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THE DECEPTIVE REARRANGEMENT OF A C_8H_9 CATION OF THE CAGE TYPE

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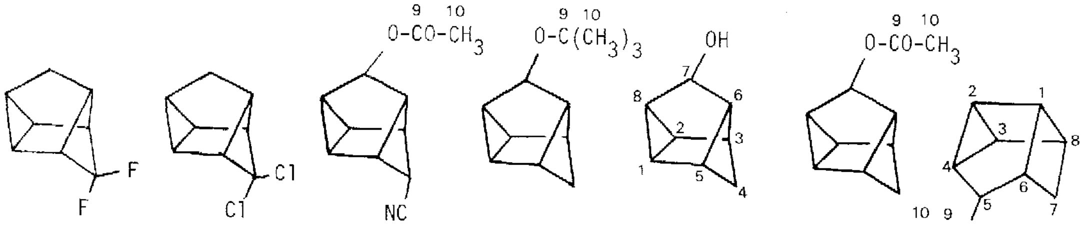
Summary. We produce evidence to show that the acetolysis of *exo-seco*-cubyl mesylate gives 7-tetracyclo[$3.3.0.0^{2,8}0^{3,6}$]octyl acetate as sole product and not 5-tetracyclo[$4.2.0.0^{2,4}0^{3,8}$]-octyl acetate.

We were surprised by the report that the acetolysis of the *seco*-cubyl mesylate 1, proceeding through the intermediacy of the C_8H_9 cation 2, merely rearranged to the cyclopropyl-carbinyl cation 3 to yield the single epimeric acetate 4.[1] A cation such as 2 would be expected to undergo a more deep-seated rearrangement.[2] In fact, we have recently obtained unequivocal proof that the Schmidt fragmentation reaction carried out on homocubanone 5 produces the rearranged cyano-mesylate 6.[3]

We believe that the latter reaction involves the initial formation of the imino-diazonium ion 7 which cleaves to the cyano-*seco*-cubyl cation 8 which further rearranges to the cyclopropylcyclobutylcarbinyl cation 9, to be finally captured by solvent, thereby affording the mesylate 6.

Doubting that two carbocations so similar as 2 and 8 would evolve differently, we converted the mesylate 6 into the acetate 10 and compared its ^{13}C-NMR spectra with that of the compound purported to have structure 4. The similarity of the spectra was striking (Table). In order to confirm that the acetate which was assigned structure 4 had in reality structure 11, we decided to prepare, in unequivocal manner, the acetate 11 and its alcohol 12.

Table. ^{13}C-Resonances of Some Derivatives of Tetracyclo$[3.3.0.0^{2,8}0^{3,6}]$octane.^{a,c}

