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CONTIGUOUS CONCERTED PARTICIPATION IN THE REARRANGEMENT OF ANTI-TRICYCLO[4.2.1.1.^{2,5}]DECA-3,7,-DIENE-9,10-DIOL, A HIGHLY HINDERED SYSTEM.

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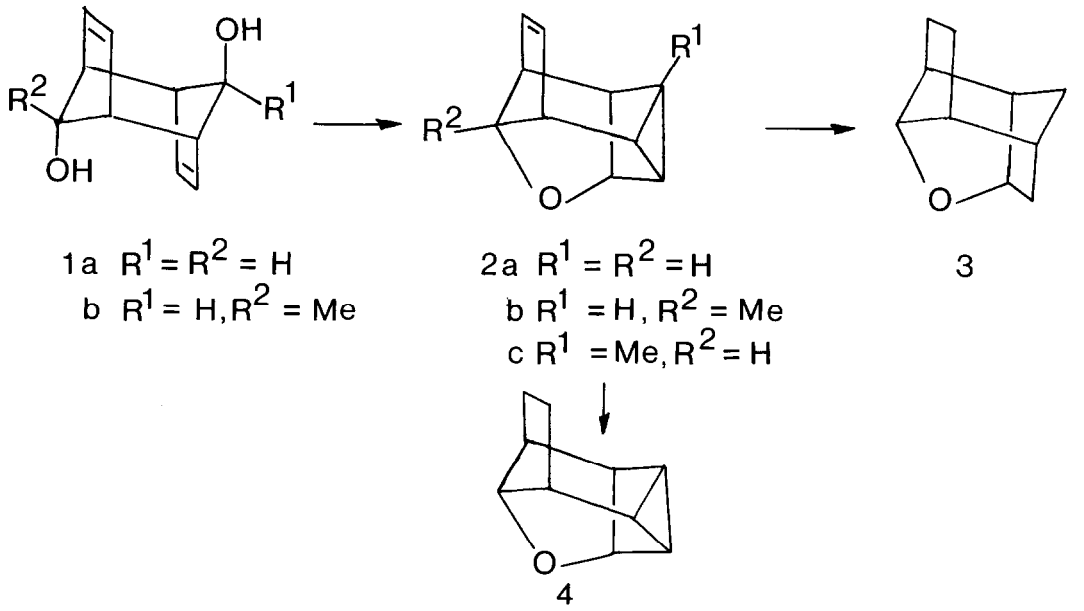
Summary: The acid catalysed rearrangement of anti-tricyclo[4.2.1.1.^{2,5}]*deca-3,7-diene-9, 10-diol* (1a) *to* 2a *is shown to proceed through concommitant electrophilic and nucleophilic attack on an alkene by an incipient carbonium ion and the remaining alcohol function.*

Carbocation rearrangements have played a central part in the development of both mechanistic and synthetic organic chemistry.[1] Such rearrangements occur with participation of bonding electron pairs in a step subsequent to, or consecutive with, the formation of the carbocation, the exact nature of this interaction having been contentious.[2] We would like to describe a rearrangement of a highly hindered substrate in which two groups participate and in which the participation appears to occur very early in the bond breaking process leading to the putative carbocation.

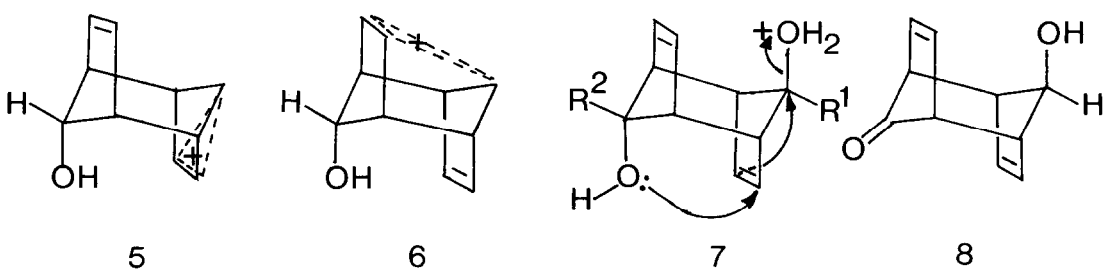
The diol 1a,[3] prepared from anti-tricyclo[4.2.1.1.^{2,5}]deca-9,10-dione[4] by reduction with $LiAlH_4$,[5] was treated in THF with a trace of HCl whereupon 2a was formed in 60-75% yield. The structure assigned to 2a is based on its spectral and chemical properties. The ^{1}H NMR spectrum ($CDCl_3$,δ) had signals at 1.27-1.30(m,1H), 1.54-1.60(m,1H), 2.09-2.17(m,2H), 2.55-2.57(m.2H), 4.57-4.63(m,1H), 4.84-4.87(m,1H), 5.77-5.81(m,1H), 6.12-6.16(m,1H), and the ^{13}C NMR spectrum ($CDCl_3$,ppm) had signals at 12.70, 17.20, 19.70, 35.0, 35.95, 44.30, 75.50, 90.65, 126.65 and 136.25, each signal representing a single methine carbon. Catalytic reduction of 2a over Pd-$CaCO_3$ gave 3,[6,7] and reduction of 2a with diimide gave 4.[6,7]

The formation of 2a from 1a can readily be envisaged as the formation of the carbocation promoted by the stabilising participation of the double bond, the resulting delocalised carbocation 5 then being trapped by intramolecular attack of the hydroxyl group. However, in the free carbocation participation of the other double bond might be anticipated (i.e. 6) particularly in view of recent findings for a saturated analogue[8].



