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THE PREDICTABLE BEHAVIOUR OF CATIONS DERIVING FROM *endo*-4-CHLOROTETRACYCLO[3.3.0.0.^{2,8}0.^{3,6}]OCTANE.

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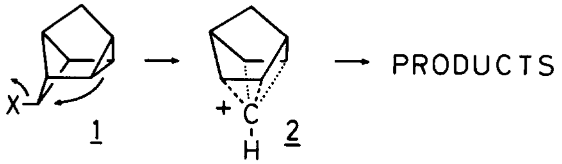
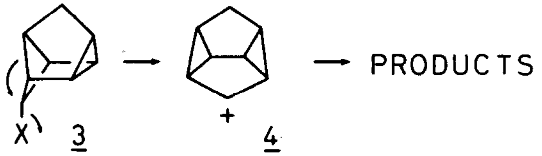
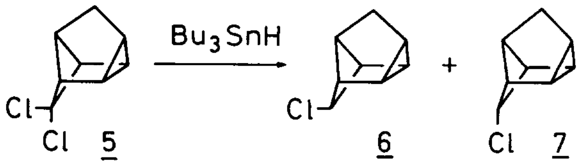
Silver cation-initiated ionization of the title compound in aqueous dioxane gives the *exo* and *endo*-tetracyclo[3.3.0.0.^{2,8}0.^{4,6}]octane-3-ols (35 and 65%). Thermal isomerization in chloroform gives the *exo* and *endo* isomers of 4-chlorobicyclo[3.2.1]octa-2,6-dienes (3.5 and 1.5%) and 6-chlorotricyclo[3.2.1.0.^{2,7}]oct-3-ene (90 and 5%). The behaviour of the cations involved is compatible with MINDO/3 calculations.

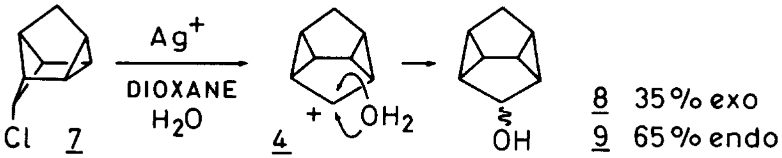
We have recently provided a theoretical basis for the observation that *exo*-4 derivatives of tetracyclo[3.3.0.0.^{2,8}0.^{3,6}]octane (1) give rise to the strongly delocalized pyramidal cation 2. We have also calculated that the *endo* epimer 3 would generate initially, in as yet unrealized reactions, the bis-cyclopropylcarbinyl cation 4.[1] We now describe experiments which strikingly confirm our theoretical predictions.

The *homo*-1,4 adduct (5)[2] obtained from dichlorocarbene and norbornadiene was treated with tri-*n*-butyltin hydride. Reductive dechlorination occurred, giving the *exo* and *endo*-4-chloro derivatives 6 and 7 in a ratio of 15:85 in a yield of 63%. Separation was achieved by preparative gas-liquid chromatography (15% FFAP on Chromosorb W, using nitrogen as carrier, with the injector, column and outlet temperatures maintained at 100°). Submission of the *endo* epimer 7 in aqueous dioxane (1:2) to an equivalent of silver nitrate in the same solvent gave an instant precipitate of silver chloride. Neutralization and extraction of the solution with ether afforded a 92% yield of the *exo* and *endo* alcohols 8 and 9 in a ratio of 35:65.[3] This result reveals that the first-formed cation is the bis-cyclopropylcarbinyl structure 4, which is immediately quenched.









In the absence of nucleophile, cation 4 is expected to rearrange *via* the calculated minimum energy reaction pathway to give the tricyclo[3.2.1.0.^{2,7}]octenyl cation 10 and ultimately the bicyclo[3.2.1]octadienyl cation 11 (Fig. 1). Once again, experiment accurately bears out this prediction. Thermolysis of 7 in chloroform at 180° caused isomerization to the *exo* and *endo* epimers respectively of the tricyclic (12 and 13) and bicyclic (14 and 15) skeletons. Clearly, the products and their ratios are a consequence of thermodynamic control. The bis-cyclopropyl-carbinyl cation 4 has had time to equilibrate to the pair of enantiomeric tricyclic cations 10 and 10' and the allylic cation 11, which are then captured by chloride ion.

A further intriguing question arises. Does the allylic cation 11 undergo circumambulation ? Two different processes are possible. 1,2 Migration of the vinyl group in 11 would generate the bicyclo[2.2.2]octadienyl cation 16, which by further 1,2 migration generates a new cation 11'. Successive shifts would result in scrambling of all five [sp^2] hybridized carbon atoms.[4] Alternatively, 1,2 migration of the methylene bridge in 11 would give a new cation 11' . However, this way all seven CH groups are scrambled.

