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CYCLIZATION OF α-TERPENOLS AND THEIR ACETATES BY FLUOROSULFONIC ACID

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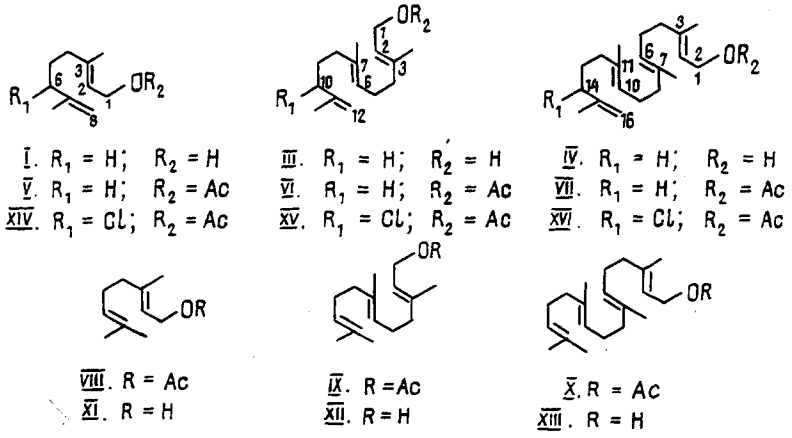
It has been shown that the superacid cyclization of α-terpenols and their acetates takes place with structural selectivity and chemo- and stereospecificity and leads to cyclic isoprenoids with higher yields than the cyclization of the corresponding β-terpenols and their acetates.

We have previously investigated the superacid cyclization of aliphatic β-terpenols and their acetates with $C_{10}-C_{25}$ compositions containing terminal isobutylidene groups [1-5]. According to the literature [6], the double bond of the isobutenyl group present in terpenoids of the α-series is more accessible for protonation. It might therefore be expected that aliphatic α-terpenoids should cyclize more readily and more effectively than the β-isomers.

Recently in the superacid cyclization of α-geraniol (I), α-cyclogeraniol (II) was obtained with a yield of 86% [7].

We have undertaken systematic investigations of the superacid cyclization of α-terpenols and their acetates. In the present paper we give the results of the superacid cyclization of α-geraniol (I), α-E,E-farnesol (III), and α-E,E,E-geranylgeraniol (IV) and their acetates (V)-(VII), which are considered in comparison with the results on the cyclization of their β-isomers (VIII)-(XIII).

Compounds (I) and (III)-(VII) were synthesized by a procedure developed for monoterpenoids [8], starting from the acetates of geraniol (VIII), of E,E-farnesol (IX), and of E,E,E-geranylgeraniol (X). On interaction with sulfuryl chloride in methylene chloride at −60°C these acetates gave the chlorine-substituted acetates (XIV)-(XVI). The chloroacetates (XIV)-(XVI) were reduced with sodium tetrahydroborate in dimethylformamide in the presence of sodium iodide by the procedure of Novak et al. [9] to the acetates of α-geraniol (V), of α-E,E-farnesole (VI), and of α-E,E,E-geranylgeraniol (VII), respectively. The structures of compounds (V)-(VII) and (XIV)-(XVI) were established on the basis of the results of elementary and spectral analyses. Compounds (V)-(VII) were also obtained, with approximately the same yield, on the reduction of the chloroacetates (XIV)-(XVI) with a mixture of zinc dust, sodium iodide, nickel chloride, and triphenylphosphine in aqueous DMFA according to the protocol of Odinokov et al. [8], but this procedure is less convenient in use.



