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CYCLOPROPYLCARBINYL CATION REARRANGEMENTS IN THE BICYCLO[4.1.0]HEPT-2-YL SYSTEM

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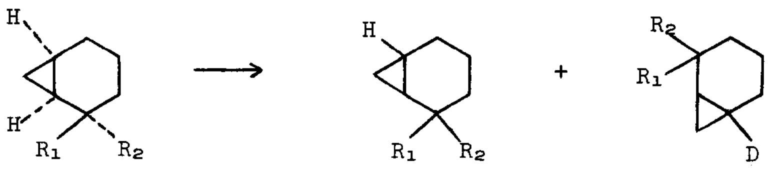
Goering and Rubenstein[1] reported that identical product mixtures were obtained in the solvolyses of the cis- and trans-bicyclo[4.1.0]hept-2-yl p-nitrobenzoates. This observation led them to suggest that each isomer ionized to form a common cyclopropylcarbinyl cation intermediate.

In recent work on the cis- and trans-bicyclo[5.1.0]oct-2-yl 3,5-dinitrobenzoates we[2] observed that both isomeric esters also gave similar (but not identical) hydrolysis product mixtures. The cis and trans esters, however, gave very different rates of degenerate cyclopropylcarbinyl cation rearrangement, as measured using both deuterium scrambling and racemization techniques. After 81% reaction the alcohol products from the cis isomer possessed no scrambled deuterium atoms; after 93% reaction the deuterium in the alcoholic products from the trans isomer, however, was found to be greater than 90% scrambled. Thus, it appears that measurement of the rates of degenerate cyclopropylcarbinyl cation rearrangement for isomeric cyclopropylcarbinyl systems provides a more sensitive measure of structurally different cyclopropylcarbinyl cation intermediates than do simple product studies. Based on the above reasoning, it is important to carry out a careful study of the rates of degenerate cyclopropylcarbinyl cation rearrangement for the solvolyses of both isomeric bicyclo[4.1.0]hept-2-yl derivatives. For our work we used deuterium scrambling for measuring the maximum possible amount of degenerate cyclopropylcarbinyl rearrangement primarily because a very sensitive mass spectrometric method of analysis was available.

A mixture of cis- and trans-bicyclo[4.1.0]heptan-2-ols-2-d_1 was prepared by lithium aluminum deuteride reduction of bicyclo[4.1.0]heptan-2-one. Vpc separation of the isomeric alcohols followed by treatment with p-nitrobenzoyl chloride gave the cis and trans esters, **1** and **2**, which were shown by vpc to be 94% and 99+% pure, respectively, after hydrolysis back to the alcohol. Nmr analysis of trans ester **2** showed no absorption for hydrogen at C-2. A portion of each ester was solvolyzed to 50-90% completion in 80% aqueous acetone at ca. 79° in the presence of undissolved sodium carbonate. These conditions have been shown[1] to give a relatively stable mixture of kinetically controlled products arising only via alkyl-oxygen cleavage. The alcoholic products were separated from unreacted ester either by trituration with cold pentane in which only the alcohols were soluble, or by bulb-to-bulb vacuum transfer. The alcoholic mixture from each solvolysis was analyzed by vpc to determine the cis-trans ratio. The ratio in each solvolysis was ca. 3-4 as observed before[1] and therefore any acyl-oxygen cleavage was precluded. Each alcohol mixture was finally oxidized with Jones' reagent to bicyclo[4.1.0]heptan-2-one[3] which was collected by vpc and analyzed by mass spectral techniques. A portion of each starting ester was also hydrolyzed as a control sample under acyl-oxygen cleavage conditions to the respective alcohol. These alcohols were similarly oxidized, collected by vpc, and analyzed by mass spectrometry. If the degenerate cyclopropylcarbinyl rearrangement occurred, a product mixture of alcohols **3a** and **4a** would lead to bicyclo[4.1.0]heptan-2-one containing more deuterium than the control sample of ketone.



