

SMALL RING COMPOUNDS XXVII
THE MIGRATORY APTITUDE OF THE CYCLOPROPYL GROUP
IN THE β -CYCLOPROPYLETHYL CATION SYSTEMS

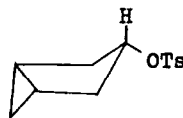
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The remarkable degree of the interaction of a cyclopropane ring with the neighbouring vacant p-orbital in the cyclopropylcarbinyl systems has been well established. On the other hand, the similar interaction (i.e., σ - π interaction) in the β -cyclopropylethyl cation and related systems is strongly influenced by the relative geometrical arrangement of the cyclopropane ring and the vacant p-orbital. Generally, a rigid configuration (i.e., 1^{a} , 2^{b} , etc.) which allows the maximum overlap of the developing vacant p-orbital with the cyclopropane pseudo π -orbital is required to observe the σ - π interaction in the solvolytic reaction in which the β -cyclopropylethyl cation is generated.

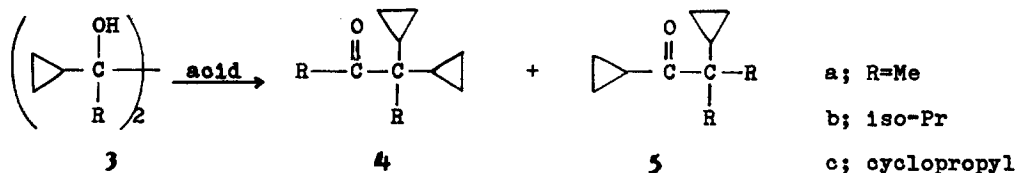
Previously, however, the preferential migration of the cyclopropyl group was found in the pinacol rearrangement of a series of pinacol bearing cyclopropyl group as the substituent². In some open chain β -alkyl, β -cyclopropylethyl cation systems, the similar exclusive Wagner-Meerwein rearrangement of cyclopropyl group was also observed by Y.E. Rhodes, et al.³, and M. Hanack, et al.⁴. In the present study, we wish to report the further details of the migratory aptitude of the cyclopropyl



1



2



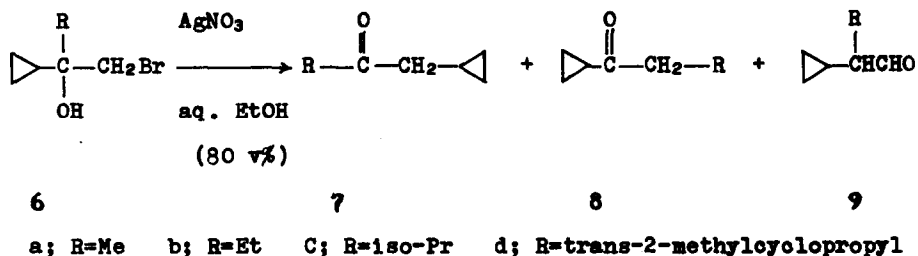
Scheme 1

Table 1 a) Yield of 4 b) (%)

<u>acid</u> c)	<u>4a</u>	<u>4b</u>	<u>4c</u> d)
6N-H ₂ SO ₄	84.4		77.7
HCO ₂ H	n.q. e)	n.q. e)	89.6
aq. CF ₃ CO ₂ H (50 vol%)	n.q. e)		90.0

a) The structures of the products were determined by nmr, ir and mass spectra and elemental analyses. b) The product **5** was not detected by means of vpc. c) The reaction of **3** with 6N-HCl or trifluoroacetic acid gave a ring cleaved compound as a main product together with **4**. e) nearly quantitatively.

group and to consider the transition state of the migration. The results are summarized in Scheme 1 and 2, and Table 1 and 2, where **4** and **7** were formed from the rearrangement of cyclopropyl group and the migration of R gave **5** and **8**. Although the total yield in the reaction of **6d** was relatively low, the ratio **7d/8d** correctly represents the relative migratory aptitude since the ratio was not affected by the further treatment of the mixture of **7d** and **8d** under the same reaction condition. The results show that the cyclopropyl group has far greater migratory aptitude than the alkyl group (cyclopropyl/methyl=44 in the present study, =56³) and that the introduction of one methyl group on the cyclopropane ring brings three times increment on the migratory aptitude. Although the present results may not be sufficient to discuss in detail the character of the transition state of the rearrangement of the cyclopropyl group, it would be suggested that



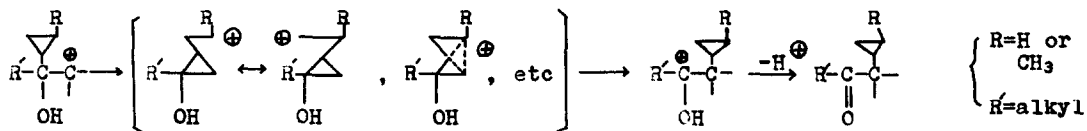
Scheme 2

Table 2^{a)}. Yields of 7, 8 and 9 (%)

	<u>7</u>	<u>8</u>	<u>9</u>
a	35.0	0.8	37.8
b	30.0	0.5	48.0
c	33.4	<0.1	42.7
d	4.6	13.8	4.6

a) The products were identified by the comparison of their nmr, ir, and mass spectra and vpc retention times with those of the corresponding authentic compounds.

the delocalization of the positive charge into the cyclopropane ring in the transition state lowered the activation free energy of the rearrangement of the cyclopropyl group (Scheme 3). The observation that the cyclopropane ring was not cleaved and the stereochemistry of the trans-2-methylcyclopropyl group was retained in the rearranged product seems to be interesting because it would afford a clue to examine the nature of the transition state of the rearrangement. More detailed studies on the transition state are currently in progress.



Scheme 3

References

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