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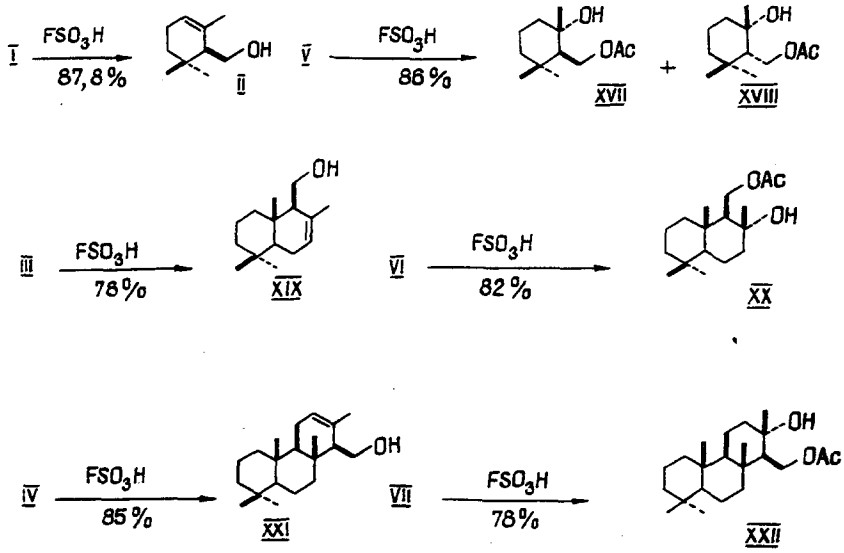
Compounds (I), (III), and (IV) were obtained as the result of the saponification of the acetates (V)-(VII) with an alcoholic solution of caustic soda or by reducing the chloroacetate (XIV)-(XVI) with lithium tetrahydroaluminate in tetrahydrofuran [9]. The structures of compounds (I), (III), and (IV) were confirmed by their spectral characteristics.

The superacid cyclization of compounds (I) and (III)-(VII) was carried out with fluorosulfonic acid in 2-nitropropane at −80°C. On the cyclization of α-geraniol (I) under the conditions that we used previously (ratio of (I) to FSO_3H (in moles) = 1:5, 5 min), the yield of α-cyclogeraniol (II) was 87.8%. The cyclization of α-geranyl acetate (III) (ratio of (III) to FSO_3H = 1:10, 5 min) led to a mixture (8:1) of the hydroxyacetataes (XVII) and (XVIII) (yield 86%).



The yields of the products of the cyclization of geraniol (XI) and of geranyl acetate (VIII) by fluorosulfonic acid were lower, amounting to 72 and 73%, respectively [4].

On the cyclization of α-E,E-farnesol (III) and its acetate (VI) (molar ratio of substrate to FSO_3H = 1:10, time 30 and 40 min, respectively), drimenol (XIX) (78%) and drimanediol monoacetate (XX) (82%) were formed. Under analogous conditions, E,E-farnesol (XII) and its acetate (IX) gave drimenol (XIX) and the hydroxyacetate (XX), again with lower yields (66 and 76%) respectively) [2].

The cyclization of α-E,E,E-geranylgeraniol (IV) and its acetate (VII) with fluorosulfonic acid under the same conditions as for α-farnesol (XII) and its acetate (IX) (time 30 min) led, respectively, to (±)-14αH-isoagath-12-en-15-ol (XXI) (yield 85%) and (±)-14α-H-isoagathane-13α,15-diol 15-monoacetatae (yield 78%). The yields of these substances when the reactions were performed with the β-isomers (XIII) and (X) (82 and 72%) were not much lower than on the cyclization of their α-isomers.

The identification of all the reaction products was achieved by chromatographic and spectral comparison with samples of the substances that we had obtained previously [1, 2, 4].

Thus, as a result of a comparative study of the superacid cyclization of α- and β-terpenols with the $C_{10}-C_{20}$ composition and their acetates, we have shown that the cyclization of compounds of the α-series takes place more easily and leads to cyclic terpenoids with higher yields than the cyclization of aliphatic terpenols of the β-series and their acetates.

EXPERIMENTAL

IR spectra were taken on a Specord 74 IR instrument in CCl_4, and PMR spectra on Tesla BS 476 (60 MHz) and Bruker AC-80 (80 MHz) spectrometers in CCl_4. The signals are given in the δ scale, with tetramethylsilane as internal standard. GLC analysis was conducted on a Chrom-5 chromatograph with a flame-ionization detector and a 3 × 1500 mm glass column, the stationary phase being 5% of SE-30 on Chromaton N-AW-DMCS and the carrier gas helium at V = 45 ml/min, t_{column} = 210°C, $t_{evaporator}$ = 250°C. For column chromatography we used Chemapol silica gels L 40/100 μ and L 100/250 μ. Silica gel impregnated with silver nitrate was obtained by the method of Norin and Westselz [10].

