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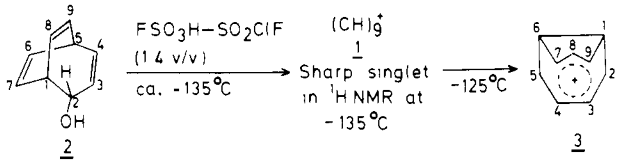
The Totally Degenerate $(CH)_9^+$ Ion 9-Barbaralyl Cation Studied by ^{13}C Labeling and Isotopic Perturbation by Eight Deuteriums

Carin Engdahl, Göran Jonsäll, and Per Ahlberg*

Contribution from the Department of Organic Chemistry, Institute of Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden. *Received May 3, 1982*

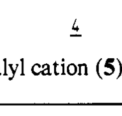
Abstract: There has been controversy regarding the structure and mechanisms of rearrangement of the totally degenerate $(CH)_9^+$ carbocation **1** obtained from bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**2**) in superacid. Ion **1** appears as a sharp singlet in the ^1H NMR spectrum at −135 °C and rearranges rapidly at −125 °C to the 1,4-dihomotropylium ion (**3**). Among others, bicyclo[3.2.2]nona-3,6,8-trienyl cation (**4**), 9-barbaralyl (tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-yl) cation (**5**), and the D_{3h} structure **6** have been proposed as structures of ion **1**. The present paper presents complete results of studies of ^{13}C labeled ion **1** and isotopic perturbation by eight deuteriums of ^{13}C-labeled **1**. The ion precursors [3-^{13}C]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**10**) and [3-^{13}C,1,2,4,5,6,7,8,9-$^2H_8$]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**12**) have been synthesized. From these alcohols the corresponding ions $[(CH)_8{}^{13}CH]^+$ (**11**) and $[(CD)_8{}^{13}CH]^+$ (**13**) have been generated in superacid. On the basis of the ^{13}C NMR spectrum of **11** and its temperature dependence, structure **4** is excluded as candidate for ion **1**. Perturbation of the rapid degenerate equilibria of **11** by eight deuteriums as in **13** results in shifts of the ^{13}C NMR signals relative to those of ion **11**. These results exclude **6** as a candidate for the structure of ion **1** but are consistent with structure **5**. Ion **5** undergoes a 9-fold degenerate rearrangement ($\Delta G^{\ddagger} = 21$ kJ mol^{-1}) presumably via **4** as an intermediate. Ion **5** also undergoes an even faster rearrangement, a 6-fold degenerate rearrangement ($\Delta G^{\ddagger} < 16$ kJ mol^{-1}) via divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cation mechanism.

There has been controversy regarding the structure of the $C_9H_9^+$ ion **1** and its mechanisms of rearrangement. Ion **1**, obtained by reaction of the bicyclic alcohol **2** with superacid, is observed as a sharp singlet by ^1H NMR at −135 °C.[1] Since there can be no regular polyhedron with nine corners, the observed sharp singlet suggests a rapid equilibration among the nine CH's rather than a single structure with nine equivalent CH's. Obviously carbocation **1** is extremely reactive compared with its neutral counterpart, bullvalene, which does not exchange its 10 CH's rapidly on the ^1H NMR time scale until the temperature has been raised to 100 °C.[2] Ion **1** is also very sensitive to nondegenerate rearrangement. At ca. −120 °C it is rapidly transformed into a 1,4-dihomotropylium ion **3**.[1] Therefore, ion **1** has to be generated and observed at very low temperatures.



Ion **1** has also been studied under conditions for short life, i.e., solvolytic conditions, by Schleyer and co-workers[3] and by Grutzner and Winstein[4] using deuterium-labeled nitrobenzoates and dinitrobenzoates of 9-barbaralol and bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**2**). The deuterium distribution in the products indicated the intermediacy of a carbocation which can be partially or totally degenerate or have D_{3h} symmetry.

Among others, bicyclo[3.2.2]nona-3,6,8-trienyl cation (**4**), 9-barbaralyl cation (**5**), and the D_{3h} structure **6** have been proposed as structures of ion **1**.[5] Calculations (CNDO/2) by Yoneda et al.[6] and an orbital correlation study by Hoffmann et al.[7] have suggested structure **6**.



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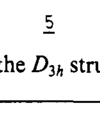

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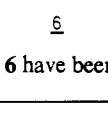

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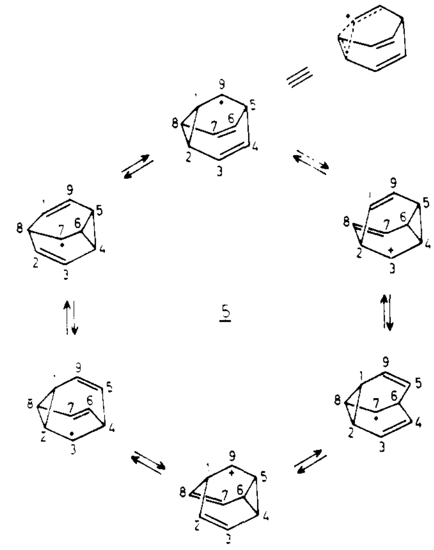
Scheme I



If ion **1** has structure **5** it undergoes a 6-fold partially degenerate rearrangement which has been proposed to proceed via a new type of mechanism, the divinylcyclopropylcarbinyl cationic rearrangement in Scheme I. Total degeneracy can be achieved through ion **4** as an intermediate or transition state (Scheme II).[1,3]

In a group theoretical study Bouman and Trindle have concluded that if ion **1** has structure **5**, then **6** can be neither a transition state nor intermediate in its rearrangements.[8] McIver's rules also exclude **6** as a transition state in the rearrangement of **5**.[9]

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(5) (a) Leone, R. E.; Schleyer, P. v. R. *Angew. Chem.* **1970**, *82*, 889–919. (b) Ahlberg, P.; Jonsäll, G.; Engdahl, C. *Adv. Phys. Org. Chem.* **1982**, *19*, 223–379.

(6) Yoneda, S.; Winstein, S.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2510–2512.

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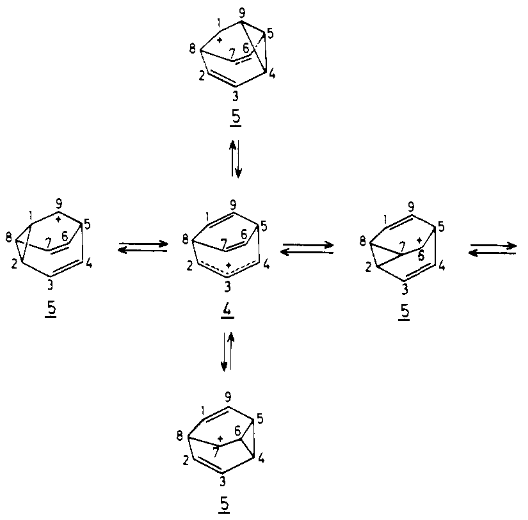
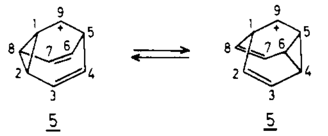
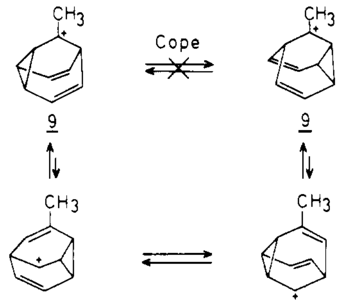
Scheme II



