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METHYL SUBSTITUENT EFFECTS ON CYCLOPROPYLCARBINYL-CYCLOPROPYLCARBINYL CATION REARRANGEMENTS IN THE 2-BICYCLO[4.1.0]HEPTYL SYSTEM

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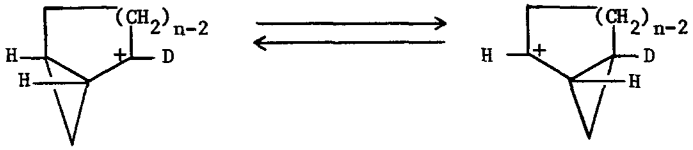
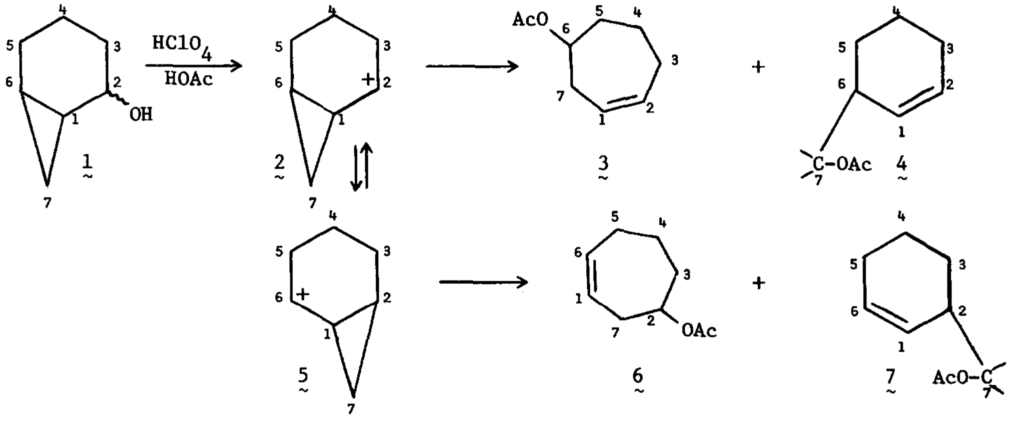
We recently reported[1] a study of cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangements[2] in perchloric acid catalyzed acetolyses[3] of the 2-deuterio-_endo_- and _exo_-2-bicyclo[n.1.0]alkanols (n = 3 to 6). In none of the systems examined was the amount of rearrangement observed to be dependent on the leaving group geometry. However, ring size effects upon the rearrangement were important. Thus, little or none of the rearrangement was observed in the products from the small and medium ring 2-bicyclo[3.1.0]hexyl and [6.1.0]nonyl systems. On the other hand, significant amounts had taken place prior to formation of the cycloalken-4-yl acetate products from the 2-bicyclo[4.1.0]heptyl and [5.1.0]octyl systems.



In an attempt to learn more of the structural and electronic requirements for cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangements, we have now examined the effects of individual 1,2,6 or _exo_-7-methyl substitution upon the amounts of the rearrangement $\underset{\sim}{2} \rightarrow \underset{\sim}{5}$ in perchloric acid catalyzed acetolyses in the 2-bicyclo[4.1.0]heptyl system $\underset{\sim}{1}$.



The 2-bicyclo[4.1.0]heptyl system was chosen for this study because of its intermediate position in the spectrum of behaviors observed in our earlier study[1] of the unsubstituted 2-bicyclo[n.1.0]alkanols. The perchloric acid catalyzed acetolysis procedure provides primarily the homoallylic acetate products of thermodynamic control *via* repeated reionization of any initially formed bicyclic acetate products of kinetic control. In the reaction scheme shown, the numbering of the carbon atoms in 1 has been retained in all of the structures 2 to 7 to illustrate the consequences of the cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement of 2 → 5 in the possible homoallylic products.

For cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement to occur in the 2-bicyclo[4.1.0]heptyl system, several likely pathways may be envisioned. These are shown below using localized charges for simplicity. The species 8 and 9 either may represent intermediates in a two step process or activated complexes in a one step process. For both possibilities it would be anticipated that if the pathway for rearrangement of 2 to 5 involves charge buildup at C_1 as in 8, a methyl substituent at C_1 should increase the importance of the rearrangement relative to other processes. Correspondingly, if charge buildup at C_7 as in 9 is important, 7-methyl substitution should be effective. On the other hand, 2-methyl or 6-methyl substitution might actually decrease rearrangement through either 8 or 9 by increasing charge localization elsewhere relative to that at C_1 or C_7.