The petroleum ether used had bp 40-60°C. Solutions of the substances in organic solvents were dried with anhydrous sodium sulfate.

Synthesis of the Chloroacetates (XIV)-(XVI) (General Procedure). At −60°in an atmosphere of argon, a solution consisting of 3.5 ml of SO_2Cl_2 and 15 ml of CH_2Cl_2 was added dropwise to a stirred solution of 17.8 mmole of one of the acetates (VIII)-(X) in 40 ml of CH_2Cl_2 and 2.6 ml of dried pyridine. The reaction mixture was heated to 0°C for 10 min and was worked up in the usual way.

6-Chloro-α-geranyl Acetate (XIV). By the method described above, 3.5 g of geranyl acetate (VIII) yielded 3.86 g of a reaction product which was chromatographed on a column containing 65 g of SiO_2. Petroleum ether−ethyl acetate (9:1) eluted 2.59 g (63%) of 6-chloro-α-geranyl acetate (XIV), a colorless viscous liquid. IR spectrum (cm^{-1}): 1230, 1735 ($OCOCH_3$), 890, 1648 (>C=H_2), 1660 (>C=C<$_H$). PMR spectrum (ppm): 1.76 (s, 3H), 1.82 (s, 3H) (CH_3, s, at C-3 and C-7), 2.01 (s, 3H, $OCOCH_3$), 3.96 (m, 1H, >CHCl), 4.23 (m, 2H, CH_2O−), 4.85 (br.s) and 4.96 (br.s) (2H, >C=CH_2), 5.18 (t, J = 8 Hz, 1H, >C=C<$_H$). The spectral characteristics of compound (XIV) coincided with those given in the literature [9].

10-Chloro-α-E,E-farnesyl Acetate (XV). By the method described above, 1.52 g of E,E-farnesyl acetate (IX) yielded 1.42 g of a reaction product which was chromatographed on a column containing 30 g of SiO_2. Petroleum ether−ethyl acetate (9:1) eluted 1.28 mg (75%) of 10-chloro-α-E,E-farnesyl acetate (XV), a colorless viscous liquid. IR spectrum (cm^{-1}): 1222, 1742 ($OCOCH_3$), 900, 1635 (>C=CH_2), 1645 (>C=C<$_H$). PMR spectrum ($CDCl_3$, ppm): 1.56 (s, 6H), 1.63 (s, 3H), 1.67 (s, 3H), (CH_3 at C-3, C-7, and C-11), 2.09 (s, 3H, $OCOCH_3$), 3.94 (m, 2H, >CHCl), 4.45 (d, J = 7 Hz, 2H, CH_2−O−), 4.58 (m, 2H, >C=CH_2), 5.10 (m, 1H, 6-H), 5.52 (m, 1H, 2-H). Found %: C 68.14; H 8.96; Cl 12.11. $C_{17}H_{27}ClO_2$. Calculated %: C 68.32; H 9.11; Cl 11.86.

14-Chloro-α-E,E-E-geranylgeranyl Acetate (XVI). By the procedure described above, 0.80 g of E,E,E-geranylgeranyl acetate (X) yielded 0.77 g of reaction product, which was chromatographed on a column containing 17 g of SiO_2. Petroleum ether−ethyl acetate (9:1) eluted 634 mg (72%) of 14-chloro-α-E,E,E-geranylgeranyl acetate (XVI), a colorless viscous liquid. IR spectrum (cm^{-1}): 1230, 1735 ($OCOCH_3$), 900, 1644 (>, >C=CH_2), 1670 (>C=C<$_H$). PMR spectrum ($CDCl_3$, ppm): 1.60 (s, 6H), 1.70 (s, 3H) and 1.81 (s, 3H) (CH_3 at C-3, C-7, C-11, and C-15), 2.05 (s, 3H, $OCOCH_3$), 4.34 (t, J = 6 Hz, 1H, > CHCl), 4.58 (d, J = 7 Hz, 2H, CH_2−O−), 4.89 (s) and 4.76 (s) (2H, >C=CH_2), 5.36 (m, 3H, 2-H, 6-H, and 10-H). Found %: C 71.87; H 9.84; Cl 9.38. $C_{22}H_{35}ClO_2$. Calculated %: C 72.01; H 9.61; Cl 9.66.

