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THE PREDICTABLE REARRANGEMENT OF TETRACYCLIC C_8H_9 CATIONS

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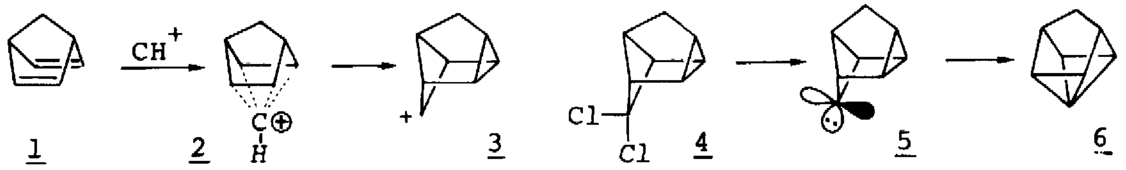
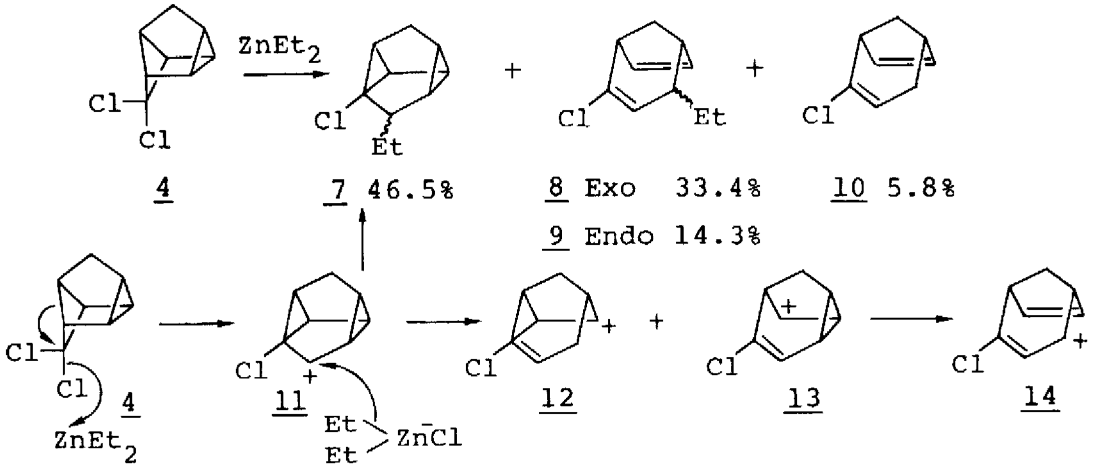
Summary. The homo-1,4 adduct obtained by addition of dichlorocarbene to norbornadiene on reaction with diethylzinc in ether solution gives 2-chloro-3-ethyltetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (46.5%), 2-chlorobicyclo[3.2.1]octa-2,6-diene (5.8%) and its 4-ethyl derivative (47.7%). The *exo* and *endo* monochloro derivatives (obtained from the homo-1,4 adduct) on reaction with diethylzinc, are inert for the former, whereas the *endo* isomer reacts as before, undergoing reductive dechlorination with rearrangement. The C_8H_9 cations involved behave as predicted by MINDO/3 calculations.

Pyramidal cations constitute a new class which is formally derived by the cheletropic reaction of carbyne cation (CH^+) to annulenes containing 4n π electrons.[1] We have recently[2] explored the potential energy surface surrounding the C_8H_9 square pyramidal cation 2 formed on adjunction of CH^+ or obtained in more practical fashion by addition of halocarbene to norbornadiene (1).[3] The high energy species 2 possesses the particularity of collapsing by haptotropic shift to the cyclobutyl cation 3. The present work, which bears on the experimental confirmation of predictions made in the C_8H_9 cation series, emanated from the idea of generating the bridged cyclobutylidene carbene 5 from the *gem*-dichloro adduct 4 in the expectation that reverse haptotropic rearrangement would furnish the novel C_8H_8 hydrocarbon 6 incorporating a pyramidal carbon atom.[5]



The treatment of 4 by slow addition over 10 h of a two-fold molar excess of diethylzinc in ethereal solution at 35° (conditions appropriate[6] for generating 5), gave five products in quantitative yield.[7] The overall result was rearrangement with reductive mono-dechlorination to give the pair of ethyl substituted tetracyclic epimers 7 (46.5%), the *exo* (33.4%) and *endo* (40.3%) bicyclo[3.2.1]octadienes (8 and 9) and the parent diene 10 (5.8%).

Clearly, carbene 5 is not formed and the results can be best explained in terms of the Lewis acid action of diethylzinc. Of the two chlorine substituents, as will be shown later, the one in the *endo* position is selectively removed engendering the predictably easy 1,2 shift. The bis-cyclopropylcarbinyl cation 11 thus formed is then rapidly captured by ethide ion. However, despite its stability, 11 has the chance to evolve further. Successive migrations of the cyclopropyl bonds yield initially the pair of tricyclic cations 12 and 13 and finally the common allylic cation 14, all of which are expected to lie close in energy to each other and to 11 (*cf.* Fig. 1). The presence of the chlorine substituent stabilizes the positive charge and ensures that reaction is completed by nucleophilic attack of ethide or hydride ion on the least substituted allylic terminus of 14, thereby giving 8, 9 and 10.



In order to confirm that the departure of the *endo* chlorine substituent really characterizes the reactivity of 4, both the *endo* and *exo*-chloro epimers 15 and 16 were independently submitted to diethylzinc under the same conditions as before. The *endo* derivative 15 gave a 95% yield of four rearranged products. Reductive dechlorination had occurred to give the tetracyclic *exo* and *endo* ethyl epimers 17 (29.3%), accompanied by its parent hydrocarbon 18 (3.3%), the *exo* and *endo* ethyl bicyclo[3.2.1]octadienes 19 (46.5%) together with bicyclo[3.2.1]octa-2,6-diene (20, 20.4%).