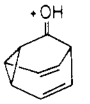
Scheme III



Scheme IV



In NMR studies of the influence of positive charge on the rate of the Cope rearrangement (Scheme III), it was found that protonated barbaralone **7** has a considerably higher barrier (56.2 kJ mol^{-1} (13.4 kcal mol^{-1}) at −44 °C) than barbaralone **8** (42.8 kJ mol^{-1} (10.2 kcal mol^{-1}) at −93 °C).[1b,10] Apparently the positive charge is retarding the Cope rearrangement.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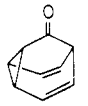
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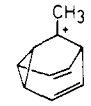
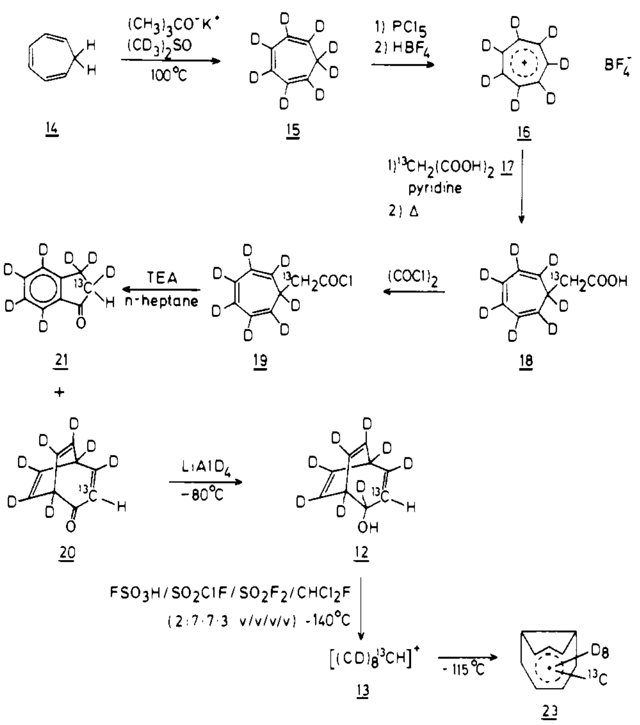

9

Extrapolation predicts an even higher barrier for the 9-methyl-9-barbaralyl cation (**9**) than for **7** since the charge is more delocalized in **9**. However, the observed barrier for **9** is only 31.9 kJ mol^{-1} (7.63 kcal mol^{-1}) at −129 °C,[10b] which is even lower than that for the neutral compound **8**. Therefore, it was concluded that **9** is using the new type of mechanism, e.g., a divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cationic rearrangement (Scheme IV) which yields the same exchange pattern as a Cope rearrangement.

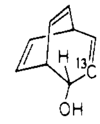
For the parent barbaralyl cation (**5**) an even higher Cope barrier would thus be predicted than for **9** and on this basis there has been support of the proposed 6-fold degenerate mechanism (Scheme I).[1]

Scheme V



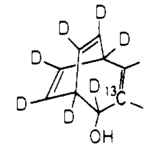
For a recent review of degenerate carbocation rearrangements ($C_9H_9^+$ and other cations), refer to Ahlberg et al.[5b] The ^{13}C NMR spectrum of an ionic solution of **1** containing natural abundance ^{13}C did not show any carbocation signal distinguishable from the noise.[10b] Obviously, the degenerate rearrangement of ion **1** has such a rate (on the ^{13}C NMR time scale) that the result is a very broad signal which is concealed by the noise. This result necessitated the use of ^{13}C labeling to get further insight into the structure of ion **1** and the reaction mechanisms it follows.

The present paper presents complete results; preliminary accounts were previously reported.[11] Alcohol **2** containing 3-^{13}C (**10**) was prepared and converted into ^{13}C-labeled ion **11**, and the temperature dependence of its ^{13}C NMR spectrum was studied. The results supported the possibility of one or two degenerate processes and excluded **4** as a possible structure for ion **1**.


10

$[(CH)_8{}^{13}CH]^+$

11


12

$[(CD)_8{}^{13}CH]^+$

13

The final discrimination between the candidates **5** and **6** was made by using the isotopic perturbation technique.[12-14] For this purpose the specifically labeled octadeuterated **10** (**12**) was synthesized and converted into octadeuterated ^{13}C-labeled ion **1** (**13**) by reaction with superacid. ^{13}C NMR chemical shifts of **13** compared with those of **11** showed that ion **1** has the 9-barbaralyl cationic structure (**5**) rather than the D_{3h} structure (**6**). The rearrangement barriers have also been measured.

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(10) (a) Ahlberg, P.; Grutzner, J. B.; Harris, D. L.; Winstein, S. *J. Am. Chem. Soc.* **1970**, *92*, 3478–3480. (b) Engdahl, C.; Ahlberg, P. *Ibid.* **1979**, *101*, 3940–3946.

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(13) (a) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070–8071. (b) Saunders, M.; Kates, M. R. *Ibid.* **1977**, *99*, 8071–8072. (c) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *Ibid.* **1977**, *99*, 8072–8073.

(14) Saunders, M. "Stereodynamics of Molecular Systems"; Sarma, R., Ed.; Pergamon Press: New York, 1979; p 171.

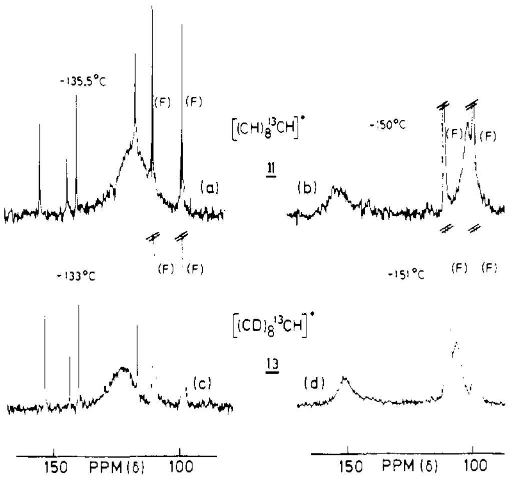

Figure 1. (a, b) ^{13}C NMR spectra for the mono ^{13}C-labeled barbaralyl cation (**11**) obtained at −135.5 and −150 °C, respectively, using a double-pulse sequence to suppress the solvent signal. (c, d) Spectra of the octadeuterated mono-^{13}C-labeled barbaralyl cation (**13**) at −133 and −151 °C, respectively, recorded with single pulses. The peaks marked F are due to $CHCl_2F$ (δ 110.3, 98.6) used as the solvent and internal standard reference. The other sharp signals originate from labeled 1,4-dihomotropylium ions (**3**).

