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INTERMEDIATES ON THE TRICYCLOUNDECANE REARRANGEMENT SURFACE

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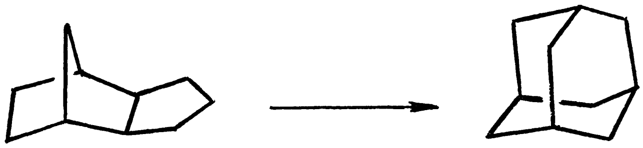
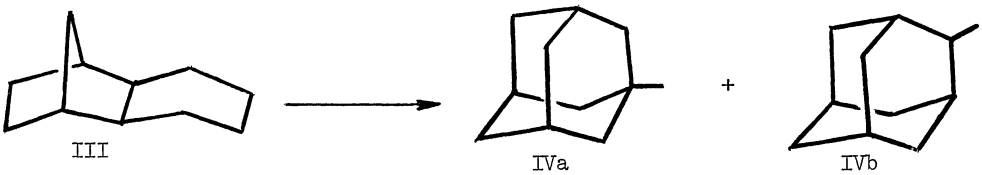
Tricyclo[5.3.1.$0^{3,8}$]undecane (VI) was identified as one of the several intermediates observed during the aluminum halide isomerization of 2,3-tetramethylene norbornane (III) to the methyl adamantanes (IV). Empirical force field (strain) calculations predict that many tricycloundecanes have comparable stabilities.

One of the earliest generalizations of the rearrangement leading to adamantane, I → II,[2] was the analogous isomerization, III → IV.[3]



I II



III IVa IVb

	III	IVa	IVb
ΔH_f^o calc. kcal/mol	E[4] = -21.67 A[4] = -21.79	E = -41.92 A = -42.89	E = -37.94 A = -39.04

A more detailed study of the latter process was carried out a number of years ago;[1,7] at least three intermediates were detected by glc, but homoadamantane (V) was not among them. One of these intermediates, analyzing for $C_{11}H_{18}$, was isolated in crystalline form, m.p. 66.6-67.0°, by preparative gas chromatography. A sample was unsuccessfully submitted for X-ray analysis. ^{1}H-nmr and mass spectra indicated that none of the intermediates possessed a methyl group but provided insufficient data for structural assignments.

Very recently Majerski[8] discovered that the major product from the hydride transfer reduction of 4-homoadamantane was VI (tricyclo[5.3.1.0^{3,8}]undecane). The initial identification of VI by ^{13}C-nmr was confirmed by comparison with an authentic sample.[9] The mass and ^{1}H-nmr spectra, and gas chromatographic behavior of VI and the intermediate of m.p. 66.6-67.0^{o} are identical.[8] We have now learned that Dr. Y. Inamoto has independently identified VI as an intermediate in the III $\longrightarrow$ IV isomerization.[10]

Empirical force field (strain) calculations using two different force fields have been carried out on many $C_{11}H_{18}$ isomers.[4] Predicted heats of formation for some of the most stable structures are summarized under III and IV and in Figure 1. These structures are good candidates for the other intermediates observed during the III $\longrightarrow$ IV isomerization. Enthalpy differences between tricycloundecane isomers tend to be smaller than those on the tricyclodecane rearrangement graph,[11] and entropy factors should play a significant role in determining the relative stabilities.[12]

The rearrangement of homoadamantane (V) to 1-and 2-methyladamantane (IVa and IVb) has also been studied.[1] At room temperature with $AlBr_3$ as catalyst and cyclohexane as solvent, the rearrangement of V was more rapid than that of III, and only small concentrations of intermediates were detected.[1] 2-Methyladamantane (IVb) was formed in larger than thermodynamic amounts,[13] indicating that there must be some pathway leading directly to this less stable isomer. The mechanism of ring contraction giving rise to alkyl groups in adamantane rearrangements is of considerable current interest to us, and we would like to point out that many methylprotoadamantanes are calculated to be quite stable (ΔH_f^o's as low as -30.6 kcal/mole)[14] relative to the tricycloundecanes (Figure 1). Only a few other methyl-substituted tricyclodecanes appear to be as stable.

The $C_{11}H_{18}$ rearrangement graph has been constructed[15] and it is hoped that further work will elucidate the mechanistic pathways following during isomerization.

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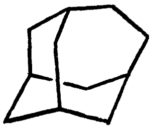
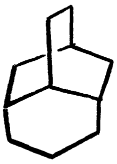
Figure 1. Calculated enthalpies of formation for some $C_{11}H_{18}$ tricycloalkanes, kcal/mole.[4]



V

E = -29.84

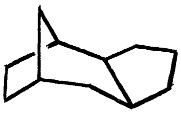
A = -27.77



VI

E = -28.60

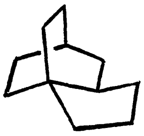
A = -30.32



VII

E = -24.87

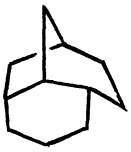
A = -25.54



VIII

E = -24.77

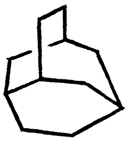
A = -25.54



IX

E = -26.32

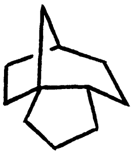
A = -25.93



X

E = -24.97

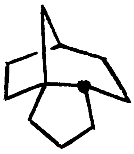
A = -26.10



XI

E = -26.05

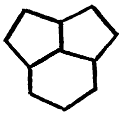
A = -26.72



XII

E = -26.20

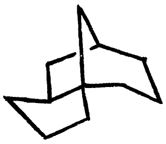
A = -27.32



XIII

E = -29.52

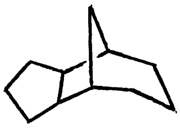
A = -25.89



XIV

E = -28.19

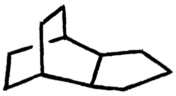
A = -28.38



XV

E = -27.79

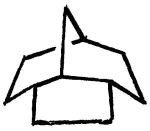
A = -27.57



XVI

E = -24.25

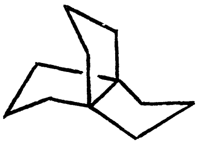
A = -26.77



XVII

E = -26.14

A = -24.12



XVIII

E = -30.28

A = -28.98

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