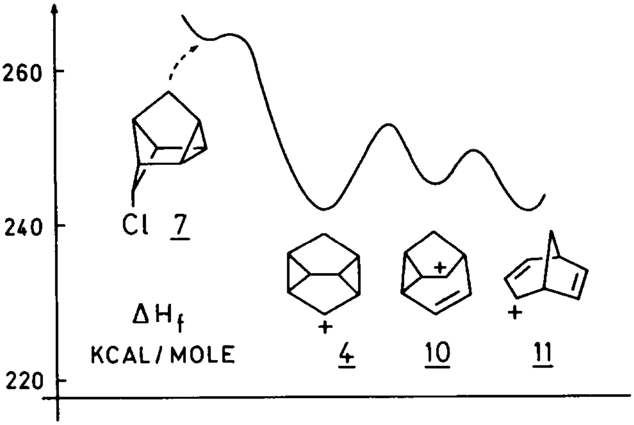
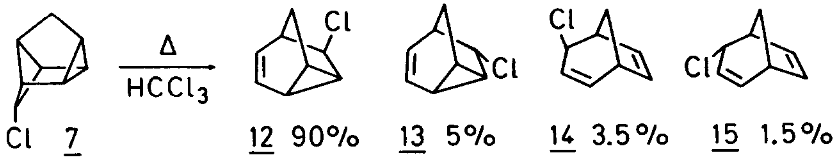
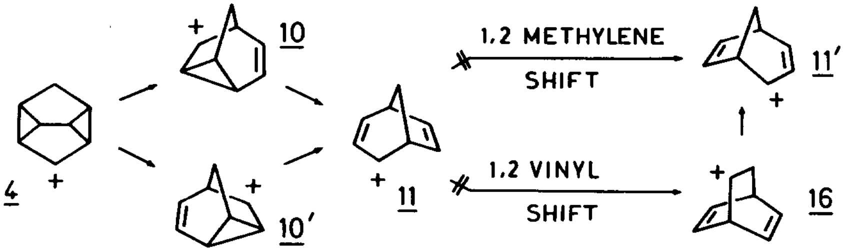
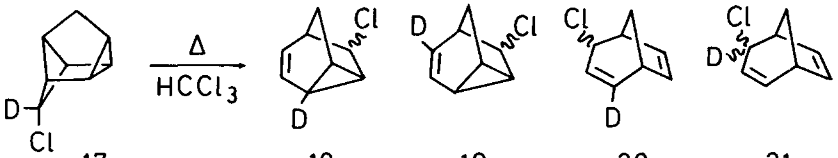


Fig. 1. Calculated minimum energy reaction paths interconverting C_8H_9 cations 4, 10 and 11 (ref. 1)

To test these important mechanistic points, the *exo*-4-deuterio-*endo*-4-chloro derivative 17 was prepared by reducing 5 with tri-*n*-butyltin deuteride. Thermolysis as before gave the same proportion of isomers. However, the deuterium label was distributed equally between the cyclopropyl and vinyl sites (as shown) of the tricyclo[3.2.1.0.^{2,7}]octenyl chlorides (18 and 19) and equally between the allylic termini of the bicyclo[3.2.1]octadienyl chlorides (20 and 21).







17 18 19 20 21

Moreover, no isomers having label on the ethene bridge or on the central carbon atom of the allylic part of the latter skeleton were detected. Therefore, circumambulation by either of the two possible processes does not occur. Consequently, under our conditions cation 4 generates first the enantiomeric pair of tricyclic cations 10 and 10', which in turn give the symmetrical bicyclic cation 11. Once formed, these cations exist as discrete species.

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REFERENCES AND NOTES

1) C.W. Jefford, J. Mareda, J.C. Perlberger & U. Burger, J. Am. Chem. Soc. 101, 1370 (1979).

2) C.W. Jefford, V. de los Heros & U. Burger, Tetrahedron Letters 1976, 703; C.W. Jefford, J. Mareda, J.C.E. Gehret, nT. Kabengele, W.D. Graham & U. Burger, J. Am. Chem. Soc. 98, 2585 (1976).

3) The alcohols 8 and 9 were easily identified. Their structures were assigned by comparing their NMR spectra with those of the known methyl ethers (W. Kirmse & T. Olbricht, Ber. 108, 2616 (1975); A.F. Diaz, M. Sakai & S. Winstein, J. Am. Chem. Soc. 92, 7477 (1970)). Traces of olefinic products were also detected.

4) It has been reported that the permethyl derivative of 11 undergoes circumambulation *via* the appropriate cation 16 (H. Hart & M. Kuzuya, J. Am. Chem. Soc. 97, 2459 (1975)).

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