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CYCLOPROPYLCARBINYL-CYCLOPROPYLCARBINYL CATION REARRANGEMENTS IN 2-BICYCLO[n.1.0]ALKYL SYSTEMS

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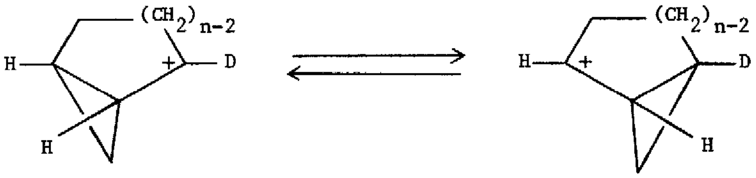
Cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangements are well characterized in monocyclic systems.[1] However, in bicyclic[2] and polycyclic[3] systems they are only occasionally observed. For example, evidence for such rearrangements occurring during hydrolysis in 80% aqueous acetone has been sought with all of the _cis_-ring fused 2-deuterio-_exo_- and _endo_-2-bicyclo[n.1.0]alkyl 4-nitro- or 3,5-dinitrobenzoates (n = 3 to 6).[2] However, only with the 2-deuterio-_exo_-2-bicyclo[5.1.0]octyl 3,5-dinitrobenzoate was any significant amount of rearrangement of the type shown below observed to occur during hydrolysis.[2d]

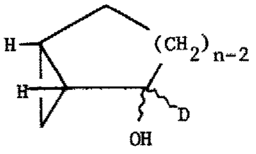
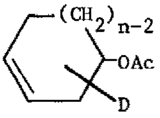


In connection with our continuing interests in the effects of structural and electronic differences upon the nature and behavior of cyclopropylcarbinyl cation intermediates,[2a,b] we have examined the perchloric acid catalyzed acetolyses of all of the 2-deuterio-_exo_- and _endo_-2-bicyclo[n.1.0]alkanols (n = 3 to 6) to obtain information regarding just how unfavorable is the cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement process with the various members of the series for which it was not observed in the ester hydrolysis studies. We have already described elsewhere[2b] the procedure for the perchloric acid catalyzed bicyclo alkanol acetolysis method. Its advantages and greater sensitivity over the ester hydrolysis method lie partly in the lower nucleophilicity of acetic acid as compared to 80% aqueous acetone, thus allowing the 2-bicyclo[n.1.0]alkyl cations more time to undergo possible cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement before solvent attack occurs to give products. Also, any initially formed _exo_- or _endo_-bicyclic acetate products of kinetic control will be eventually completely converted to the products of thermodynamic control _via_ repeated reformation of the 2-bicyclo[n.1.0]alkyl cations. These thermodynamic products, in all cases except with the _exo_-2-bicyclo[6.1.0]nonyl system, should be primarily the homoallylic _cis_-cycloalken-4-yl acetates[2] containing deuterium only at their 1-positions if none of the cyclopropylcarbinyl-

cyclopropylcarbinyl cation rearrangement occurs. However, if the rearrangement does occur, the deuterium in a portion of the *cis*-cycloalken-4-yl acetate product should also be found at the 4-position. With the 2-deuterio-*exo*-2-bicyclo[6.1.0]nonyl system, the thermodynamic product should be predominantly *trans*-bicyclo[5.2.0]nonan-*trans*-8-yl acetate[2e] containing deuterium only at C-1 if none of the rearrangement occurs but also at C-7 if rearrangement takes place.

In our earlier study of perchloric acid catalyzed acetolyses in the 2-deuterio-2-bicyclo-[3.1.0]hexyl system, the results showed that less than 2% cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement had occurred during formation of the deuteriocyclohexen-4-yl acetate obtained from either *exo*- or *endo*-starting materials.[2b] These results were in accord with the corresponding 3,5-dinitrobenzoate hydrolysis results.[2a] However, in our present studies of perchloric acid catalyzed acetolyses of the 2-deutero-*exo*- and *endo*-2-bicyclo[4.1.0]heptyl, *endo*-2-bicyclo[5.1.0]octyl, and *exo*- and *endo*-2-bicyclo[6.1.0]nonyl alcohols which are summarized in Table I, at least small amounts of cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrange-

Table I. Cyclopropylcarbinyl-Cyclopropylcarbinyl Cation Rearrangements in Reactions of *ca.* 25 µl of 2-Deuterio-*exo*- and *endo*-2-Bicyclo[n.1.0]alkanols with *ca.* 400 µl of 0.037 *M* $HClO_4$ in Acetic Acid at 40°.

	Time,[a] hr.	% Total Yield		% Rearranged[b]
exo-[4.1.0]	0.3-70	96±2[c]		34±2
endo-[4.1.0]	0.2-30	96±2[c]		36±2
exo-[5.1.0]	0.3-45	100		38±2
endo-[5.1.0]	0.3-50	100		38±2
exo-[6.1.0][d]	---	---		---
endo-[6.1.0]	0.2-30	100		10±2

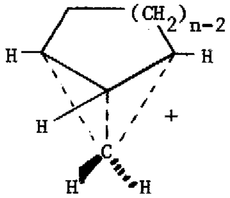
[a] Range of times over which the reaction mixtures were examined by nmr and found to be further unchanged. [b] Determined from nmr vinyl to α-proton ratios. The products were shown by nmr and also in certain cases by mass spectral examination to still contain approximately one deuterium per molecule. [c] About 4% of deuterio-3-acetoxy methylcyclohexene is also formed.

