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THE 1,6-π CLEAVAGE OF THE NORBORNYL SKELETON

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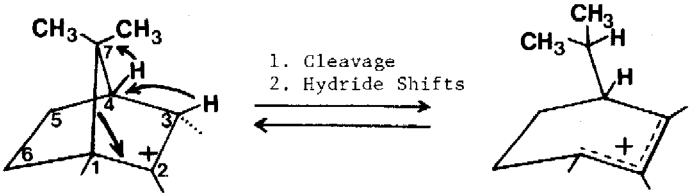
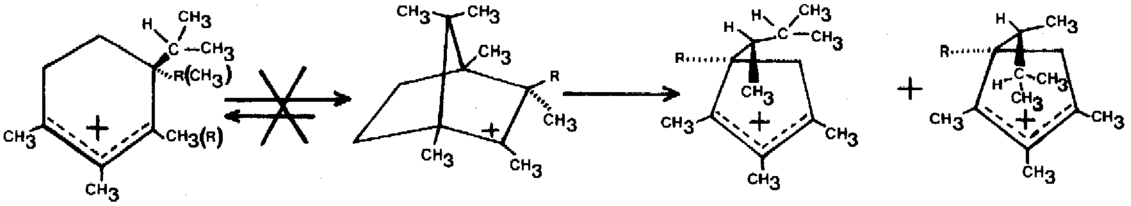
In 1964, Deno (1) first reported that norbornyl cations were cleaved under observable ion conditions, to yield cyclohexenyl cations. Subsequently, this 1,7-π cleavage has been observed in other norbornyl systems, is in some cases reversible and can even be made to proceed in the right to left direction depending on the substituents (2).

Eq. 1



The corresponding 1,6-π cleavage had not been observed (3) but we now report that the hexamethyl and heptamethyl 2-norbornyl cations 1 and 2, previously described (4), are preferentially cleaved by this 1,6-π route. The cation 1 rearrangement is exceptionally clean ($k_{rearr.} = 4.8 \times 10^{-4} s^{-1}$ at -50, $\Delta G^{\neq} = 16.3$ kcals/mole) and the most clear-cut to analyze (n.m.r. spectrum Fig. 1) (5). From decoupling experiments (6), recovery experiments giving substituted cyclopentadienes and from reasoning analogous to that used in a similar structural elucidation (7), the product is the diastereomeric cyclopentenyl cations 3a and 3b. Initially, the product mixture is richer in 3b but on standing at 25°C, the proportions change and after 24 hours (equilibrium), there is *ca.* twice as much of 3a in the mixture.



1 R = CH_3
2 R = H

3a R = CH_3
4a R = H

3b R = CH_3
4b R = H

The hexamethyl cation 2 rearrangement is also very clean, $k_{rearr.} = 2.7 \times 10^{-4} s^{-1}$ at -3°, $\Delta G^{\neq} = 20.2$ kcals/mole. The high field methyl n.m.r. peaks of the product are more overlapped than in 3a and 3b, however it is clear from the lower field part that the product is a cyclopentenyl cation with methyl groups at positions 1, 2, 3, but not, like 3a and 3b, at positions 4 (or 5) (8) Knowing the results from 1 and using decoupling experiments, one can assign the diastereomeric structures 4a and 4b to the rearrangement products from 2. The initially formed ratio of 4a and

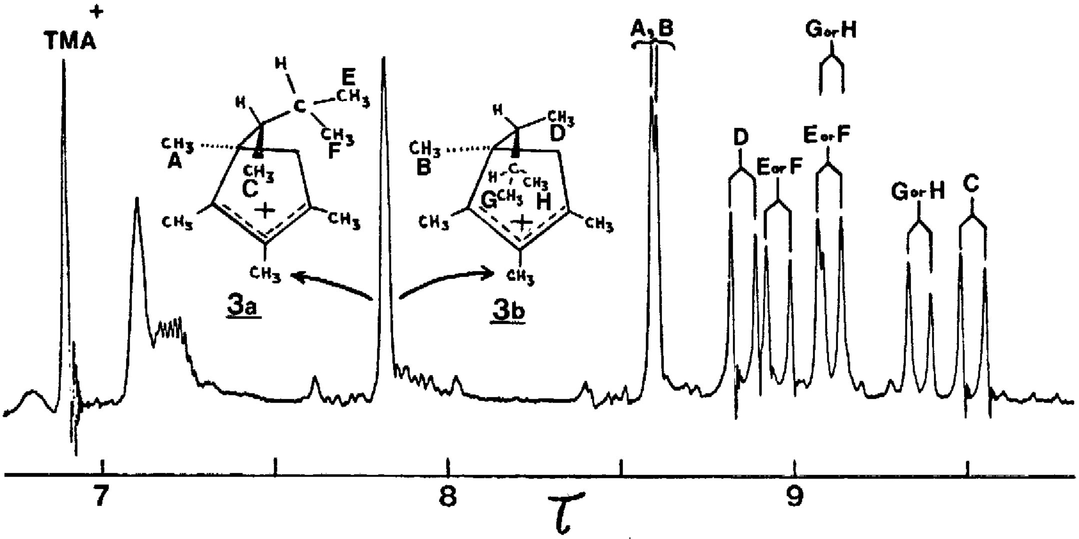
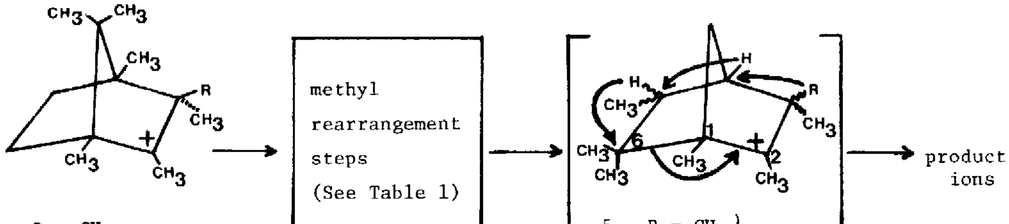