Results

The ^{13}C-labeled alcohols [3-^{13}C]bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**10**) and [3-^{13}C,1,2,4,5,6,7,8,9-$^{2}H_8$]bicyclo[3.2.2]-nona-3,6,8-trien-2-ol (**12**) were prepared, with some modifications, in the same way as was the corresponding nonlabeled bicyclic alcohol.[4b,15] The route is illustrated in Scheme V by the preparation of **12**. In the preparation of **10**, nonlabeled tropylium tetrafluoroborate was used together with 90% enriched [2-^{13}C]-malonic acid (**17**). No purification was performed before the mixture of ketones **20** and **21** was obtained; these were separated by GLC.

$[(CH)_8{}^{13}CH]^+$ (11). A solution of pure **10** (with 90% ^{13}C in the 3-position) in CD_2Cl_2 was rapidly mixed into a solution of $FSO_3H–SO_2ClF–SO_2F_2$ at −135 °C in a 5-mm NMR tube by using an ion generation apparatus which has been previously described.[10b,16] The pale yellow ionic solution obtained provided fairly well-resolved ^{13}C NMR spectra down to −144 °C, when the solution turned solid. A solution of **10** in $CHCl_2F$ was added to a mixture of $FSO_3H–SO_2ClF–SO_2F_2–CHCl_2F$ to obtain resolved spectra at even lower temperatures. Solutions more concentrated than ca. 0.1 M could not be prepared without the formation of byproducts.

Figure 1a,b shows ^{1}H-noise-decoupled ^{13}C NMR spectra of ion **11** at two different temperatures. At −135.5 °C only one broad singlet is associated with **11** (118.5 ppm) which confirms the total degeneracy of **11**. The sharp peaks in Figure 1a marked (F) originate from the freon and the others from the 1,4-dihomotropylium ion **3** which was formed while accumulating the spectral data. When the temperature is lowered, the broad singlet is further broadened and becomes unsymmetric, splitting into two new bands centered at 101 and 152 ppm, respectively, with an area ratio of 6:3. Figure 1b shows the spectrum at −150 °C. Further lowering of the temperature to −152 °C sharpened the two singlets. No peaks from **3** appear in this spectrum since the experiment was actually started at −150 °C, and at this temperature the rate of formation of **3** is slow.

The rate constant $k_{obsd} = 4900$ s^{-1} (rate constant for exchange from the six-carbon group to the three-carbon group) at −135.5 °C, for the totally degenerate rearrangement which corresponds to a barrier $\Delta G^* = 21$ kJ mol^{-1} (5.0 kcal mol^{-1}), has been estimated assuming the Scheme II mechanism, which involves ion **4** as intermediate, and the band width $\Delta\nu_{1/2} = 324$ Hz and a natural bandwidth of $\delta\nu_0 = 14$ Hz. At about −150 °C $\delta\nu_0$ is estimated to be ca. 40 Hz.

If it is assumed that the formation of the two singlets from **11** in Figure 1b is a result also of rapid degenerate processes, we can then estimate a lowest possible rate constant $k_{obsd} > 2 \times 10^5$ s^{-1} (rate constant for exchange from the two-carbon group C-3, C-7 with C-9) from the bandwidths at ca. −150 °C. Assuming the Scheme I mechanism, this corresponds to the barrier $\Delta G^* < 16$ kJ mol^{-1} (~3.8 kcal mol^{-1}).

$[(CD)_8{}^{13}CH]^+$ (13). The octadeuterated ^{13}C-labeled alcohol **12**, containing ca. 90 atom % ^{13}C in position 3, ca. 99 atom % ^{2}H in position 2, and ca. 97 atom % ^{2}H in each of the other deuterium-labeled positions, was dissolved in $CHCl_2F$ at −15 °C. This freon solution was transferred to a 5-mm NMR tube containing a mixture of $FSO_3H–SO_2ClF–SO_2F_2–CHCl_2F$ (2:7:7:3, v/v/v/v) at about −140 °C; after they were mixed, a homogeneous pale yellow solution resulted. Figures 1c and 1d show ^{1}H-noise-decoupled ^{13}C NMR spectra of the octadeuterated ^{13}C-labeled cation $[(CD)_8{}^{13}CH]^+$ (**13**) at −133 and −151 °C, respectively. The deuteriums have had the effect of perturbing the rapid equilibria exhibited by nondeuterated **11**, the broad singlet of **13** at −133 °C (123 ppm) being 4.5 ppm downfield from that of **11**. As the temperature was lowered the broad singlet of **13**, like that of **11**, split into two new signals centered at 107 and 151 ppm, respectively, with an area ratio 5:3 (Figure 1d). Thus these signals have been shifted downfield by 6 ppm and upfield by 1 ppm, respectively, compared to those of ion **11**.

When the temperature was lowered from −151 to −157 °C, the S/N ratio decreased but the half-height bandwidth ($\Delta\nu_{1/2}$) of the singlet at 151 ppm was unchanged while those of the freon (F) increased. Change of the temperature from −157 to −159 °C broadened all signals in the spectrum including the one at 151 ppm. The $\Delta\nu_{1/2}$ of the freon signals increased by 33%. Even at −157 °C the 107-ppm singlet is merged into the low-field solvent signal.

The deuterium substitution of **11** did not have a noticeable effect on the rate of rearrangement of the cation.

Discussion

The ^{13}C NMR data of the ^{13}C-enriched ion $[(CH)_8{}^{13}CH]^+$ (**11**) preclude the simple bicyclic allylic ion **4** as the structure of **1**. A nonequilibrating allylic ion (**4**) would, of course, exhibit more peaks than the two observed (101 and 152 ppm) at −150 °C. Consistent with the area ratio 6:3 between these two peaks is an ion **4** undergoing partially degenerate rearrangements in which either C-3 exchanges with C-2 and C-4 and the remaining six carbons (C-1, C-5–C-9) exchange with each other or C-3 exchanges with C-1 and C-5, and C-2, C-4, and C-6–C-9 exchange among themselves. The observed area ratio does not allow any other exchange possibilities. However, the estimated average chemical shifts for these two cases show large deviations from observed values.

Does the data obtained with ion **11** allow a discrimination between ions **5** and **6**? Ion **5** undergoing the 6-fold degenerate rearrangement shown in Scheme I would exhibit the observed area ratio 6:3 since this mechanism exchanges C-3, C-7, and C-9 with each other and C-1, C-2, C-4–C-6, and C-8 among themselves.

The ^{13}C chemical shifts of **5** could be estimated by using the data shown in Table I. The 9-methyl-9-barbaralyl cation (**9**) is used as a reference substance. It is assumed that the shift differences ($\delta_{25} - \delta_{24}$) between carbons 1, 2, 4, 6, and 7 of 3-methyl-3-nortricyclyl cation (**24**) and 3-nortricyclyl cation (**25**)[17] are transferable to the 9-barbaralyl system. If it is also assumed that there are no differences in chemical shift between carbons 3, 4, 6, and 7 of **5** compared to those of **9**, then the chemical shifts in the last column of Table I are obtained for **5**. From these values the average chemical shifts of the two peaks with area ratio 6:3 which results from the assumed operation of the Scheme I mechanism, are 106 and 153 ppm, respectively. These values are in reasonable agreement with the observed values for ion **1**, 101

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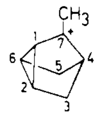
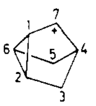
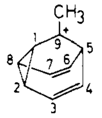
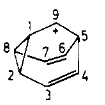
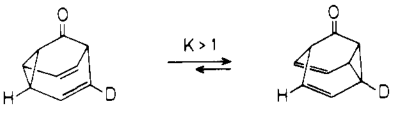
(17) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920–1927.