[d] After 5 hr reaction time, only formation of deuterio-*trans*-bicyclo[5.2.0]nonan-*trans*-8-yl acetate was detected. Using $Eu(fod)_3$ nmr shift reagent, this was found to contain 20±10% of rearranged material.

ment were observed which had been too small to be detected in the previous nitrobenzoate ester hydrolysis studies. Thus, large amounts of material which must result *via* cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement were found in the deuterio-*cis*-cycloalken-4-yl acetate products obtained from both the *exo*- and *endo*-[4.1.0]heptyl and [5.1.0]octyl alcohols. Also, in formation of the deuterio-*cis*-cyclononen-4-yl acetate product from the *endo*-[6.1.0]nonanol, and in the deuterio-*trans*-bicyclo[5.2.0]nonan-*trans*-8-yl acetate product from the *exo*-[6.1.0]nonanol, it could be concluded that real, although small, amounts of cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement had occurred.

The observation that nearly identical amounts of cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement were found in the perchloric acid catalyzed acetolyses of both of the isomeric 2-deuterio-2-bicyclo[5.1.0]octanols requires some comment. In the ester hydrolysis study,[2d] none of the rearrangement was observed with the *endo* starting material. However, after a time at 110° sufficient for 93% acid production, the alcoholic products from the *exo* starting material were all greater than 45% rearranged. Thus, one might have anticipated that in the perchloric acid catalyzed 2-bicyclo[5.1.0]octanol acetolyses less rearrangement would have been observed starting with the *endo*-alcohol than with the *exo*-alcohol. Also, in the deuterio-*cis*-cycloocten-4-yl acetate product from the *exo*-starting material, greater than the observed 34±2% of rearranged material might have been expected. This may result from different preferences for the reacting conformations of the bicyclic alcohols or acetates in acetic acid versus the 3,5-dinitrobenzoates in 80% aqueous acetone. Also, in the less neucleophilic acetic acid any initially formed 2-bicyclo[5.1.0]octyl cation conformation which is not favorable for rearrangement should have more time to convert to a favorable conformation before solvent attack occurs.

As to why the cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement process is so much more favorable in the 2-bicyclo[4.1.0]heptyl and [5.1.0]octyl systems than in the [3.1.0]-hexyl and [6.1.0]nonyl systems is likely related to angle strain or H-H repulsions in the [3.1.0]-hexyl and [6.1.0]nonyl systems which destabilize the species necessary for the rearrangement to such an extent that it does not occur at all or only slowly in competition with solvent attack. Current views,[1a,b,c;3f] based on both experimental and theoretical considerations, seem to favor a puckered cyclobutyl-type C_s symmetric activated complex or intermediate for the rearrangement process. Such a species, which may be considered[3f] as similar to that which would be obtained through a 1 + 3 cycloaddition of nonlinear methylene with an allyl cation, is shown below for



for the 2-bicyclo[n.1.0]alkyl cation system. However, molecular models do not clearly show why such a species should be less favorable in the 2-bicyclo[3.1.0]hexyl and [6.1.0]nonyl systems than in the [4.1.0]heptyl and [5.1.0]octyl systems. Work is in progress which it is anticipated will help to clarify this.

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REFERENCES

1. For examples and leading references to earlier work see:
    (a) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).
    (b) Z. Majerski and P. von R. Schleyer, *ibid.*, **93**, 665 (1971).
    (c) G. A. Olah, C. L. Jewell, D. P. Kelly and R. D. Proter, *ibid.*, **94**, 146 (1972).
    (d) C. D. Poulter and C. J. Spillner, *ibid.*, **96**, 7591 (1974).

2. (a) E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971).
    (b) E. C. Friedrich and M. A. Saleh, *J. Amer. Chem. Soc.*, **95**, 2617 (1973).
    (c) L. E. Friedrich and G. B. Schuster, *Tetrahedron Lett.*, 3171 (1971).
    (d) L. E. Friedrich and F. R. Wight, *J. Amer. Chem. Soc.*, **92**, 1807 (1970).
    (e) K. B. Wiberg and T. Nakahira, *ibid.*, **93**, 5193 (1971).

3. (a) L. A. Paquette, O. Cox, M. Oku and R. P. Henzel, *J. Amer. Chem. Soc.*, **96**, 4892 (1974).
    (b) P. G. Gassman, R. N. Steppel and E. A. Armour, *Tetrahedron Lett.*, 3287 (1973).
    (c) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **93**, 1275 (1971).
    (d) W. G. Dauben and L. E. Friedrich, *Tetrahedron Lett.*, 1735 (1967).
    (e) W. G. Dauben and E. I. Aoyagi, *Tetrahedron*, **26**, 1249 (1970).
    (f) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4303, 4311 (1968).
    (g) G. A. Olah, G. Liang, K. A. Babiak, T. K. Morgan, Jr., and R. K. Murray, Jr., *ibid.*, **98**, 576 (1976).