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AN ADAMANTANE REARRANGEMENT. A NEW PATHWAY

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Summary: Tricyclo(4.2.2.0^{1,5})decane (7) in the presence of $AlBr_3$ rearranges partly "forwards" to adamantane (1) and partly "backwards" to tetrahydrodicyclopentadiene (2, largely the exo isomer). Intermediate 14, characterizing the 7 → exo-8 → 14 → 3 → 1 forward pathway, is found only in small amounts. The detection of a new intermediate, 12, also shows that a second major rearrangement route from 7 to 1 is being utilized (see dashed lines in Figure 1).

The graphical analysis of the adamantane rearrangement[1,2] originated by Whitlock and Siefken[3] (Figure 1, after ref. 2) reveals the potential complexities of such multistep processes. Based on fragmentary chemical evidence, Whitlock and Siefken suggested that the most likely rearrangement pathway from tetrahydrodicyclopentadiene (2)[1,2] proceeded via intermediates 7 → exo-8 → 14 → 3 to adamantane (1). Empirical force field calculations on the tricyclodecanes and their carbocation intermediates supported this conclusion; the pathways shown by darkened lines in Figure 1 were suggested to be the most likely.[2] Tricyclo(4.2.2.0^{1,5})decane (7) was recognized to be the energetic "bottle neck" through which the isomerization must proceed. The next intermediate in the sequence, exo-8, was examined experimentally.[2] As predicted, rearrangement to adamantane (1) occured via 14 and protoadamantane (3). Labelling studies provided more detailed information concerning this pathway.[4] We now report the synthesis and the isomerization behaviour of the "bottle neck" tricyclodecane, 7. An unanticipated new rearrangement route leading to adamantane is found to compete with the one formerly identified.

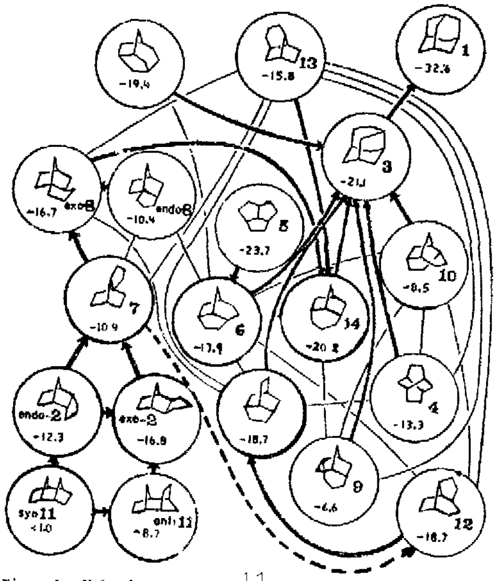
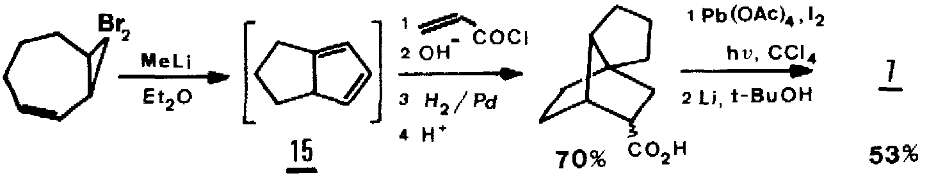
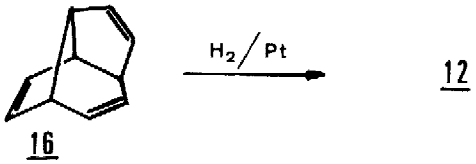


Figure 1 Tricyclodecane graph[11]

Our preparation of 7[5] was based on the demonstration that the tetrahydropentalen 15, generated by a carbene rearrangement, could be trapped by Diels-Alder dienophiles.[6] Use of acrylyl chloride for this purpose followed by removal of the functional groups gave 7 (IR (film): 2930 s, 2940 m, 1740 w, 1260 w, 660 w; ^{13}C nmr (δ, CCl_4): 60.23 (C-5), 58.35 (C-1), 37.29, 36.51 (C-6), 32.62, 32.10, 30.08, 28.78, 28.52, 21.25):