Table I. ^{13}C Chemical Shifts[a] of **5** Estimated from Those of the Models **9**, **24**, **25**, and 1,9-Dimethyl-9-barbaralyl Cation[b]

	 δ_{24}[c]	 δ_{25}[c]	$\delta_{25} - \delta_{24}$	 δ_{9}[b]	 δ_{5}
C-1	67.5	86.3	18.8	72.5	91.3
C-2	83.7	111.6	27.9	86.2	114.1
C-3	43.7	46.6		116.2	116.2
C-4	47.0	42.4	−4.6	130.2	130.2
C-5	43.7	46.6		59.2	54.6
C-6	83.7	111.6	27.9	130.2	130.2
C-7	293.2	258.5	−34.9	116.2	116.2
C-8				86.2	114.1
C-9				260.0	225.1
CH_3	33.7			33.2	

[a] In ppm relative to Me_4Si. [b] Cf. ref 10b. [c] Cf. ref 17.

Scheme VI



26 a 26 b

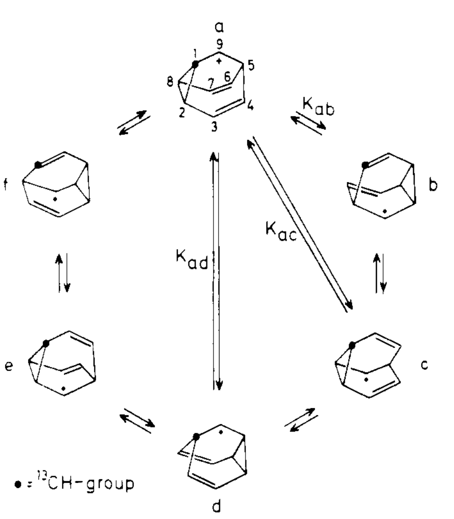
and 152 ppm, respectively, at −150 °C. However, because of the lack of proper model compounds, it is impossible to make accurate enough estimates of the chemical shifts of structure **6**. Therefore, the data obtained so far did not seem to allow a discrimination between the two candidates **5** and **6**.

Inspired by the elegant work of Saunders in discriminating between equilibrating classical and nonclassical carbocations by means of isotopic perturbation and its influence on the NMR spectra of the cations,[12-14,18] we analyzed the consequences of deuterium substitution in our totally degenerate $C_9H_9^+$ ions.

Substitution of H with D at ^{13}C was purposely avoided since this would result in a drastically decreased ^{13}C NMR S/N because of ^{13}C–D coupling and the absence of a nuclear Overhauser effect. To make the effect of the isotopic perturbation as large as possible and simultaneously maintain the S/N, it was decided to exchange all H with D except on the ^{13}C label (C-3). The synthetic route shown in Scheme V was designed for $[(CD)_8{}^{13}CH]^+$. The different C–H bonds in ions **5** and **6** have different zero-point energies, and the CD groups will preferentially be found in those positions which have the highest zero-point energy since this will result in the lowest total zero-point energy (and lowest total energy). Earlier studies (e.g., with deuterated barbaralone (**26**); see Scheme VI) have shown D to prefer C–H bonds in the following order: C(aliphatic) > C(cyclopropyl) > C(vinylic).[19]

If the totally degenerate ion **1** has structure **5**, a CD group in $[(CD)_8{}^{13}CH]^+$ (**13**) is expected to prefer any of the positions 1, 2, 5, or 8 over any of the remaining ones. Consequently, the ^{13}CH group is more likely to be in one of the positions 3, 4, 6, 7, and 9 (the carbon at the 9-position is assumed to be similar to a vinylic one) than in any of the other positions. Since for **5** the estimated ^{13}C NMR signals of C-3, C-4, C-6, C-7, and C-9 are at lower field than those of C-1, C-2, C-5, and C-8 (Table I), the average ^{13}C NMR signal of **13** is predicted to be at somewhat lower field than that for **11** in which the ^{13}CH group is about evenly distributed among the nine positions. This prediction is in agreement with the experimental observation; i.e., the singlet in Figure 1c is shifted 4.5 ppm downfield relative to the one in Figure 1a. However, by similar reasoning it is found that a downfield shift is also expected if ion **1** has structure **6**, and therefore the observed downfield shift does not allow differentiation between structures **5** and **6**.

Scheme VII



Ion **6** has two groups of equivalent positions, C-3, C-7, C-9 and C-1, C-2, C-4–C-6, C-8, respectively. Since the carbons in a group are equivalent, there is an equal probability that ^{13}CH will be found in any of the positions within that group. Therefore, essentially no difference in the chemical shifts between the two signals in Figure 1d and those in Figure 1b would be expected. The area ratio of the two peaks is predicted to change when going from **11** (6:3) to **13**. While the observed decreased area ratio is consistent with the predictions, the observed large shift differences are not. This result excludes **6** as a candidate for the structure of ion **1**.

Are the results consistent with ion **1** having structure **5**? If ion **5** is the rearranging ion, then the low-field peak of Figure 1b originates from ^{13}C in the 3-, 7-, and 9-positions and the high-field one from positions 1, 2, 4–6, and 8, respectively. Now, since the positions in each group are not equivalent, the ^{13}CH group will preferentially be found in certain positions of the group. In the six-carbon group of **13** the probability of finding ^{13}CH at position 4 or 6 is larger than that of finding it at position 1, 2, 5, or 8, and, therefore, a larger six-carbon weighted average chemical shift is predicted for **13** than for **11**. For the three-carbon group, on the other hand, the nonequivalence of positions 3, 7, and 9 is probably small, and consequently only a small shift difference between low-field peak of **13** and that of **11** is expected. The observed shift differences are +6 and −1 ppm for the high- and low-field peaks, respectively. Consistently the area ratio has decreased from 6:3 for **11** to ca. 5:3 for **13**. These data, therefore, are at least qualitatively consistent with ion **1** having structure **5**.

The results presented above were next analyzed quantitatively assuming that ions **11** and **13** have the 9-barbaralyl cation structure (**5**). Let us first consider scrambling of the ^{13}CH group only among the six positions 1, 2, 4–6, and 8 (Scheme VII). Scheme VII is aimed to show primarily the equilibria considered among the structures a–f rather than the mechanisms by which these equilibria are obtained. Consequently, the chemical shift (δ^6) for upfield ^{13}C NMR singlet is

$$\delta^6 = f_a\delta_1 + f_b\delta_4 + f_c\delta_2 + f_d\delta_5 + f_e\delta_8 + f_f\delta_6 \qquad (1)$$

The mole fraction of the x isomer among the isomers a–f is denoted f_x, and δ_i is the chemical shift of ^{13}C in position i. The symmetry of ion **5** implies that $\delta_2 = \delta_8$ and $\delta_4 = \delta_6$, and $f_b = f_f$ and $f_c = f_e$. By these simplifications eq 2 is obtained from eq 1.

$$\delta^6 = f_a\delta_1 + 2f_b\delta_4 + 2f_c\delta_2 + f_d\delta_5 \qquad (2)$$

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(18) (a) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867–6868. (b) Saunders, M.; Siehl, H.-U. *Ibid.* **1980**, *102*, 6868–6869. (c) Saunders, M.; Kates, M. R.; Walker, G. E. *Ibid.* **1981**, *103*, 4623–4624. See also: (d) Schmitz, L. R.; Sorensen, T. S. *Ibid.* **1980**, *102*, 1645–1648. (e) Hogeveen, H.; van Kruchten, E. M. G. A. *J. Org. Chem.* **1981**, *46*, 1350–1353. (f) Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Singh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 588–596. (g) Kirchen, R. P.; Okazawa, N.; Ranganayakulu, K.; Rauk, A.; Sorensen, T. S. *Ibid.* **1981**, *103*, 597–604.