Reduction of the Chloroacetates (XIV)-(XVI). Method A (General). A solution of 15.2 mmole of one of the chloroacetates (XIV)-(XVI) in 35 ml of DMFA was added dropwise to a stirred solution of 1.54 g of $NaBH_4$, 2.28 g of NaI, and 19 ml of DMFA. The reaction mixture was stirred at 60°C for 3 h and was then diluted with water and acidified with 5% HCl solution (20 ml). The mixture was extracted with ether (3 × 20 ml). The extract was washed with water, with saturated $NaHCO_3$ solution, and again with water, and was dried, and the solvent was distilled off.

Method B (General). In an atmosphere of argon, with stirring at 50°C, a solution of 17.5 mmole of one of the chloroacetates (XIV)-(XVI) in 20 ml of DMFA−H_2O (24:1) was added to a suspension of 2.02 g of zinc dust in a solution of 0.98 g of NaI, 1.28 g of $NiCl_2$, and 1.52 g of $P(C_6H_5)_3$ in 28 ml of DMFA−H_2O (24:1). The reaction mixture was stirred at the same temperature for 4 h and was then worked up.

Method C (General). A solution of 1.1 mole of one of the chloroacetates (XIV)-(XVI) in 0.8 ml of abs. THF was added to a stirred suspension of 40 mg of $LiAlH_4$ in 1.8 ml of abs. THF. The reaction mixture was boiled under reflux for 3 h and was worked up.

Saponification of the α-Terpenol Acetates (V)-(VII) (General Procedure). A solution of 2.30 mmole of one of the acetates (V)-(VII) in 2 ml of ethanol was treated with 5 ml of a 10% alcoholic solution of KOH, and the mixture was boiled under reflux for 1.5 h and was then diluted with water (10 ml) and extracted with ether (3 × 5 ml). The ethereal extract was washed with water to neutrality and was dried, and the solvent was distilled off.

α-Geranyl Acetate (V). a) By method A, 3.50 g of 6-chloro-α-geranyl acetate (XIV) yielded 2.70 g of reaction product, which was chromatographed on a column containing 55 g of SiO_2. Petroleum ether−ethyl acetate (19:1) eluted 2.1 g (yield 70.6%) of α-geranyl acetate (V). IR spectrum (cm^{-1}): 1226, 1735 ($OCOCH_3$), 890, 1645 (>C=CH_2). PMR spectrum ($CDCl_3$): 1.59 (s, 3H, CH_3 at C-7), 1.69 (s, 3H, CH_3 at C-3)), 1.96 (s, 3H, $OCOCH_3$), 4.47 (d, 2H, J = 7 Hz, CH_2−O−), 4.63 (s, 1H) and 4.76 (s, 1H) (>C=CH_2), 5.28 (t, J = 7 Hz, 1H, >C=C<$_H$). The spectroscopic characteristics of compound (V) coincided with those given in the literature [9].

b) By method B, 4.03 g of 6-chloro-α-geranyl acetate (XIV) yielded 3.47 g of a reaction product which was chromatographed on a column containing 60 g of SiO_2. Petroleum ether–ethyl acetate (19:1) eluted 2.08 g (61%) of α-geranyl acetate (V), identical in its chromatographic properties with the sample obtained above.

α-Geraniol (I). a) By method B, 250 mg of 6-chloro-α-geranyl acetate (XIV) yielded 152 mg of a reaction product, which was chromatographed on a column containing 3 g of SiO_2. Petroleum ether–ethyl acetate (17:3) eluted 127 mg (76%) of α-geraniol (I), a colorless viscous liquid. IR spectrum (cm^{-1}): 1050, 3400, 3600 (OH-group), 890, 1643 (>C=CH_2), 835, 1665 (>C=C<$_H$). PMR spectrum ($CDCl_3$, ppm): 1.70 (s, 3H) and 1.75 (s, 3H) (CH_3 at C-3 and C-7), 4.09 (d, J = 6.5 Hz, 2H, CH_2O–), 4.69 (s) and 4.78 (s) (2H, >C=CH_2), 5.32 (t, J = 6.5 Hz, 1H, >C=C<$_H$). The spectral characteristics of compound (I) agreed with those given in the literature [9].

b) The saponification of 450 mg of α-geranyl acetate (V) by the procedure described above gave 348 mg of a reaction product, which was chromatographed on a column containing 7.5 g of SiO_2. Petroleum ether–ethyl acetate (17:3) eluted 334 mg (94%) of α-geraniol (I), identical with the sample obtained above.