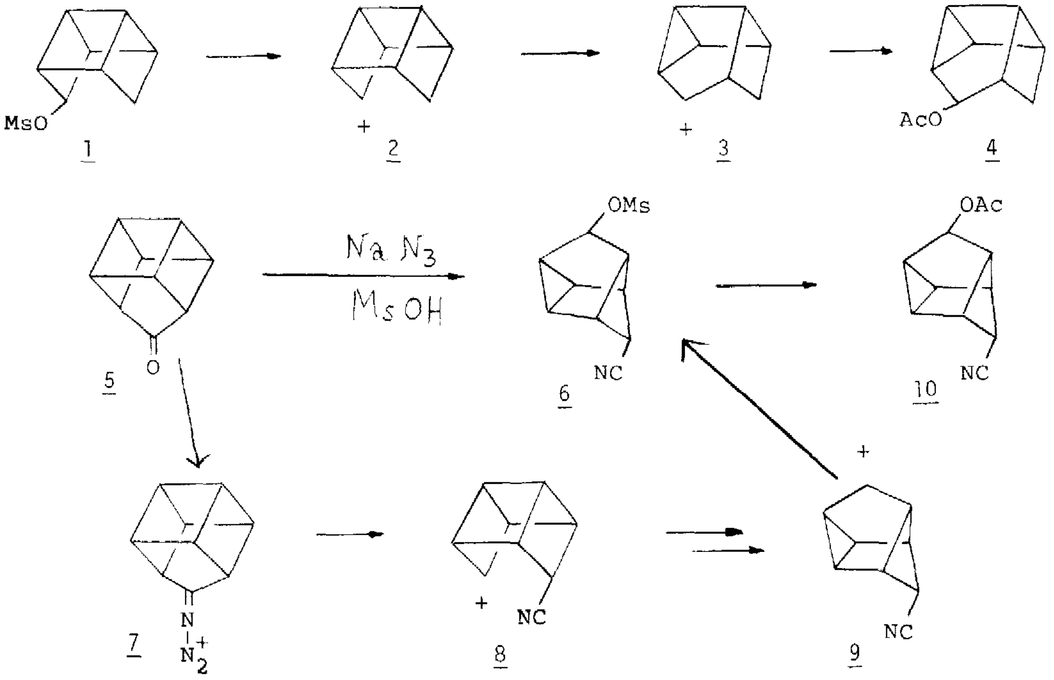


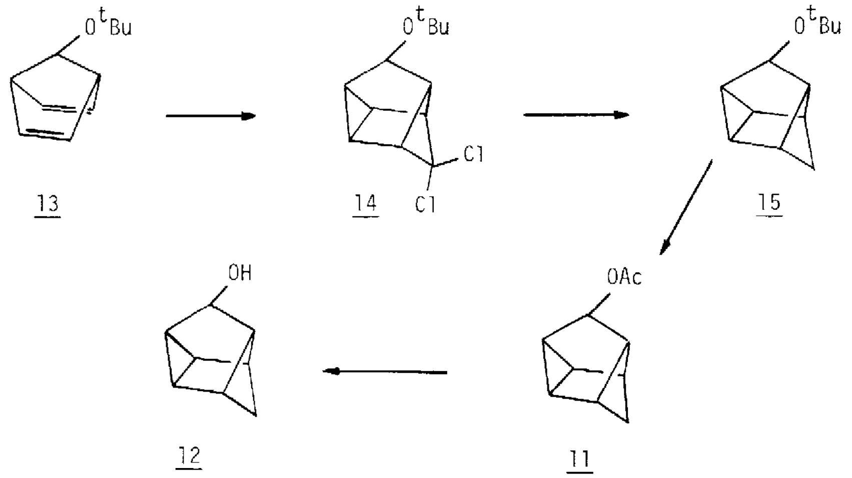
	16	17	10	15	12	11		4^b
C1	12.91	18.95	18.95 D	19.31 D	19.83 D	20.03 D	C2	20.0 D
C2	12.91	18.95	19.68 D	20.63 D	20.53 D	20.49 D	C3	20.5 D
C3	49.19	58.20	41.85 D	38.99 D	39.66 D	39.40 D	C8	39.4 D
C5	49.19	58.20	43.61 D	40.98 D	40.03 D	40.97 D	C1	41.0 D
C4	128.10	91.69	44.29 D	43.45 T	43.10 T	43.30 T	C7	43.4 T
C6	33.81	40.62	45.80 D	48.96 D	49.13 D	46.23 D	C6	46.2 D
C7	31.77	34.38	79.82 D	78.60 D	78.54 D	81.16 D	C5	81.3 D
C8	25.61	30.65	34.45 D	34.37 DD	35.13 DD	32.03 DD	C10	32.0 Q
C9	-	-	171.30 S	72.83 S	-	170.94 (S)	C9	171.3 S
C10	-	-	20.90 (Q)	28.67 Q	-	21.22 Q	C4	21.2 D