(19) Barborak, J. C.; Chari, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 5275–5277.

The three equilibrium constants (equilibrium isotope effects) that characterize the equilibria in Scheme VII are defined as follows:

$$K_{ab} = f_b/f_a \qquad K_{ac} = f_c/f_a \qquad K_{ad} = f_d/f_a \tag{3}$$

Each of these three equilibrium constants for ion **11** is assumed to be close to 1 since the ^{13}C is expected to impart only a very small perturbation on the equilibria. With this assumption and the fact that the sum of the mole fractions is unity ($f_a + 2f_b + 2f_c + f_d = 1$), eq 2 is transformed into eq 4.

$$\delta_{11}{}^6 = \frac{1}{6}(\delta_1 + 2\delta_2 + 2\delta_4 + \delta_5) \tag{4}$$

The introduction of eight deuteriums in **11** to yield ion **13**, on the other hand, causes large perturbations of the equilibria in Scheme VII. Using the equilibrium constants defined in eq 3, we derive for the mole fractions $f_a - f_f$:

$$f_a = 1/(1 + 2K_{ab} + 2K_{ac} + K_{ad}) \tag{5}$$

$$f_b = K_{ab}/(1 + 2K_{ab} + 2K_{ac} + K_{ad}) \tag{6}$$

$$f_c = K_{ac}/(1 + 2K_{ab} + 2K_{ac} + K_{ad}) \tag{7}$$

$$f_d = K_{ad}/(1 + 2K_{ab} + 2K_{ac} + K_{ad}) \tag{8}$$

and that

$$\delta_{13}{}^6 = \frac{\delta_1 + 2K_{ab}\delta_4 + 2K_{ac}\delta_2 + K_{ad}\delta_5}{1 + 2K_{ab} + 2K_{ac} + K_{ad}} \tag{9}$$

The chemical shift difference between the "six carbons" of ions **11** and those of **13**, which is found to be −6 ppm, may be expressed with eq 2 and 9.

$$\delta_{11}{}^6 - \delta_{13}{}^6 = \frac{a_0 + a_1K_{ab} + a_2K_{ac} + a_3K_{ad}}{6(1 + 2K_{ab} + 2K_{ac} + K_{ad})} = -6 \tag{10}$$

In eq 10

$$a_0 = -5\delta_1 + 2\delta_4 + 2\delta_2 + \delta_5$$

$$a_1 = 2\delta_1 - 8\delta_4 + 4\delta_2 + 2\delta_5$$

$$a_2 = 2\delta_1 + 4\delta_4 - 8\delta_2 + 2\delta_5$$

$$a_3 = \delta_1 + 2\delta_4 + 2\delta_2 - 5\delta_5$$

The following set of a_i values is obtained with the predicted ^{13}C chemical shifts for ion **5** shown in Table I: $a_0 = 86.7$, $a_1 = -293.4$, $a_2 = -100.2$, and $a_3 = 306.9$ ppm, respectively. From these values and the assumption that K_{ac} is close to unity (a ^{13}CD group most likely show almost the same preference for any of the cyclopropane positions in **5**) and that $K_{ad} = 0.59$[20] (such a value has been measured for the corresponding [1-^2H]- and [5-^2H]-9-barbaralone),[19] a value of 1.34 is estimated for K_{ab} from eq 10. This value corresponds to an isotope effect of 1.13 at room temperature (assuming the free energy difference to be only a zero-point energy difference). This K_{ab} value is in the expected range. By similar reasoning for the 1-ppm upfield shift of the downfield peak, the equilibrium constant for the equilibrium of structures with ^{13}CH in the 9- and 3- or 7-positions (and with eight CD groups) is found to be small (1.04 at −150 °C), as expected. Thus, a CD group only slightly prefers the charged 9-position over the olefinic 3- or 7-position. Thus, our observations qualitatively and quantitatively support the 9-barbaralyl cation structure **5** for the degenerately rearranging ion **1**.

The D_{3h} structure **6** has also been proposed as an intermediate or transition state in the rearrangements of **5**. However, in their group theoretical study of ions **4**–**6** and their rearrangements, Bouman and Trindle using nuclear spin functions concluded that if the $C_9H_9^+$ ion has the 9-barbaralyl cation structure, then the D_{3h} structure **6** can be neither a transition state nor an intermediate in the rearrangements of **5**.[8] Under these conditions McIver's rules[9] also exclude **6** as a possible transition state.

Furthermore, preliminary STO-3G calculations yield the following energy ordering for the ions considered: **6** > **4** > **5** > **3**.[21]

All results taken together therefore strongly suggest that the observed ion **5** undergoes a 6-fold degenerate rearrangement by divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cationic rearrangements shown in Scheme I rather than by any of the other proposed mechanisms. The measured barrier for the 6-fold degenerate rearrangement of **5** is ~16 kJ mol^{-1} (~3.8 kcal mol^{-1}). The barrier for the totally degenerate rearrangement, i.e., the 9-fold rearrangement, is found to be only about 5 kJ mol^{-1} higher, i.e., 21 kJ mol^{-1} (5.0 kcal mol^{-1}). In this latter rearrangement of ion **5**, ion **4** is likely to be an intermediate.

Experimental Section

The ^1H NMR and the proton-noise-decoupled ^{13}C NMR spectra were obtained with a JEOL-FX100 pulse spectrometer equipped with a 5-mm variable-temperature $^1H/^{13}C$ dual probe, external ^7Li lock, and quadrature phase detector. Data autostacking programs FAFT 20/21/22 and FAFT 70-791221 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 7.24]), and CD_3CN ([δ_H 2.0]) were used (figures in square brackets represent ^1H NMR signals from the residual protonated species).

The temperature determinations in the NMR probe were performed with a precalibrated chemical shift thermometer (CH_3OH in a mixture of $CHCl_2F$–$CDClF_2$ 1:1, v/v). At the lower temperature (i.e., −150 °C) the maximum error limits are ±1 °C. Spectra were usually taken with the sample solution at the lower temperature first and then at the higher ones. Consequently, there are no signals from nondegenerate rearranged 1,4-dihomotropylium cation (**3**) in spectra b and d in Figure 1.