1, R_1 = OPNB, R_2 = D
2, R_1 = D, R_2 = OPNB

3a, R_1 = D, R_2 = OH
3b, R_1 = R_2= =O

4a, R_1 = H, R_2 = OH
4b, R_1 = R_2= =O

Since an M-1 mass spectral peak persisted even at low ionization energies, a computer program was written to subtract the M-1 isotopic ion cluster from the observed peaks in the molecular ion region. The only assumption is that no deuterium was lost in the M-1 fragmentation. This assumption, however, introduces negligible error if the ketone has a very small deuterium content. The calculated $M^{+\cdot}$ isotopic cluster was analyzed by a weighted least-squares analysis to determine the deuterium content of the various ketone samples, see Table I.

Table I

Deuterium Content of Bicyclo[4.1.0]heptan-2-one Obtained from Oxidation of the Solvolysis Products of the cis- and trans-Bicyclo[4.1.0]hept-2-yl-2-d_1 p-Nitrobenzoates, (**1**) and (**2**).

Sample Source	Deuterium Content	DF[a]
cis-PNB, **1**	0.0041 ± 0.0023	5
Control	0.0055 ± 0.0019	5
trans-PNB, **2**[b]	0.0052 ± 0.0015	4
Control	-0.0019 ± 0.0076	4
trans-PNB, **2**[b]	0.0061 ± 0.0018	5
Control	-0.0002 ± 0.0014	5
trans-PNB, **2**[c]	0.0026 ± 0.0015	5
Control	-0.0041 ± 0.0016	5

[a] Internal degrees of freedom from repetitive scans on a Perkin-Elmer RMU6E mass spectrometer. The exit slit was opened wider than the ion beam so that flat-topped peaks were produced whose heights are directly proportional to the ion currents. All errors are standard deviations.

[b] Duplicate samples from same product run.

[c] Different product run.

A weighted least-squares calculation of the difference in deuterium content between the ketone and control samples for solvolysis of the trans ester gave an average deuterium difference of 0.0065. This difference corresponds to 1.3% deuterium scrambling under conditions where ca. 0.5% scrambling could have been detected. Even though *trans* ester **2** does scramble to a small extent and *cis* ester **1** doesn't,[4] the amount of scrambling is so small that it doesn't distinguish different mechanistic pathways for the solvolyses of the two isomeric esters.

In summary, all data obtained by Goering and Rubenstein and in the present work from solvolysis studies of the *cis*- and *trans*-bicyclo[4.1.0]-hept-2-yl ester systems indicate the intervention of only a single common intermediate cation. Similar results have also been reported recently by Friedrich and Saleh for the bicyclo[3.1.0]hex-2-yl system.[5] The larger ring bicyclo[n.1.0]alk-2-yl esters, n = 5-7,[2,6] however, lead to different catonic intermediates from solvolysis of the *cis* and *trans* esters. The reasons for this contrast must be associated with the different conformations available to the cyclic methylene chains in the different ring systems. Presumably the *inherent* chemistry of the cationic cyclopropylcarbinyl moiety is independent of the bicyclo[n.1.0] ring size and is the same as would be observed in the 1-(*cis*-2-methylcyclopropyl)ethyl system. A detailed interpretation of the solvolysis data in the bicyclic cyclopropylcarbinyl series should await the study of this model acyclic system.

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References

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3. W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).
4. Goering and Rubenstein[1] reported a 1.7% loss of optical activity in the alcoholic products formed from solvolysis of optically active *cis* isomer **1**. This result may mean that intermediate cations are racemizing without rearrangement by reversible fragmentation to the 3-cyclohepten-1-yl cation.
5. For the latest and most complete study of the bicyclo[3.1.0]hex-2-yl cyclopropylcarbinyl system, see E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971). See also G. H. Schmid and A. Brown, *ibid.*, 4695 (1968); P. R. Brook, R. M. Ellam and A. S. Bloss, *Chem. Comm.*, 425 (1968).
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