,3-$^{13}C_2$]Bicyclo[3.2.2]nona-3,6,8-trien-2-ol[10c] (24 mg, 0.18 mmol) was dissolved in DME (0.35 ml) and added at 0 °C to a mixture of sodium hydride (8.7 mg, 0.29 mmol; washed with dry n-pentane) and methyl iodide (16.5 µl, 0.26 mmol) in DME (0.4 ml). Addition of methyl iodide (4 µl, 0.07 mmol) and stirring for 4 h was followed by work-up by the normal procedure, giving (**7**) (16 mg, 0.11 mmol, 61%). The product was 95% pure by g.l.c., $\delta_H(CD_2Cl_2)$ 6.72 (t, *J* 7.0 Hz, 7- and 8-H), 6.29 (t, *J* 7.3 Hz, 6- and 9-H), 6.2—6.0 (m, *J* 10.2 and 7.0 Hz, 2-H), 5.01 (d, d, m, $^1J_{CH}$ 157.4 and *J* 10.7 Hz and d, m, *J* 10.5 Hz, 3-H), 3.60 (d, m, $^1J_{CH}$ 139 Hz, 4-H), 3.60 (m, 5-H), 3.39 (d, $^3J_{CH}$ 4.9 Hz and s, CH_3), and 3.24 (m, 1-H), δ_C 141.5 (C-7 or -8), 140.3 (C-8 or -7), 136.5 (d, $^1J_{CC}$ 70.8 Hz, C-2), 129.1 (C-6 or -9), 128.5 (C-9 or -6), 126.6 (d, $^1J_{CC}$ 47.6 Hz and s, C-3), 73.9 (d, $^1J_{CC}$ 48.8 Hz and s, C-4), 56.5 (CH_3), 47.2 (d, $^1J_{CC}$ 39.1 Hz, C-5), and 37.1 p.p.m. (C-1).

Preparations of Ions.—Anions were prepared under vacuum line conditions in a H-shaped reaction vessel modified from Winstein and Grutzner.[3,15] A short sidearm without break-seal was used for the precursor. The precursor (**6**) or (**7**) (*ca.* 20 µl) was introduced into the sidearm with a syringe, frozen in liquid nitrogen and covered with some solvent ([$^2H_{10}$]DME) under a flow of argon. Sodium–potassium alloy (*ca.* 0.3 ml) was introduced into the reaction chamber with an all-glass syringe and frozen in liquid nitrogen. The cap was closed and the vessel evacuated to below 10^{-5} mmHg. The solvent [$^2H_{10}$]DME (*ca.* 1.5 ml) was distilled into the reaction chamber from the vacuum line by cooling the vessel in liquid nitrogen and the evacuated vessel was removed and placed in an ice–acetone bath (−10 °C). As soon as the alloy was molten, vigorous stirring (glass-covered magnet) was begun and a blue colour appeared. The precursor was kept frozen and covered with solvent during this procedure. The precursor, now molten, was rapidly poured into the reaction chamber and stirred for 1 h at −10 °C, while a deep green colour developed. The solution was filtered through the coarse fritted disk, concentrated, and poured into the 5-mm n.m.r. tube at −13 °C. The tube was sealed and kept in an ice–acetone bath at −20 °C. In the preparation of ion (**9**), lithium bromide (3 equiv.) was added to the solution after filtration.

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