Regarding $[(CH)_8{}^{13}CH]^+$ (**11**), the solvent signals (marked F in Figure 1) were suppressed with a double-pulse sequence (180°, τ, 90°), in which τ was taken as ca. $T_1 \times \ln 2$ for the $CHCl_2F$ signal but at the same time less than $5 \times T_1$ for the barbaralyl signals. A spectral width of 8 kHz, 8192 data points, data aquisition times of 0.2 s, pulse interval times (τ) of 180 and 78 ms, delay times of 0.3 and 0.1 s between the pulse sequences, and 4000 and 8000 scans for spectra a and b, respectively, in Figure 1 were used. When the data were processed, the following positive exponential and trapezoidal windows were used: exp = 9, $T_1 = T_2 = 0$, $T_3 = 0.9 \times T_4$, and T_4 chosen as the end of the data-aquisition time.

Regarding $[(CD)_8{}^{13}CH]^+$ (**13**), only single-pulse spectra were recorded, but double-length data processing was performed. The following parameters were used: pulse width, 90°; spectral width, 8 kHz; 8192 data points when recording the spectra; data aquisition time, 0.3 s; delay between the pulse sequences, 0.1 s; and 8000 and 10000 scans for spectra c and d, respectively, in Figure 1. The same exponential and trapezoidal windows as above were used when processing the data.

The rearrangement barriers given earlier[11] have been calculated directly from k_{obsd} which in turn have been estimated from the equation for exchange above the temperature of coalescence. The barriers in this paper refer to particular mechanisms and therefore deviate somewhat from those earlier given.

High-performance liquid chromatography (HPLC) was carried out with a Waters 6000A solvent delivery system and a Waters 440 absorbance detector (254 nm), on a μPorasil (10 μm) silica column (4 mm × 0.3 m) with chloroform/*n*-hexane 4:1 (spectro quality) as the mobile phase. For preparative gas chromatography (GLC) a Varian 90-P was used and the column was a 0.65 m × $^3/_8$ in. copper tube with 20% Reoplex 400 on Chromosorb W (60/80 mesh). The carrier gas flow (He) was 60 mL min^{-1} and the column temperature 144 °C. A Perkin-Elmer 990 instrument was used for analytical GLC as described in the text. Thin-layer chromatography (TLC) was performed on DC-alufolien, silica gel F254, eluted with ether/petroleum ether 7:3.

Cyclohepta-1,3,5-triene (Fluka, practical, 95%), potassium *tert*-butoxide (Fluka, practical), tetrafluoroboric acid (Riedel, 50%, "chemisch rein"), [2-^{13}C]malonic acid (Prochem, 90 atom % ^{13}C), oxalyl chloride (Merck, "zur Synthese", 97%), lithium aluminum deuteride (CIBA-GEIGY, >99 atom % ^2H), and lithium aluminium hydride (Merck, "zur Synthese", 90%) were used as purchased. Pyridine (Kebo-Grave, purum) was distilled and triethylamine (TEA) (Baker, >99%) was distilled over sodium. They as well as [$^2H_6$]dimethyl sulfoxide (CIBA-GEIGY, >99.5 atom % ^2H) were stored over molecular sieves (3 Å). Carbon tetrachloride (Merck), methylene chloride (Merck), and *n*-heptane (Merck), all analytically pure, were stored over molecular sieves (3 Å). Diethyl ether (May & Baker, anhydrous) was dried over sodium.

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[20] Recalculated to −150 °C.

[21] Huang, M. B.; Goscinski, O.; Jonsäll, G.; Ahlberg, P. *J. Chem. Soc., Perkin Trans. 2*, in press.

All reactions were carried out under dry nitrogen in glassware dried at 120 °C overnight.

[1,2,3,4,5,6,7,7-^{2}H$_8$]Cyclohepta-1,3,5-triene (15).[22] Cyclohepta-1,3,5-triene (**14**, 1.43 g, 15.5 mmol) was mixed with a suspension of 0.41 g (3.7 mmol) of potassium *tert*-butoxide in 7.6 g (90 mmol) of [^{2}H$_6$]dimethyl sulfoxide; the mixture was transferred to a glass ampule which was then sealed. The ampule was placed in a PEG-600 bath (MoDo, polyethylene glycol) at 90 °C for 24 h and then 100 °C for 15 h. A colorless fraction of cyclohepta-1,3,5-triene (ca. 80 atom % ^{2}H) was isolated by distillation (40–50 °C/(8–10 mm)) from the dark brown reaction mixture (the receiver being cooled with liquid nitrogen) and dried over molecular sieves (3 Å).

A mixture of this crude product (1.0 g, ca. 10 mmol) and a suspension of 0.31 g (2.8 mmol) of potassium *tert*-butoxide in 7.08 g (84.2 mmol) of [^{2}H$_6$]dimethyl sulfoxide in a sealed ampule was again heated at 90 °C for 15 h and then at 100 °C for 9 h. After being distilled (35–40 °C/(10 mm)) crude **15** (0.688 g, yield ca. 40%) was dried over molecular sieves (3 Å). A total of 2.31 g of distilled **15** (crude) so prepared from 5.43 g (58.9 mmol) of **14** was analyzed by GLC on a 2 m × $^1/_8$ in. column with 10% SE-30 on Chromosorb W at a column temperature of 58 °C and by ^{1}H NMR spectroscopy using benzene as the internal standard. This crude **15** contained 9 wt % of *tert*-butyl [^{2}H]alcohol. Purification of this mixture before the next reaction step is recommended (cf. note 24). Yield of **15**: 2.31 g (91% pure, 36% calculated on 21 mmol of pure product) containing 2.2 atom % ^{1}H.

[1,2,3,4,5,6,7-^{2}H$_7$]Tropylium Tetrafluoroborate (16).[23] To a suspension of 10.17 g (48.8 mmol) of phosphorus pentachloride in 65 mL of carbon tetrachloride in a 100 mL two-necked round-bottomed flask equipped with a mechanical stirrer and a gas-exit valve was added 2.2 g (20 mmol at 91% purity) of **15**, and the mixture was stirred at room temperature for 18 h.[24] The solid material was isolated by vacuum filtration, washed with cold carbon tetrachloride, and dissolved in 35 mL of ice-cold absolute ethanol with rapid stirring. Upon the addition of 5 mL of tetrafluoroboric acid, a white precipitate was formed which was separated by suction filtration, washed with cold ethanol and ether, and air-dried. The product (**16**) was analyzed by ^{1}H NMR spectroscopy, with CH$_3$CN as internal standard, to determine the ^{1}H content: yield, 1.17 g (6.35 mmol, 32%) containing 2.2 atom % of ^{1}H; ^{1}H NMR (CD$_3$CN) δ 9.32.

[1,2,3,4,5,6,7-^{2}H$_7$]Cyclohepta-2,4,6-trien-1-yl[2-^{13}C]acetic Acid (18).[25] To a magnetically stirred solution of 0.51 g (4.9 mmol) of [2-^{13}C]malonic acid in 5 mL of pyridine in a 10-mL round-bottomed flask fitted with a condenser was added 0.895 g (4.84 mmol) of **16**, and the mixture was refluxed for 42.5 h.[26] After being acidified with 25 mL of 4 M hydrochloric acid, the mixture was extracted 12 times with 12-mL portions of diethyl ether, and the combined extracts were dried over MgSO$_4$, filtered, and evaporated to yield 0.75 g (4.7 mmol, 98%) of a brown viscous product (**18**) which was used without purification: ^{1}H NMR (CD$_2$Cl$_2$) δ 11.62 (s, 1 H), 2.79 (s, 0.2 H and d, $^1J_{CH}$ = 128.9 Hz, 1.8 H), residual protons at δ 6.74, 6.28, 5.32.

