

ADAMANTANE REARRANGEMENT MECHANISMS. 1,2-TRIMETHYLENENORBORNANES¹

Malvina Farcasiu

Mobil Research and Development Corporation, Central Research Division,
P.O. Box 1025, Princeton, New Jersey 08540, USA

Edward W. Hagaman and Ernest Wenkert^{1a}

Department of Chemistry, Indiana University, Bloomington, Indiana 47401, USA

Paul von Ragué Schleyer*

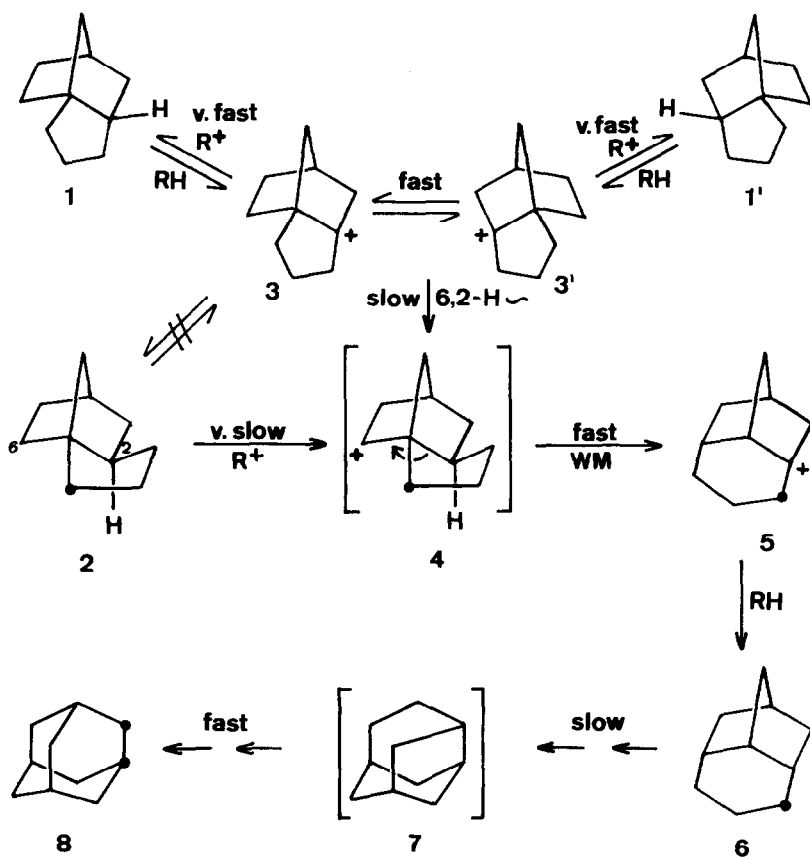
Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg,
D-8520 Erlangen, Federal Republic of Germany

Summary: Unexpected differences in the aluminium bromide-catalyzed rearrangement behaviour of 1,2-endo-trimethylenenorbornane (1) and its 1,2-exo-isomer (2) are interpreted. Isotopic labelling studies indicate that reversible abstraction of the tertiary 2-endo hydride in 2 does not occur (Scheme 1). Instead, rearrangement to 6 is favored. The label scrambling in the final product, adamantane (8), is attributed to degenerate isomerization in the proto-adamantyl precursor, 7.

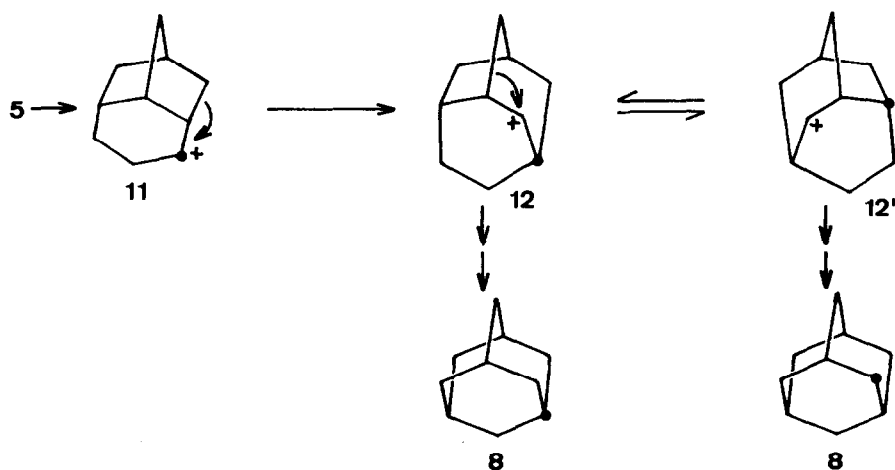
Since the discovery of the adamantane rearrangement in 1957,² the elucidation of the mechanism of this necessarily complex transformation has progressed significantly.³⁻⁶ The recent report by Klester, Jäggi, and Ganter⁷ describing the rearrangement of 1,2-endo-trimethylenenorbornane (1) with aluminium bromide prompts us to describe our results with the corresponding 1,2-exo-isomer (2), ¹³C labelled at the position designated by the dot.^{1,8} Scheme 1 presents a mechanistic interpretation of the intriguing differences in behaviour of 1 and 2 described by Ganter, et al. Previous studies had established that the rearrangement of 2 to adamantane 8 involves 2,6-endo-trimethylenenorbornane (6) and protoadamantane (7) intermediates.^{1,3-6,9}

