CYCLIZATION AND REARRANGEMENTS OF DITERPENOIDS

X. SUPERACID CYCLIZATION OF E,E,E- AND Z,E,E-GERANYLGERANIC ACIDS AND THEIR ESTERS

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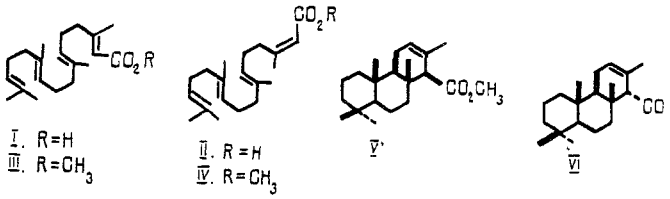
The superacid cyclization of aliphatic terpenols and their acetates is an effective route to the cyclization of terpenoids [1-3]. Continuing these studies, in the present communication we report results of the superacid cyclization of E,E,E- and Z,E,E-geranylgeranic acids (I and II) and their esters (III and IV). There is practically no information in the literature on their cyclization [4].

The acid (I) (55 mg, 0.18 mmole) reacted with fluorosulfonic acid (360 mg, 3.60 mmole) in 2-nitropropane (0.6 ml) at −(50-55)°C for 40 min to give, after the usual working up and the methylation of the reaction product with diazomethane, methyl (±)-(14αH)-isoagath-12-en-15-oate (V) (49.6 mg, 86.2%), mp 85-88.5°C (from CH_3OH). Under the same conditions, the cis- acid (II) gave the liquid methyl (±)-(14βH)-isoagath-12-en-15-oate (VI) (yield 81%, reaction time 1 h).



I. R=H
III. R=CH_3

II. R=H
IV. R=CH_3

V

VI

As was to be expected, the esters (III and IV) cyclized more readily than the acids (I and II), themselves. Thus, on interaction with fluorosulfonic acid (415 mg, 4.15 mmole) in 0.7 ml of 2-nitropropane at −(60-65)°C for 25 min, methyl E,E,E-geranylgeranate (III) (66 mg, 0.21 mmole) gave the isoagathenate (V) with a yield of 92.5%. Under the same conditions, the Z,E,E-geranylgeranate (IV) was converted into the isoagathenate (VI) (yield 85%, reaction time 40 min).

Compounds (V and VI) were identified by chromatographic and spectral comparison with specimens of their optically active forms [5].

The facts given show that fluorosulfonic acid is an effective reagent for converting aliphatic diterpene acids and their esters into tricyclic derivatives. The reaction takes place stereospecifically and structurally-selectively.

LITERATURE CITED

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