[1,2,3,4,5,6,7-^{2}H$_7$]Cyclohepta-2,4,6-trien-1-yl[2-^{13}C]acetyl Chloride (19).[25] Crude **18** (0.75 g, 4.7 mmol) was dissolved in 10 mL of methylene chloride, containing one drop of pyridine, in a 100-mL round-bottomed flask equipped with magnetic stirrer, reflux condenser, and gas-exit valve. After the addition of 1.8 mL of oxalyl chloride, the solution was stirred at room temperature for 5.5 h. Evaporation of the solvent and removal of hydrogen chloride under vacuum (oil pump) left 0.80 g (4.5 mmol) of **19** as a brown oil, which was used without purification.

[3-^{13}C,1,4,5,6,7,8,9-^{2}H$_7$]Bicyclo[3.2.2]nona-3,6,8-trien-2-one (20).[4b,15,27] A solution of **19** (0.80 g, 4.5 mmol) in 50 mL of *n*-heptane in a dropping funnel on top of a bulb condenser fitted onto a three-necked, round-bottomed flask, equipped with reflux condenser, magnetic stirrer, and capillary nitrogen inlet, was added dropwise over a 22-h period into a refluxing solution of 1.6 mL of triethylamine in 55 mL of *n*-heptane. Two 0.4-mL portions of triethylamine were added during the period. Reflux was continued for another 2.5 h after the addition of **19** was completed.[28] After being cooled, the mixture was filtered and the residual triethylamine hydrochloride precipitate in the filtrate removed by centrifugation. *n*-Heptane and triethylamine were removed by distillation and the residue was flash-distilled under vacuum (oil pump). The distillate contained 65% of **20**, 30% of **21**, and 5% of a third product presumed to be [2-^{13}C,3,3a,4,5,6,7,7a-^{2}H$_7$]-3a,7a-dihydroinden-1-one (**27**),[15,29] as analyzed by GLC on a 2.0 m × $^1/_8$ in. column with 5% Reoplex 400 on Chromosorb W at a column temperature of 133 °C. Separation of the mixture by preparative GLC gave 116.6 mg of **20** (0.834 mmol; 17% yield from **16**) and 152.5 mg of **21** (1.090 mmol; 22.5% yield from **16**).

[3-^{13}C,1,2,4,5,6,7,8,9-^{2}H$_8$]Bicyclo[3.2.2]nona-3,6,8-trien-2-ol (12).[4b,15] From a suspension of 1.07 g of lithum aluminium deuteride in 10 mL of diethyl ether was taken 1 mL, which was cooled to −80 °C. A solution of 65 mg (0.46 mmol) of **20** in 1 mL of diethyl ether was added dropwise. After the addition was completed, stirring was continued for 5 h at −80 °C when the reduction, monitored by TLC, was finished.

The product was worked up by the normal procedure[4b] and purified by sublimation (40 °C/(0.05 mm)), leaving 31.5 mg (0.220 mmol) of **12** as white needles. Analysis by ^{1}H NMR spectroscopy showed ca. 1 atom % of ^{1}H in the 2-position and ca. 3 atom % in the other deuterated positions: ^{1}H NMR (CD$_2$Cl$_2$) δ 4.98 (s, 0.1 H, and d, $^1J_{CH}$ = 157.7 Hz, 0.9 H), 2.36 (s, 1 H), and residual protons at δ 6.80, 6.70, 6.32, 6.21, 6.13, 3.27, 3.20 (in total 0.2 H).

Cyclohepta-2,4,6-trien-1-yl[2-^{13}C]acetic Acid (28).[25] Reaction of tropylium tetrafluoroborate (0.86 g, 4.9 mmol) with [2-^{13}C]malonic acid (0.51 g, 4.9 mmol) gave 0.72 g of crude **28** by the same procedure used to obtain **18**.

Cyclohepta-2,4,6-trien-1-yl[2-^{13}C]acetyl Chloride (29).[25] Treatment of **28** with oxalyl chloride in the same manner as **18** gave 0.80 g of **29** as a brown oil.

[3-^{13}C]Bicyclo[3.2.2]nona-3,6,8-trien-2-one (30).[4b,15,27] Elimination of HCl from **29** in refluxing triethylamine/*n*-heptane over a 6-h period followed by reflux for 13 h gave **30** and [2-^{13}C]indan-1-one (**31**) in the ratio 53:47 (analytical GLC; see **20**). Separation by preparative GLC yielded 63 mg (0.47 mmol) of **30** and 94 mg (0.70 mmol) of **31**. **30**: ^{1}H NMR (CDCl$_3$) δ 7.04 (d, d, J_{HH} = 8.2 and 10.9 Hz, 1 H), 6.70 (t, J_{HH} = 6.7 Hz, 2 H), 6.34 (t, J_{HH} = 6.8 Hz, 2 H), 5.05 (d, d, $^1J_{CH}$ = 164 Hz, J_{HH} = 10.6 Hz, 0.9 H, and d, J_{HH} = 10.8 Hz, 0.1 H), 4.17 (1 H), 3.83 (m, J_{HH} = 7 Hz, 1 H); ^{13}C NMR δ 189.2 (d, $^1J_{CC}$ = 52.5 Hz) 153.0 (d, $^1J_{CC}$ = 64.7 Hz), 138.1, 128.3, 124.4, 59.1 (d, $^2J_{CC}$ = 12.2 Hz), 41.3. **31**: (CDCl$_3$) ^{1}H NMR δ 7.8–7.2 (m, 4 H), 3.1 (t, J_{HH} = 6 Hz, 2 H), 2.6 (d, t, $^1J_{CH}$ = 132 Hz, J_{HH} = 6 Hz, 0.9 H, and t, J_{HH} = 6 Hz, 0.1 H); ^{13}C NMR δ 206.6 (d, $^1J_{CC}$ = 39.1 Hz), 154.8, 136.7 (d, $^2J_{CC}$ = 18.3 Hz), 134.2, 126.9, 126.3, 123.2, 35.9, 25.4 (d, $^1J_{CC}$ = 34.2 Hz).

[3-^{13}C]Bicyclo[3.2.2]nona-3,6,8-trien-2-ol (10).[4b,15] To a stirred suspension of 22.4 mg (0.59 mmol) of lithium aluminium hydride in 6 mL of ether at −80 °C was added a solution of 63 mg (0.47 mmol) of **30** in 10 mL of ether dropwise. Stirring was continued for 2 h after the addition was completed. The usual workup procedure[4b] was followed by purification using HPLC. The fraction containing **10** was evaporated and the residue sublimed (35 °C/(0.04 mm)) to give 27 mg (0.20 mmol) of **10** as white needles: ^{1}H NMR (CD$_2$Cl$_2$) δ 6.88–6.63 (m, 2 H), 6.41–6.05 (m, 3 H), 4.99 (d, d, m, $^1J_{CH}$ = 158 Hz, J_{HH} = 10.8 Hz, 0.9 H, and d, m, J_{HH} = 10.8 Hz, 0.1 H), 4.02 (br, 1 H), 3.51 (m, 1 H), 3.26 (m, J_{HH} = 7.4 Hz, 1 H), 1.80 (br, 1 H); ^{13}C NMR δ 140.6, 139.4, 135.4 (d, $^1J_{CC}$ = 70.8 Hz), 127.8, 65.0 (d, $^1J_{CC}$ = 46.4 Hz), 44.8, 37.6.