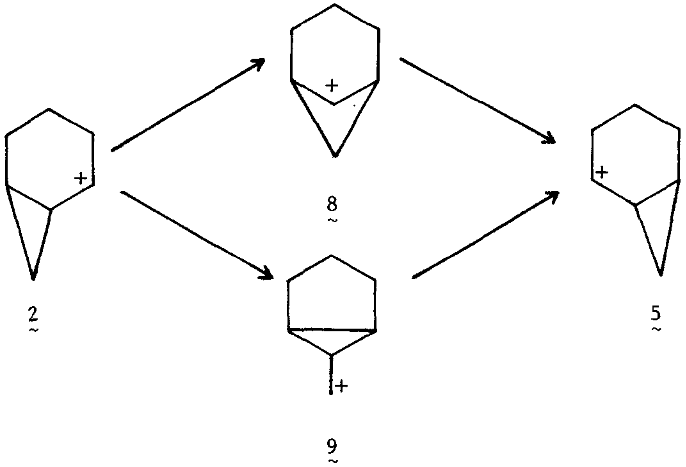


Table I summarizes the nature and yields of the various possible homoallylic products obtained in the reactions of the different 2-bicyclo[4.1.0]heptanols with perchloric acid in acetic acid. These were determined using a combination of glc and nmr techniques. The slightly lower temperatures used in the reactions of the 2-methyl and 6-methyl substituted bicycloheptanols were necessary because at higher temperatures poor material balances due to polymer formation were encountered. For the study of the effects of methyl substitution at C_7, only the *exo*-7-methyl isomer was examined because of potential complications resulting from steric interactions for the *endo*-7-methyl isomer.

In considering the results in Table I, it is felt that the relative yields of the

Table I. Homoallylic Acetate Products from Reactions of *ca.* 25 μl of some 2-Bicyclo-[4.1.0]heptanols with *ca.* 400 μl of 0.037 *M* $HClO_4$ in Acetic Acid.[a,b]

Starting 2-Bicyclo [4.1.0]heptanol	Temp. °C	Products, **3** + **6**	% Yield[c] **4** + **7**
2-D	40	96 ± 2	4 ± 2
1-CH_3, 2-D	40	96 ± 2	4 ± 2[d]
2-CH_3	23	81 ± 2	19 ± 2
6-CH_3	23	55 ± 5	---[e]
exo-7-CH_3, 2-D	40	---	100 ± 2

[a] Within experimental error, identical product mixtures were observed starting with either the *endo* or *exo*-alcohol isomer in each system. Microanalytical and spectral data were consistent with the structures proposed for all new compounds. [b] In each case the reaction mixtures were initially examined after about 5-10 min. Further reaction times of at least a factor of five longer caused no change within experimental error in the product compositions. [c] Yields are normalized to 100%. Material balances were observed in all cases to be greater than 90%. [d] The structure for this minor product has not been definitely established. [e] A 45 ± 5% yield of 1-methyl-1,3-cycloheptadiene was also observed.

two homoallylic acetate product types resulting from cyclopropylcarbinyl-allylcarbinyl cation rearrangement for the 1-methyl and *exo*-7-methyl substituted systems are in accord with expectations based on the behavior seen in the unsubstituted system. The higher yield of 3-acetoxymethylcyclohexane product type (**4** and/or **7**) from the 2-methyl substituted system was unexpected, but may be a result of the substituent significantly decreasing the amount of charge delocalized over the cyclopropane ring.[4] The absence of a 3-acetoxymethylcyclohexene product (**4** or **7** type) from the 6-methyl substituted system together with the formation of large amounts of diene is most likely the result of ionization in this system proceeding directly with ring opening to give a non-delocalized tertiary 4-methylcyclohepten-4-yl cation from which the products are formed.

The results in Table II show the effects of methyl substitution at various positions upon the importance of the cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement process in the 2-bicyclo[4.1.0]heptyl system. For the non-methyl, 1-methyl and exo-7-methyl substituted systems, deuterium labeling at the 2-positions was necessary to be able to observe the rearrangement, which is degenerate in these systems in the absence of a label. However, with the 2-methyl and 6-methyl systems, the methyl groups act simultaneously as substituents and as labels. It is seen that 1-methyl substitution increases the amount of cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement to the theoretical maximum expected if equilibrium is established between **2** and **5**, whereas 2, 6, or *exo*-7-methyl substitution cause a decrease relative to the unsubstituted system. These results appear to indicate that significant amounts of charge delocalization at C_1 are critical for the cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement to take place in the 2-bicyclo[4.1.0]-

Table II. Cyclopropylcarbinyl-Cyclopropylcarbinyl Cation Rearrangements in the Reactions of Some 2-Bicyclo[4.1.0]heptanols with $HClO_4$ in Acetic Acid.[a,b]

Starting 2-Bicyclo-[4.1.0]heptanol	% Rearrangement [c]
2-D	35 ± 2
1-CH_3, 2-D	50 ± 2
2-CH_3	3 ± 1 [d]
6-CH_3	1 ± 1
exo-7-CH_3, 2-D	--- [d]

[a] The results given were obtained concurrently with those reported in Table I and the conditions are the same. [b] Within experimental error, identical results were obtained starting with either the *endo*- or the *exo*-alcohol in each system. [c] This corresponds to the percentages of **6** formed subsequent to cyclopropylcarbinyl-cyclopropylcarbinyl cation rearrangement which are contained in the **3** + **6** mixtures. [d] For the 2-CH_3 and *exo*-7-CH_3, 2-D systems, the percentages of **7** in the **4** + **7** mixtures were less than 10% and 15 ± 5%, respectively.

heptyl system. Any substituent effects which increase charge elsewhere and thereby decrease charge delocalization at C_1 decrease the likelihood of rearrangement. This suggests that the most favorable pathway for the rearrangement is *via* a puckered cyclobutyl (or related delocalized species) **8** rather than through another cyclopropylcarbinyl species such as **9**. The conclusion is in accord with theoretical predictions.[2]

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