Fig. 1

4b is ca. 2:1.

It is not obvious that 3a, 4a etc. are products of a 1,6-norbornyl cation cleavage because the mechanism (9) requires a prior shuffling of the methyl substituents on the norbornyl skeleton so that one ends up with an intermediate cation (5 or 6, respectively, from 1 and 2). Similar methyl rearrangements have previously been studied using graph theory together with estimates of the barriers for each individual step in the total graph (10). One can determine that not only

Eq. 3



1. R = CH3
2. R = H

5. R = CH3
6. R = H
not observed

are there many routes from 1 to 5 (Table 1), but also that one of these should be quite rapid (in fact rapid enough to accommodate the observed $\Delta G^{\neq}$ for 1 → 3a, 3b). Isomer 5 is statistically only one of 210 tertiary isomers of this 2-norbornyl system but is important because it is relatively accessible from 1 and because of an Achillean skeletal weakness, the presence of a potential tertiary cation at C6 upon cleavage of the C1 - C6 bond (11). The much slower rearrangement rate observed for 2 can also be explained using graph theory. In 1, a rather expeditious three step route (see Table 1) leads to 5. To get from 2 to 6 (Table 1), we require a minimum of five steps, and also a predicted higher $\Delta G^{\neq}$ barrier. Whereas the highest barrier in 1 → 3a, 3b may be the actual cleavage step, it is possible that in 2, the highest barrier is in getting from 2 to 6.

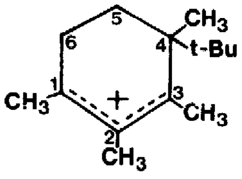
Since typical 1,7-π cleavage reactions (illustrated by Eq. 1) normally occur at faster rates than 2 → 4a, 4b (1,2), we also looked at cations 7 (12) and 8 (13), the expected 1,7-cleavage pro-

Table 1 Computer Generated Routes (see Eq. 3)

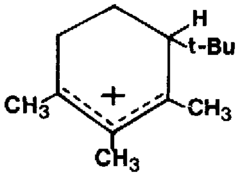
Rearrangement	Sequence[a]	Calc'd Highest Barrier[b] ($\Delta G^{\neq}$, kcals/mole)
1 → 5(exo or endo CH_3 at C5)	312	11.0
	32121312321	15.9 + 15.7
	3121231313121	15.7 (twice)
	321213121313121	15.9 + 15.7
2 → 6(exo or endo CH_3 at C3 or C5)	32132	15.9
	312321212	15.9
	3213212121	15.9 + 15.7 (twice)
	+ one of 11 steps, 3 of 14 steps, one of 15 steps	15.9 or more

a) symbols 1 ≡ Wagner-Meerwein rearrangement; 2 ≡ exo-3,2-shift; 3 ≡ endo-6,2-H shift, maximum number of steps considered = 15. (b) barriers taken from refence 10.

ducts of 1 and 2, respectively. Based on previous work, it seemed possible that 7 and 8 might be in equilibrium with 1 and 2, respectively, and that the equilibrium might favour the norbornyl cations to the extent that 7 (or 8) would be unobservable by n.m.r. (2). However, both 7 and 8 turn out to be relatively stable at the temperatures where 1 and 2, respectively, rearrange.



7



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Thus, it appears likely that the 1,7-π cleavage barrier in both cases is considerably higher than that for the combined "methyl shuffling" - 1,6-π cleavage reaction steps. The reason for this slow 1,7-π cleavage in 1 or 2 is not obvious.