To further investigate the details of this process we prepared the analogous monomethyl derivative of 1a by treatment of anti-tricyclo[4.2.1.1.^{2,5}]deca-9,10-dione with methyl magnesium bromide, which reacts only at one carbonyl group[9], followed by reduction of the remaining carbonyl group with $LiAlH_4$ to give 1b. Compound 1b was transformed to a mixture (ca 6:1) of 2b and 2c by stirring in $CHCl_3$[10]. The isomers were separated by HPLC (Et_2O : pentane 1:9) and identified by the characteristic signals for the methyl protons in the ^{1}NMR spectra[11].

The preponderance of 2b over 2c in this latter reaction clearly suggests that the stability of the carbocation is not the factor determining the ratio of the observed products. We believe that this preference arises because of the greater inaccessability of the tertiary hydroxyl group to protonation. Protonation of the hydroxyl group is presumed to lead to invariable cleavage of the C-O bond with the double bond and hydroxyl group participating at an early stage in the process (i.e. 7).[12]



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It could be argued that the participation of the hydroxyl group is subsequent to the stabilisation of the carbocation by the double bond. Although we believed that the evidence from the rearrangement of 1b is contrary to this view, in order to clarify this point we examined the protonation of the keto-alcohol 8.[3] Neither under the conditions for the rearrangement of 1a nor under harsher conditions could we effect the rearrangement of 8 to products related to 2a.[13] We conclude that the rearrangement of 1a to 2a involves a contiguous concerted participation of both the olefin and hydroxyl functions, equivalent to concommitant electrophilic and nucleophilic attack on an alkene by the incipient carbonium ion and remaining alcohol function, respectively.[14]

Acknowledgment: We thank Professor K. Schafner (Mulheim) for advice regarding the preparation of anti-tricyclo[4.2.1.1.^{2,5}]deca-9,10-dione, and the SRC (UK) for support. C.W.D. is the recipient of a NATO Fellowship.

References and Footnotes

1. See Carbonium Ions, eds Olah, G.A., von Schleyer, P., Vol. 1, Interscience, N.Y., 1968.

2. See Brown, H.C., The Nonclassical Ion Problem, Plenum, N.Y., 1977.

3. Amman, W.; Ganter, C. Helv. Chim. Acta., 1977, 60, 1924.

4. Baggliolini, E.; Herzog, E.G.; Iwanaki, S.; Scharta, R.; Schaffner, K., Helv. Chim. Acta., 1967, 50, 297; Klimsmann, U.; Gauthier, J.; Schaffner, K.; Pasternak, M.; Fuchs, B. ibid, 1972, 55, 2643.

5. We found reduction with $LiAlH_4$ to be simpler than the method employing $NaBH_4$ described in ref. 3.

6. Satisfactory high resolution mass spectral data were obtained for this compound.

7. Satisfactory ^1H and ^{13}C NMR spectral data were obtained for this compound.

8. Ohkata, K.; Doecke, C.W.; Klein, G.; Paquette, L.A.; Tetrahedron Lett., 1980, 3253.

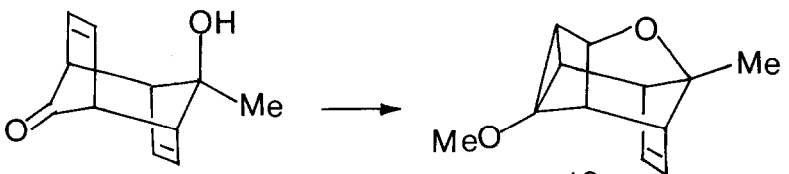
9. Pfund, R.A.; Ganter, C.; Helv. Chim. Acta., 1979, 62, 228.

10. Commercial $CHCl_3$ is sufficiently acidic to promote this rearrangement.

11. ^1H NMR, 200 MHz, $CDCl_3$,δ : 2b, 1.25 (s, CH_3), 4.73-4.82 (m, 1H, H-C-O-C): 2c, 1.15 (s, CH_3) 4.53-4.63 (m, 1H, H-C-O-C), 4.74-4.84 (m, 1H, H-C-O-C).

12. The overall process is equivalent to intramolecular addition to a double bond. The preference for loss of the secondary rather than the tertiary hydroxyl group may in part reflect a ground state interaction of this latter group with the double bond, steric congestion at the tertiary centre forcing them into proximity.

13. Interestingly, the related ketone 9 undergoes a base catalysed rearrangement to give 10, a product closely related to 2b[9]. This reaction proceeds by deprotonation of the alcohol and nucleophilic attack of the oxanion on the isolated double bond.



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14. Subsequent to the preparation of this manuscript, the rearrangement of 1a to 2a has been reported. Ammann, W.; Jaggi, F.J.; Ganter, C.; Helv. Chim. Acta., 1980, 63, 2019.

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