ELECTROPHILIC CYCLIZATION OF REGULAR α-MONOTERPENOLS CATALYZED BY BF_3 ETHERATE

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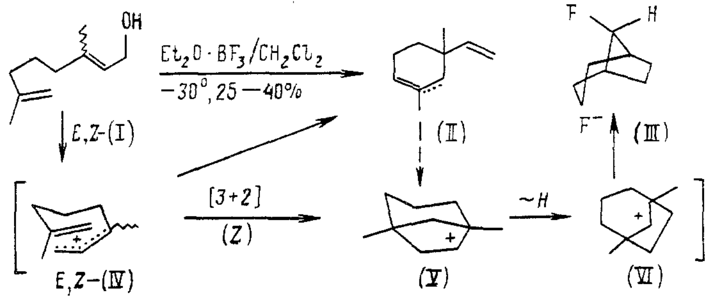
The low-temperature treatment of α-geraniol *E*-(I) and α-nerol *Z*-(I) with 1.5-2 mole-equivalents $BF_3 \cdot OEt_2$ gives a mixture of dimethylvinylcyclohexanones (II) and bicyclo[3.2.1]-octyl fluoride (III), which is readily separated on silverized silica gel. The (II)/(III) ratio is about 95:5 and 60:40, respectively, as indicated by gas–liquid chromatography and PMR spectroscopy. A comparable result was obtained in the case of α-linalool. The structures of the individual components of (II) and (III) were reliably established on the basis of their elemental and spectral data.



Diolefins (II) apparently arise by the intramolecular stabilization of allyl ion (IV) by its isopropenyl fragment. On the other hand, the formation of fluoride (III) is attributed to a nonconcerted [3 + 2] cycloaddition within the α-neryl cation *Z*-(IV) with a subsequent hydride shift (V) → (VI) and final stabilization of (VI) by an external nucleophile.

These transformations of α-monoterpenols imitate the biosynthesis of tri- and tetracyclic diterpenes from labdadienols according to Wenkert [1]. The not previously considered possibility of the generation of secondary beieranyl ion (V) from a precursor of the *Z*-(I) series is more promising than the presently employed pathway for its formation from pimaradiene precursors such as (II) [2].

LITERATURE CITED

1. E. Wenkert, Chem. Ind., 282 (1955).
2. R. M. Coates and H.-Y. Kang, J. Chem. Soc., Chem. Commun., 232 (1987); J. Org. Chem., 52, 2065 (1987).

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