Tetrahedron Letters No. 42, pp 4123 - 4126, 1973. Pergamon Press. Printed in Great Britain.

THE REARRANGEMENT OF A BIS-HOMO-(CH)$_5^+$ CATION

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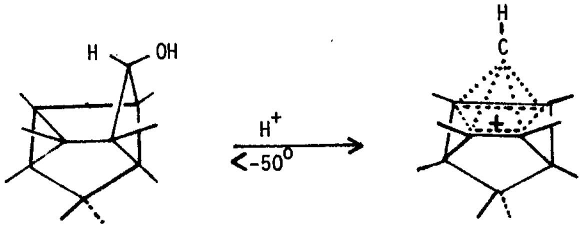
(Received in USA 23 July 1973; received in UK for publication 10 September 1973)

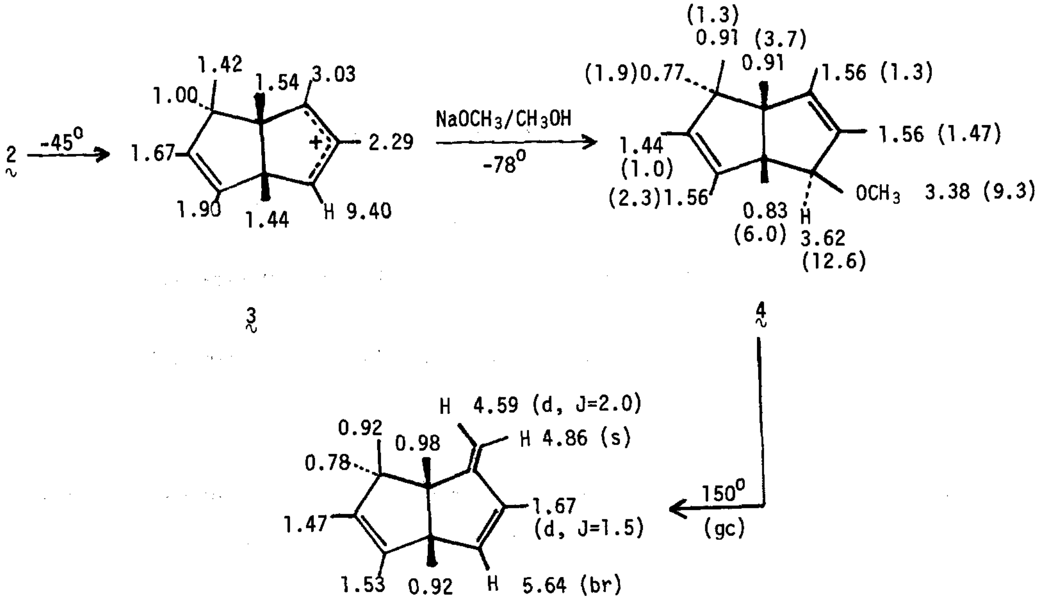
The secondary alcohol 1 was shown, on ionization in FSO_3H-SO_2ClF, to produce the pyramidal cation 2.[1,2] This ion is stable below -50°, but rearranges in a unique manner if maintained above that temperature for an extended time. In view of the current intense interest in (CH)$_5^+$-type cations,[3] we wish to communicate here the nature and mechanism of this rearrangement.



1

2

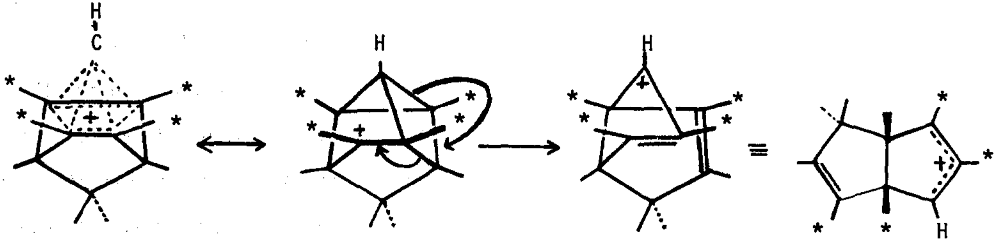
The proton nmr spectrum of 2 consists of four sharp singlets at δ(relative area)[4]: 1.80 (12), 1.33 (6), 0.77 (6), 0.74 (1). At -45 to -50°, this simple spectrum is gradually replaced by one with a single proton at δ9.40 and eight methyl signals, at δ3.03, 2.29, 1.90, 1.67, 1.54, 1.44, 1.42 and 1.00. The chemical shift of the single proton and of the lowest field methyl are consistent with their location at the termini of an allyl cation, whereas the methyl at δ2.29 must be at the central carbon of that moiety.[5] We assign the product ion structure 3. Careful quenching in methanol containing sodium methoxide gave the secondary methyl ether 4[6] which, on gas chromatography, underwent 1,4-elimination of methanol to produce the hydrocarbon 5.[7,8]



3 **4**

5, λ_{max}^{EtOH} 241 nm (ε12,000)

To obtain mechanistic information regarding the conversion of **2** to **3**, labeled **2** containing 50% D in each of the methyl groups at the 'base' of the pyramid was prepared[9] and allowed to rearrange to **3**. The intensity of the signals at δ3.03, 2.29, 1.90 and 1.44 in the resulting **3** was reduced by 50%.[13] We rationalize this result with the following mechanism (**2**' is one of four equivalent classical contributors to **2**):



2,*=1/2 CD_3 **2**' **3**,*=1/2 CD_3

The proton and ^{13}C nmr spectra of **2** show that most of the positive charge is located in the 'base' of the pyramid. It is not surprising, therefore, that the rearrangement of **2** is initiated in a manner which meets that electron demand. The polycyclic ring structure unfolds directly to the relatively unstrained bicyclo[3.3.0]octadien-2-yl cation **3**.[14]

The kinetics of the reaction 2 → 3 were determined at six temperatures in the range -39 to -55°. The rate constant at -48° was 3.1 (± 0.1) x 10^{-4} sec $^{-1}$. The activation parameters are $\Delta F^{\ddagger}$ 16.7 Kcal/mol, $\Delta S^{\ddagger}$ -2.8 eu/mol, $\Delta H^{\ddagger}$ 16.1 Kcal/mol.

