

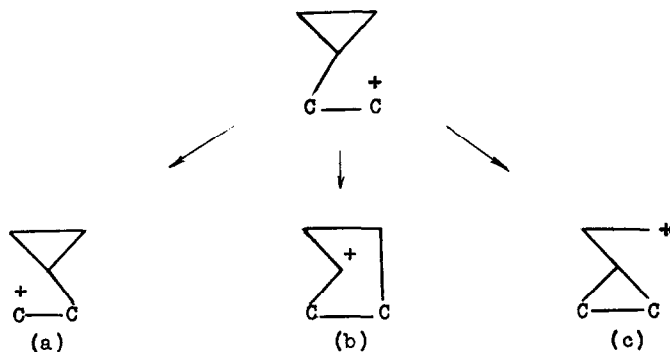
CARBONIUM ION REARRANGEMENTS OF THE

3-NORTRICYCLYL CARBINYL SYSTEM

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(Received 17 June 1964)

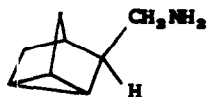
Interactions of cyclopropyl groups with carbonium ions generated at β -carbons have received considerable attention recently (1-6). Three modes of participation have been discussed which may be symbolized as follows.



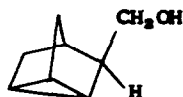
Types (a) and (b) have been implicated in the deamination of β -cyclopropylethylamine (3). Type (c) has been demonstrated in reactions of bicyclo (3.1.0)hexyl systems (1,2,6).

We wish to report a novel example of type (c) participation in a non-symmetrical system, *i.e.*, one in which tris-homocyclopropenyl ions cannot be involved.

The cationic system studied was that derived from 3-nortricyclicylcarbinyl derivatives. Specifically, 3-nortricyclicylcarbinylamine, (IV, b.p. 79-81°/19 mm.) was prepared by lithium aluminum hydride reduction of the corresponding acid amide and subjected to nitrous acid deamination in glacial acetic acid at ca. 15°. Also, the p-toluenesulfonate ester of 3-nortricyclicylcarbinol (V, b.p. 89-90°/10 mm., prepared by lithium aluminum hydride reduction of the corresponding acid) was solvolized in buffered glacial acetic acid at 110°.



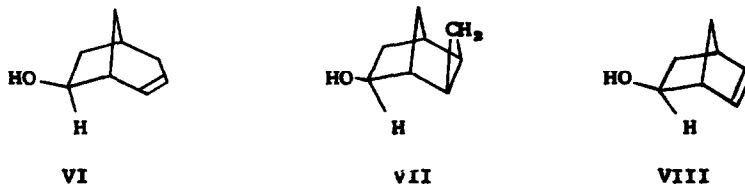
IV



V

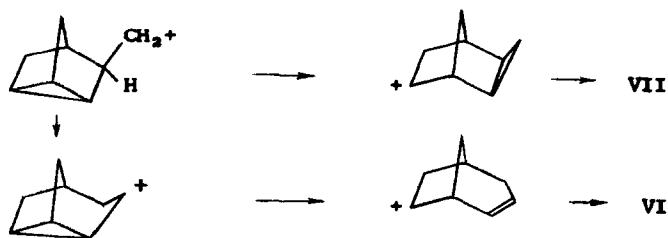
In both cases, three major products were obtained in varying proportions. In addition to 3-nortricyclicylcarbinol (V), two new compounds were identified. An olefinic alcohol was shown to be present by a combination of g.l.c. and n.m.r. data. This, and other data to be published (7) almost certainly allow structure VI for this product. The most interesting

product, formed in yields of ca. 75% (amine deamination) to ca. 34% (tosylate solvolysis) proved to be neither of the expected ring expansion alcohols but rather a new tricyclic alcohol. The analytical and spectral data for this compound were in good agreement with those expected for the tricyclic alcohol VII. An unambiguous synthesis of VII was readily achieved



by "methylene transfer" (8) to exo-5-hydroxy-2-norbornene (VIII), and the two samples were shown to be identical by comparisons of their infrared spectra.

The following scheme represents the simplest rationale for these rearrangements. Work is in progress to test the feasibility of these intermediates.



Acknowledgment.- We wish to thank the National Institutes of Health for financial support and for a U.S.P.H. predoctoral fellowship to J. A. B. (No. 1-F1-GM1,553-01).

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