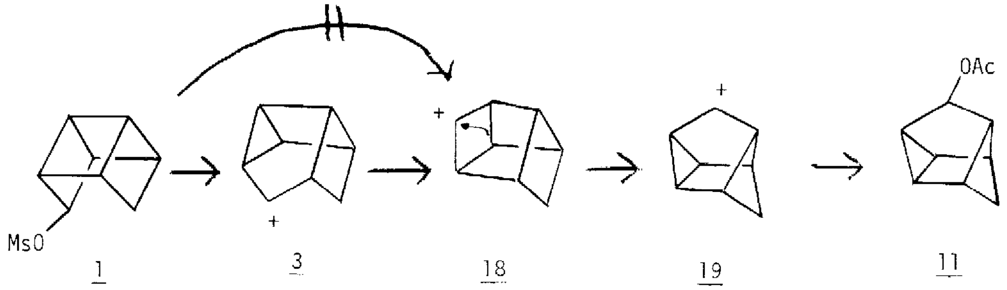
[a] Spectra recorded at 25.2 MHz in $CDCl_3$ solution; values with respect to tetramethylsilane.

[b] Structure proposed and resonances assigned thereto according to reference 1.

[c] Off-resonance multiplicities are indicated by D = doublet, etc.







Exploitation of the homo-1,4 cheletropic reaction[4] of dichlorocarbene with 7-*t*-butoxy-norbornadiene 13 gave the adduct 14. Appropriate reductive dechlorination of the *gem*-dichloro function under the Winstein conditions[5] preserved the skeleton[6] and yielded the ether of the parent hydrocarbon 15. Acid hydrolysis and acetylation gave a mixture of products. Preparative gas-liquid chromatography permitted the isolation of the desired acetate 11 in 40% yield. Reduction of 11 with lithium aluminium hydride gave the corresponding alcohol 12.

Comparison of the ^{13}C-NMR spectra of 10, 11, 12 and 15 with those of the difluoro and dichloro carbene adducts obtained from norbornadiene (16 and 17) and that reported for 4 reveals, without a shadow of doubt, that 4 in fact has the structure 11.

The spectral arguments may be briefly resumed as follows. *(1)* ^{1}H-NMR spectra of our compounds 11 and 12 correspond exactly to those described for the acetate and alcohol of the supposed structure 4. *(2)* The ^{13}C resonances of our structure 11 are identical with those of the compound assigned structure 4. *(3)* The off-resonance "quadruplet" of the signal attributed to C10 in 4 is really a doublet of doublets. On the other hand, the signal at 21.2 ppm is a quartet, in keeping with its assignment to C9 in our structure 11. *(4)* Conversion of the acetate to the alcohol (11 to 12) is most revealing; the two resonances assigned to C4 and C9 in 4 disappear, whereas the rest remain essentially unchanged, especially for those atoms furthest from the modified function. Consequently, the C4 signal has been mis-assigned.

A last question concerns the pathway by which the acetolysis of 1 leads uniquely to 11. The most economical process is the concerted Wagner-Meerwein shift which generates the cyclobutyl cation 18 directly. Subsequent ring contraction, followed by attack by solvent acetic acid on either face of the cationic center of 19 give the product 11. However, calculation reveals[7] and trapping experiments[8] have confirmed that the rearrangement occurs *via* the Dauben cation 3 which then gives 18.

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REFERENCES AND NOTES

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2) (a) *Cf.* C_8H_9 cations rearrange extensively (C.W. Jefford, J. Mareda, J.C. Perlberger & U. Burger, J. Am. Chem. Soc. 101, 1370 (1979); (b) For examples of the chemistry of cage cyclobutyl cations see: G. Mehta & V.K. Singh, Tet. Letters 1978, 4591; G. Mehta, P. Ghosh, B. Chaudhury, V.K. Singh, R. Usha, K.I. Varughese & K. Venkatesan, *ibid.* 1977, 4109.

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4) C.W. Jefford, V. de los Heros & U. Burger, Tet. Letters 1976, 703.

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6) The concordance of the ^{13}C-NMR shifts of 15 with those of 17 and 10 secures its structure. The structure of the 7-bromo derivative 10 has been determined by radio crystallography (T.S. Cameron, unpublished work).

7) The heats of formation and minimum energy reaction paths of the *seco*-cubyl cation and its congeners are being calculated by the MINDO/3 method (J.A. Zuber, unpublished work).

8) G. Mehta & S.C. Suri, unpublished results.

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