Rearrangement of ¹³C labelled 2 with AlBr₃ in CS₂ solution at -15°C gave 6; ¹³C-NMR analysis indicated the label to be at a single position (within C₃ symmetry). Unexpectedly, 2 recovered after partial rearrangement to 6, did not reveal any label scrambling which would have been expected if intermediate ions 3 and 3' had been involved. In principle, reversible abstraction of the tertiary 2-endo hydride in 2 (to give 3) might have been expected. The results indicate that this abstraction is not able to compete with attack at other positions, even though these are secondary. Thus, abstraction of a hydride from C-6 in 2 would lead (via ions 4 and 5) to 6 without label scrambling either in recovered 2 or in 6.

SCHEME 1



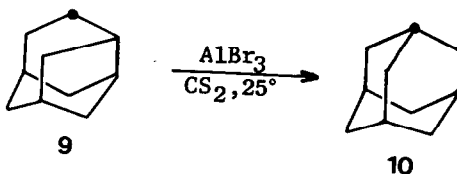
SCHEME 2



The results of Ganter, et al, with 1⁷ nicely compliment these findings. Consistent with its much higher strain energy,⁴ 1 is much more reactive than 2 with aluminium bromide catalysts. While hydrocarbons like cis- and trans-decalin epimerize¹⁰ under such conditions, this does not occur with 1; 2 is not detected in the products.⁷

However, abstraction of a secondary hydride from 1 cannot lead to 6 directly; an impossibly strained 2-exo,6-endo-trimethylenenorbornane stereoisomer of 6 would result instead. Thus, 1 gives 3 directly; equilibration via 3' leads to the expected label scrambling.¹¹ Consistent with our results, 3 does not give 2; we suggest that a 6,2-hydride shift leading from 3 to 4 occurs more rapidly. Further reaction then gives 5 and 6.

The subsequent rearrangement of labelled 6 is also of interest. Transformation of 6 to adamantane (8) by the simplest conceivable pathway should have resulted in exclusive labelling at the bridgehead position (8-1-¹³C). Instead, extensive scrambling of the label in 8 occurred. Although the small amount of 7 produced as an intermediate in the adamantane rearrangement precluded ¹³C analysis of the positional labelling, we believe that the scrambling in 8 occurs via ionic intermediates involved in the rearrangement step from 7. Although partial automerization of adamantane-2-¹⁴C by AlBr₃ has been observed,¹² the conditions were much more drastic than those employed here. As a check, we prepared protoadamantane-4-¹³C (9).¹³ Treatment with AlBr₃ under conditions similar to those used to the rearrangement of 6 gave adamantane-1-¹³C (10) exclusively; thus, no adamantane automerization took place.

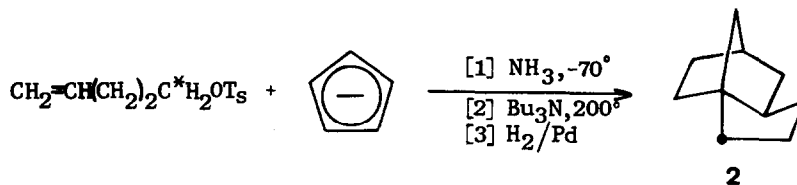


Instead, the label scrambling observed in 8 may occur according to the mechanism in Scheme 2. Intermediate cation 12, generated directly from 11 along the route leading to 8, can undergo degenerate rearrangement to 12' and thus plays the key role.

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References and Footnotes

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- (8) The specifically ^{13}C labelled **2** was prepared by adaption of the procedure of E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, **89**, 2600 (1967) as shown below.



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