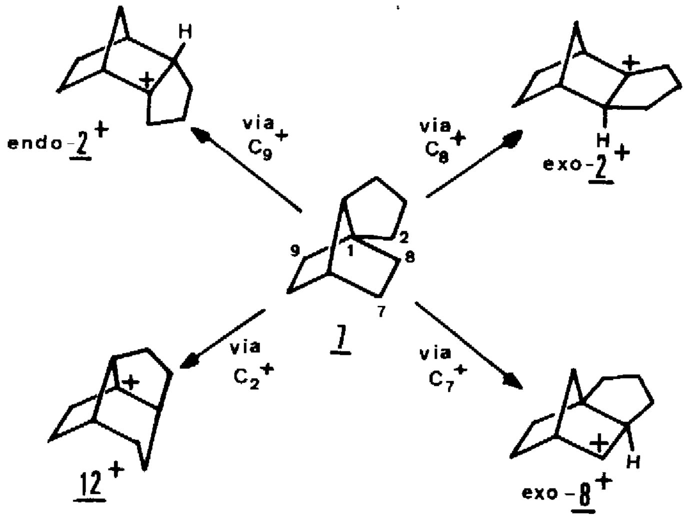


The rearrangement of 7 was carried out with $AlBr_3$ catalyst in CS_2 solution at -10°C. These conditions allowed the reaction course to be followed by glc and glc-ms. As expected, 7 acted as a "continental divide" in what Fort has called "Adamantaneland".[7] That is, about half of the reaction (40% to be more exact) proceeded "forwards" to give adamantane (1); the other 60% proceeded "backwards" to yield tetrahydrodicyclopentadiene (2) (the exo-isomer dominates at the end of the reaction). *At shorter reaction times, three intermediates are formed in* in amounts never exceeding 3-5%. In addition, traces (less than 0.5%) of protoadamantane (3) could also be positively identified (glc and glc-ms). The other intermediates were endo-tetrahydrodicyclopentadiene (endo-2), also formed from rearrangement "backwards", 14,[2] and an unknown. This unknown was assigned structure 12 (tricyclo(5.3.0.$0^{4,8}$)decane) since its glc retention data and glc mass spectra (70 eV m/e 136 (M^+, 100%, 135(60), 121(40), 107(55), 93(55), 80(90), 79(75), 67(50)) were identical with those obtained by hydrogenating 16.[8]



The "forward" part of the rearrangement of 7 thus is significantly different from that observed with exo-8.[2] While the latter gave up to 80% 14 at intermediate reaction times,[2] no more than 3% 14 was found starting from 7. This demonstrates that other rearrangement pathways leading to adamantane from 7 but by-passing 14 are being followed. The formation of 12 (maximum concentration ca 5%) indicates the most likely alternative route (dashed line in Figure 1 followed by solid lines).

Our earlier analysis[2] discounted possible rearrangements through 12 on the grounds that the necessary intermediate, 12^+, was a relatively unstable bridgehead carbenium ion. However, as we have emphasized, the relative energies of competing rearrangement transition states really determine the course of reaction. These transition states may not be approximated well by the energies of the starting and of the final carbocations. Rearrangement of 2-7^+ to 12^+ involves a strain-relieving norbornane ring expansion for which there is ample precedent.[9] Hydride abstraction from 7 occurs at the several positions summarized below.



The observation of a new adamantane rearrangement pathway from 7 proceeding via 12 indicates, but does not prove, that this pathway is followed when starting from tetrahydrodicyclopentadiene (2). Carbocation intermediates generated from 2 may not yield appreciable quantities of 7, but may rearrange sequentially to give adamantyl cations.[10] The analysis of such carbocation-based routes will be presented subsequently.

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(10) Rearrangement of tertiary tetrahydrodicyclopentadienyl cations (2^+) to the 1-adamantyl cation occurs in stable ion media where the concentrations of neutral hydrocarbons should be negligible. (P. v. R. Schleyer, W. W. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, J. Am. Chem. Soc., 86, 5679 (1964); T. S. Sorensen, Unpublished results.)

(11) Adapted with permission from ref. 2. Copyright 1973 American Chemical Society.

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