Preparation of Ions. All ions were synthesized in 5-mm NMR tubes with the ion generation apparatus earlier described in detail in ref 16 and 10b.

Barbaralyl cation [(CH)$_8$^{13}CH]$^+$ (**11**) was prepared with the precursor **10** dissolved in two different solvents, CD$_2$Cl$_2$ and CHCl$_2$F.

I. **10** (7.1 mg) was dissolved in ca. 110 mg of CD$_2$Cl$_2$ and added at −135 °C with efficient mixing to ca. 0.4 mL of a solution of FSO$_3$H–SO$_2$ClF–SO$_2$F$_2$ (1:5:2, v/v/v). After a few minutes of stirring, the reaction mixture became pale yellow and transparent.

II. **10** (7.5 mg) was dissolved in ca. 140 mg of CHCl$_2$F, which was condensed at about −10 °C (ethanol + ice) into a small test tube containing the alcohol **10**. This precursor solution was then added at −135 °C by nitrogen gas pressure through a Teflon tube to ca. 0.4 mL of a solution of FSO$_3$H–SO$_2$ClF–SO$_2$F$_2$–CHCl$_2$F (2:7:7:1, v/v/v/v) and rapidly mixed. After a few minutes of stirring, the reaction mixture became pale yellow and transparent.

Barbaralyl cation [(CD)$_8$^{13}CH]$^+$ (**13**) was prepared according to II above from ca. 8 mg of **12**. The precursor solution was added at −138 °C into ca. 0.5 mL of a solution of FSO$_3$H–SO$_2$ClF–SO$_2$F$_2$–CHCl$_2$F

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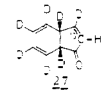
[28] The higher reflux temperature of *n*-heptane compared with *n*-hexane[4b] favors the intramolecular rearrangements and makes a faster addition of **19** possible.[27]

[29] Structure of **27**:



27

(2:7:7:3, v/v/v/v). The reaction mixture was pale yellow and transparent.

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Registry No. **9**, 28830-19-5; **10**, 84057-16-9; **11**, 84057-17-0; **12**, 77136-98-2; **13**, 84057-18-1; **14**, 544-25-2; **15**, 16675-63-1; **16**, 84057-27-2; **17**, 55514-11-9; **18**, 84057-19-2; **19**, 84057-20-5; **20**, 84057-21-6; **21**, 84057-22-7; **24**, 53959-89-0; **25**, 42289-60-1; **28**, 84057-23-8; **29**, 84057-24-9; **30**, 84057-25-0; **31**, 84057-26-1.

Chemistry of Heavy Carbene Analogues R_2M (M = Si, Ge, Sn). 8.[1] Germylenes: Singlets or Triplets? [2 + 4] Cheletropic Cycloadditions of Me_2Ge and GeI_2 to Conjugated Dienes[2]

Michael Schriewer[3] and Wilhelm P. Neumann*

Contribution from the Lehrstuhl für Organische Chemie I of the University of Dortmund, D 4600 Dortmund 50, Federal Republic of Germany. *Received February 8, 1982*

Abstract: Thermally generated germylenes Me_2Ge undergo in solution under mild conditions (70–150 °C) concerted 1,4-additions of the linear [2 + 4] cheletropic type to certain 1,3-dienes. Thus, the highly reactive meso diallene **10a** gives, in a about 1:1 ratio, only the two isomeric 1-germacyclopentenes **11a** and **11b** expected from front- and back-side attack of Me_2Ge, whereas the D,L-diallene **10b** produces only the third isomer, **11c**, in accordance with this mechanism. The yields are about 70%; the isomer purity is ≥98%. Likewise, two other *E,E*-1,4-disubstituted 1,3-butadienes give only the corresponding cis-2,5-disubstituted 1-germacyclopentenes **7a** or **9a** in 80% or 30% yields with an isomer purity of ≥98% (limit of the NMR analysis). Similarly, with GeI_2 and **10a**, only **14a** and **14b** are found, and **14c** with **10b**, as expected for a cheletropic reaction. Methylation of **14a–c** yields the corresponding compounds **11a–c**. Other mechanisms for these 1,4-additions are discussed but are highly unlikely: thermal germylenes Me_2Ge and GeI_2 behave as singlets.

The concept of carbenes R_2C as reactive intermediates was—and still is—one of the most fruitful in organic chemistry during the last three decades both in theoretical/mechanistic and in preparative respects. For the understanding of carbene reactions, Skell's rule[4] has been quite elucidating: during addition of singlet carbenes to substituted olefins, the stereochemistry of the substituents is preserved in the cyclopropane produced, whereas a cis/trans mixture follows from addition of triplet carbenes to a sterically uniform olefin, passing a biradical.

Recently much attention has been directed toward the heavier carbene analogues, the silylenes R_2Si,[5] germylenes R_2Ge,[6] and stannylenes R_2Sn.[1,7] Also in these cases the singlet/triplet problem arises. Whereas quantum chemical calculations have shown the singlet state to be the ground state for H_2Si,[8] H_2Ge,[9,10] H_2Sn,[10] Me_2Ge,[9] and Me_2Sn[10]—in contrast to H_2C and Me_2C, where the triplet is of lower energy[11]—experimental efforts with this respect are known for silylenes only: Me_2Si gives with Me_3SiH the insertion product Me_3SiMe_2SiH and no abstraction–recombination products like Me_6Si_2.[12] This is evidence for a singlet behavior of Me_2Si. The attempted cycloaddition to suited monoolefins gave for a long time no conclusive products.[5,13] Addition to both (*E*)- and (*Z*)-2-butene immediately followed by methanolysis has resulted each time in an uniform product, allowing the conclusion that also the silylene attack to the olefin has been stereospecific.[14] Addition at 420 °C to (*E,E*)-2,4-hexadiene gave mixtures of *cis*- and *trans*-2,5-dimethyl-1-silacyclopent-3-ene.[5,13] Experiments with Me_2Si under milder conditions (70 °C) were unsuccessful.[15] Lastly, no addition experiments of silylenes to 1,3-dienes could be found in the literature, elucidating definitely whether there is a stereospecific (concerted) singlet or a nonstereospecific (two-step free radical, e.g.) triplet silylene reaction. Moreover, concerted 1,4-cycloaddition was precluded for the experiments mentioned above.[5,13] Thus, this situation in the case of silylenes still remains unsatisfying.

For the heavier analogues, the germylenes R_2Ge, no experiments have been reported to our knowledge concerning the singlet/triplet problem.[16] Since we have found recently a convenient source for smooth thermal generation of germylenes within the range 70–150 °C by thermolysis of 7-germanorbornadienes **1**,[17] we wish to report now cycloadditions of dimethylgermylene Me_2Ge to

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