Ion 3 undergoes further rearrangements when warmed above -30° in FSO_3H/SO_2ClF (1:4). Details will be presented in a full paper.

Acknowledgement. We are indebted to the National Science Foundation for a grant in support of this research.

REFERENCES

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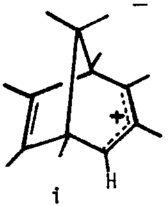
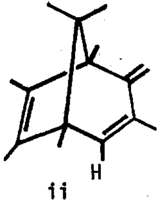
2. $(CH)_5^+$ ions were first predicted to be stable in a pyramidal geometry by W.-D. Stohrer and R. Hoffmann, J. Amer. Chem. Soc., 94, 1661 (1972).
3. For other examples, see (a) S. Masamune, M. Sakai, H. Ona and A. J. Jones, J. Amer. Chem. Soc., 94, 8956 (1972); (b) H. Hogeveen and P. W. Kwant, Tetrahedron Lett., 1665 (1973); (c) R. K. Lustgarten, J. Amer. Chem. Soc., 94, 7602 (1972). For a related $(C_{11}H_{11})^+$ cation, see M. J. Goldstein and S. A. Kline, J. Amer. Chem. Soc., 95, 935 (1973).
4. Reference compound: $(CH_3)_4N^+BF_4^-$, δ3.13.
5. See N. C. Deno in "Carbonium Ions," edited by G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, Vol II, 1970, pp. 796-7.
6. Numbers in parentheses are the relative extents to which the various signals are shifted downfield by $Eu(fod)_3$; see D. R. Kelsey, J. Amer. Chem. Soc., 94, 1764 (1972).
7. The alternative structure i for the cation can be conclusively discarded because the hydrocarbon ii which would be obtained on quenching i was independently synthesized and shown to be different from 5. Further, a direct synthetic route to i from the corresponding secondary alcohol gave solutions which behaved quite differently from those of 3.

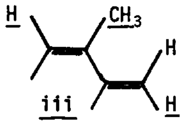


i



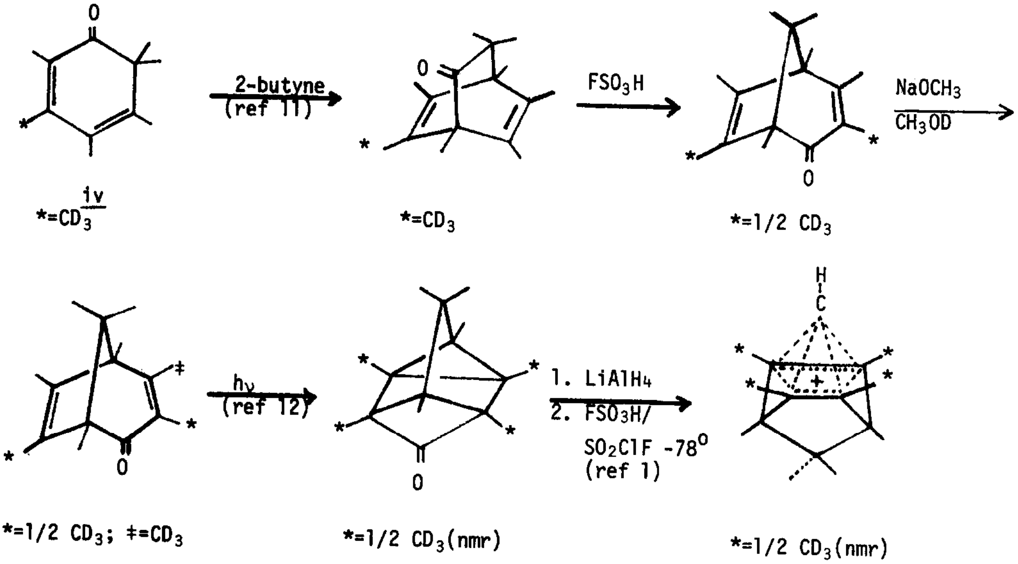
ii

8. *Anal*. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.97; H, 11.17. Irradiation of the signal at δ5.64 in **5** caused collapse into singlets of the doublets at δ4.59 and 1.67. This proves the presence of the moiety iii in **5**, the doublets being ascribed to long range



'zig-zag' and homoallylic coupling, respectively.

9. The labeled hexamethyl-2,4-cyclohexadienone iv[10] was treated as follows:



10. H. Hart, P. M. Collins and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).

11. H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6264 (1971).

12. H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6266 (1971).

13. The label distribution in **4** and **5** also was consistent with the nmr assignments as shown in the structures.

14. Less direct routes to **3**, via bicyclo[3.2.1]octadienyl cations can be excluded. Details will be presented in a full paper.