Even more puzzling is the behaviour of the related cyclohexenyl cation 9 the allyl isomer of 8. This ion is curiously situated on an energy watershed and is now seen to be rearranged to more stable cations by two competing, unrelated routes (Fig. 2). The previously described 80% route (12) leads to 10 and this in turn is rearranged to 11 by a well-known mechanism (14). The 20% route first leads to 2, which from the work in this paper, rearranges to 4a-4b. As noted by Deno (15), the cyclopentenyl cation structure is an energy minimum but the two routes in Fig. 2 leading to this are quite different. Previously we have demonstrated that a 4-isopropyl or t-butyl cyclohexenyl cation can be converted to norbornyl cations (2) (however not 7 and 8 apparently) The results with 9 demonstrate that a 1-t-butyl cyclohexenyl cation can also (and perhaps easier) enter the 2-norbornyl cation manifold and furthermore, that this 2-norbornyl cation is more stable than the fully alkylated (C1, 2, 3) cyclohexenyl cation.

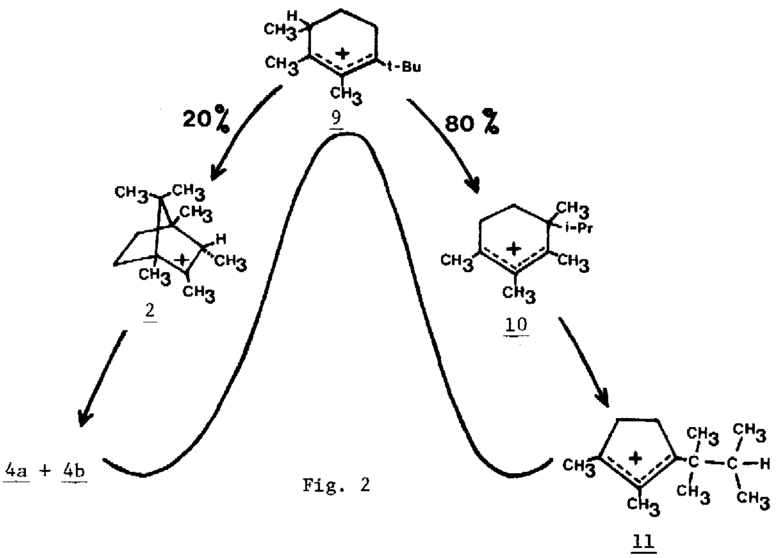

Fig. 2

ACKNOWLEDGEMENT

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(2) L. Huang, K. Ranganayakulu and T. S. Sorensen, Ibid., 95, 1936 (1973).

(3) The 1,6-π closure in solvolysis is a well-known reaction.

(4) R. P. Haseltine and T. S. Sorensen, Can. J. Chem., 53, 1067 (1975).

(5) In FSO_3H solvent; the diastereotopic methyls E and F, and G and H are not specifically assigned in either 3a, 3b or 4a, 4b.

(6) The single protons causing the C, D, EF and GH coupling are located at τ 7.98, 8.04, 8.12 and 8.88 respectively.

(7) K. Ranganayakulu and T. S. Sorensen, Can. J. Chem., 50, 3534 (1972).

(8) The corresponding methyls in 4a, 4b, using lettering as in 3a, 3b are at τ: C, 9.40, d, J = 6.5; D, 8.89, d, J = 6.5; E and F, 8.91, 8.95, both d, J = 6.5; G and H, 9.08, 9.18, both d, J = 6.5

(9) A much less plausible cleavage via a 7-norbornyl cation also rationalizes the results.

(10) C. K. Johnson and C. J. Collins, J. Amer. Chem. Soc., 96, 2514 (1974). C. J. Collins, C. K. Johnson and V. F. Raaen, ibid., 96, 2524 (1974). R. Haseltine, E. Huang, K. Ranganayakulu, T. S. Sorensen and N. Wong, Can. J. Chem., 53, 1876 (1975). R. Haseltine, K. Ranganayakulu, N. Wong and T. S. Sorensen, ibid., 53, 1901 (1975).

(11) There is an analogy here to stumbling on to the correct combination for opening a safe by randomly moving the dial.

(12) K. A. Ananthanarayan and T. S. Sorensen, Can. J. Chem., 50, 3550 (1972).

(13) N.m.r.:τ 7.76, C2 CH_3; 8.60, C4 CH_3; 8.88, C4 t-Bu.

(14) T. S. Sorensen and K. Ranganayakulu, J. Amer. Chem. Soc., 92, 6539 (1970).

(15) N. C. Deno, D.B. Boyd, J.D. Hodge, C.U. Pittman, Jr. and J.O. Turner, ibid., 86, 1745 (1964)