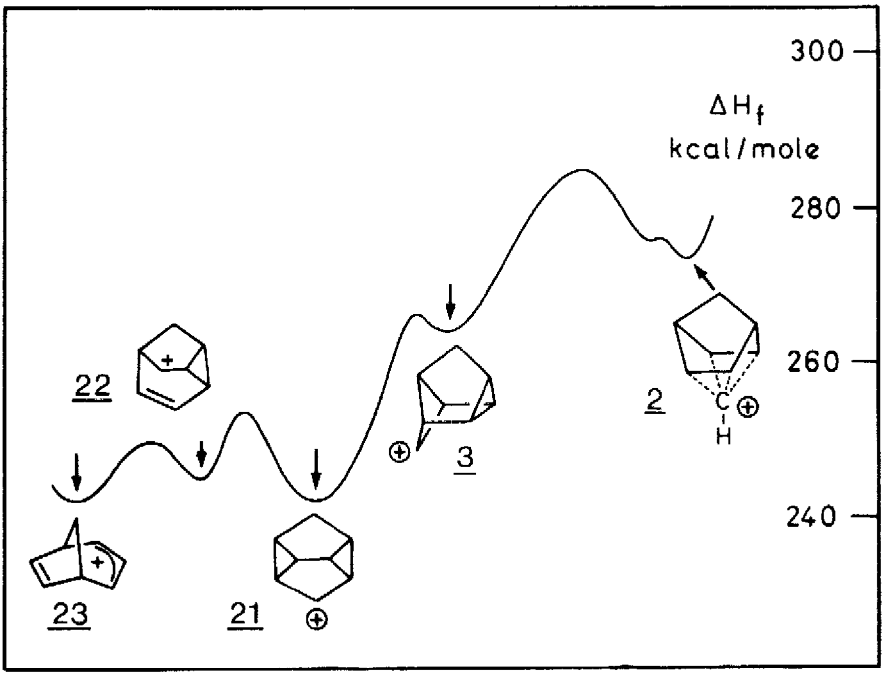
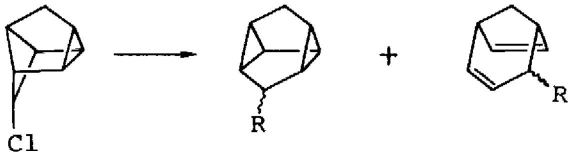
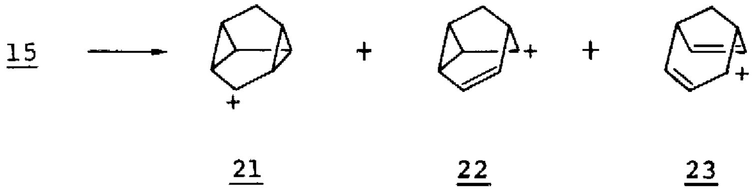


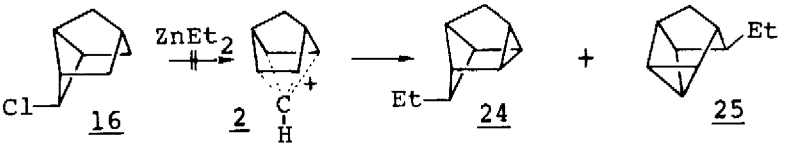
Fig. 1 Calculated minimum energy reaction paths (MERP) for some C_8H_9 cations (ref.2)



15 17 R = Et 29.3% 19 R = Et 46.5%

18 R = H 3.3% 20 R = H 20.4%





This result parallels that of 4, confirming that rearrangement to the bis-cyclopropylcarbinyl cation 21 is electronically linked to the *endo* configuration in 15. Rapid transit then occurs through the tetracyclic cation 22 to the allylic cation 23. Capture of 21 and 23 is effected by ethide or hydride ions. In striking contrast, the *exo*-chloro epimer 16 emerged unchanged after exposure to diethylzinc in boiling ether for 10 h. The participation of the cyclopropane ring in expelling chloride ion to generate cation 2 is calculated to require some 22 kcal/mol, which is evidently unattainable under the present conditions. Moreover, it is significant that no products derived from 2, *e.g.* ethyl derivatives 24 or 25, were detected in any of the experiments.

In general, the product compositions differ from that obtained by equilibration of 15,[4a] since they are kinetic in origin. Nevertheless, the predictions of the MERP diagram for these C_8H_9 cations (Fig. 1) are amply corroborated. Moreover, the bicyclo[3.2.1]octadienyl cations (14 and 23) formed, albeit fleetingly,[8] exist as such and do not undergo circumambulation[9] since 14 gave no products with a rearranged chlorine substituent.

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4) (a) Previous paper: C.W. Jefford, S. Genevay-Höck, A. Delay, J. Mareda & U. Burger, Tetrahedron Letters 1979, 2549; (b) For comparative studies on homocubyl cations, see W.L. Jorgensen, J. Am. Chem. Soc. 99, 4272 (1977).

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7) Products were separated by preparative gas-liquid chromatography on a column of 15% FFAP on Chromosorb W (2.5 m x 5 mm, 130°) and characterized by their NMR spectra.

8) Little is known about 23 (*cf.* A.F. Diaz, M. Sakai & S. Winstein, J. Am. Chem. Soc. 92, 7477 (1970)), except that attempts to obtain it in superacid media were vitiated by polymer formation (ref. 9).

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