

SMALL RING COMPOUNDS XXVIII

THE STEREOCHEMISTRY AND THE EFFECT OF METHYL SUBSTITUENT
IN WAGNER-MEERWEIN REARRANGEMENT OF CYCLOPROPYL GROUP

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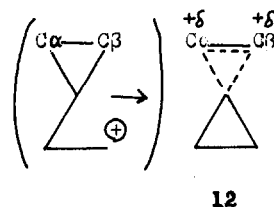
In the previous study, we have indicated that the migratory aptitude of a cyclopropyl group in Wagner-Meerwein rearrangement is far greater than a simple alkyl group¹⁾. In the present study, we wish to report the stereochemistry of the rearrangement and the effect of methyl substituent on the migratory aptitude of the cyclopropyl group.

Bromohydrins (1,3 and 5) or bromohydrin methyl ethers (6 and 9) were treated with AgNO_3 in aqueous ethanol (80%) as described in previous study. All of the products were identified by comparison of their nmr, ir and mass spectra, and vpc retention times with those of the corresponding authentic specimens. The results are summarized in Scheme I and Table I. The product ratio, 7/8 or 10/11 was not affected by further treatment of the mixture of 7 and 8 or 10 and 11 under the same reaction condition. These observations indicated that the migratory aptitude of the cyclopropyl group was larger than the methyl group as was already observed in our previous study, that the stereochemistry of the migrating cyclopropyl group was completely retained, that the migratory aptitude of the cyclopropyl group was enhanced about three times for one methyl group on the cyclopropane ring, and that the effect of methyl substitution might be multiplicative rather than additive. On the basis of the multiplicative effect of a methyl group, the transition state of the cyclopropyl migration is supposed to involve the delocalization of nearly equal positive charge to C α and

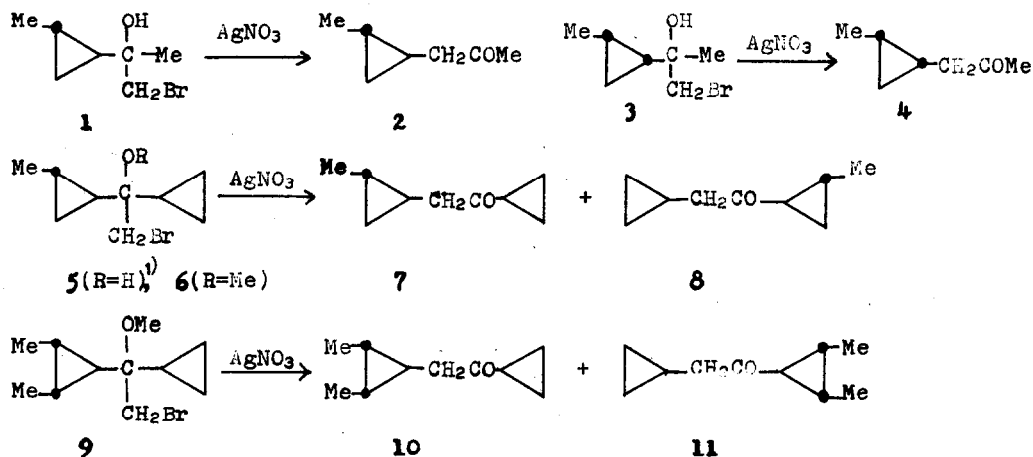
C β (see 12), and the retention of configuration would suggest that the carbon-carbon bonds of the cyclopropane are neither cleaved nor alternated in the rearrangement. In conclusion, a tentative model 12 (and related models) may be proposed as the transition state, which would be conceptually similar to a phenonium ion²⁾.

Table I Ratio of Migratory Aptitude^{a)}

	Migrating Group	
		R
R=Me	97.8	2.2
R=Et	98.2	1.8
R=isoPr	99.7	0.3
R= 	25, 24 ^b	75, 76 ^b
R= 	9 ^b	91 ^b



- a) The results obtained previously by us were also involved.
 b) The values were obtained from the reactions of the bromohydrin methyl ethers. The value without the mark was obtained from the reaction of the bromohydrin.



Scheme I

References

- 1) T. Shono, K. Fujita, S. Kumai, T. Watanabe and I. Nishiguchi, Tetrahedron Lett., 3249 (1972)
- 2) C. J. Lancelot, D. J. Cram and P. v. R. Schleyer, "Carbonium Ions", WILEY-INTERSCIENCE, NEW YORK, 1972, p 1347.