α-E,E-Farnesyl Acetate (VI). a) By method A, 1.10 g of 10-chloro-α-E,E-farnesyl acetate (XV) yielded 0.89 g of a reaction product, which was chromatograpahed on a column containing 23 g of SiO_2. Petroleum ether–ethyl acetate (19:1) eluted 620.3 mg (64% yield) of α-E,E-farnesyl acetate (VI), a colorless viscous liquid. IR spectrum (cm^{-1}): 1230, 1734 ($OCOCH_3$), 895, 1646 (>C=CH_2), 1667 (>C=C<$_H$). PMR spectrum (ppm): 1.57 (s, 3H), 1.66 (s, 3H), 1.70 (s, 3H), (CH_3 at C-3, C-7, and C-11), 1.96 (s, 3H, $OCOCH_3$), 4.45 (d, J = 7 Hz, 2H, CH_2O–), 4.53 (br.s) and 4.62 (br.s) (2H, >C=CH_2), 5.03 (m, 1H, 6-H), 5.27 (t, J = 7 Hz, 1H, 2-H). Found %: C 77.22; H 10.72. $C_{17}H_{28}O_2$. Calculated %: C 77.22; H 10.67.

b) By method B, 1.89 g of 10-chloro-α-E,E-farnesyl acetate (XV) yielded 1.57 g of a reaction product, which was chromatographed on a column containing 35 g of SiO_2. Petroleum ether–ethyl acetate (9:1) eluted 1.12 g (67%) of α-E,E-farnesyl acetate (VI), identical in its chromatographic behavior with the sample obtained above.

α-E,E-Farnesol (III). a) By method B, 360 mg of 10-chloro-α-E,E-farnesyl acetate (XV) yielded 259 mg of a reaction product which was chromatographed on a column containing 6 g of SiO_2. Petroleum ether–ethyl acetate (17:3) eluted 201.4 mg (75%) of α-E,E-farnesol (III), a colorless viscous liquid. IR spectrum (cm^{-1}): 1090, 3335, 3600 (OH-group), 890, 1641 (>C=CH_2), 835, 1660 (>C=C<$_H$). PMR spectrum ($CDCl_3$, ppm): 1.61 (s, 3H), 1.68 (s, 6H) (CH_3 at C-3, C-7, and C-11), 4.15 (d, J = 7 Hz, 2H, CH_2O–), 4.72 (m, 2H, >C=CH_2), 5.12 (m, 1H, 6-H), 5.43 (t, J = 7 Hz, 1H, 2-H). Calculated %: C 80.88; H 11.63. $C_{15}H_{26}O$. Found %: C 81.02; H 11.78.

b) The saponification of 160 mg of α-E,E-farnesyl acetate (VI) by the procedure described above yielded 131 mg of a reaction product which was chromatographed on a column containing 2.2 g of SiO_2. Petroleum ether–ethyl acetate (17:3) eluted 123.4 mg (92%) of α-E,E-farnesol, identical in its chromatographic properties with the sample obtained above.

α-E,E,E-Geranylgeranyl Acetate (VII). a) By method A, 660 mg of 14-chloro-α-E,E,E-geranylgeranyl acetate (XVI) yielded 427 mg of a reaction product which was chromatographed on a column containing 10 g of SiO_2. Petroleum ether–ethyl acetate (97:3) eluted 371.8 mg (64% yield) of α-E,E,E-geranylgeranyl acetate (VII), a colorless viscous liquid. IR spectrum (cm^{-1}): 1228, 1736 ($OCOCH_3$), 890, 1645 (>C=CH_2), 1667 (>C=C<$_H$). PMR spectrum (ppm): 1.58 (s, 6H), 1.70 (s, 6H), (CH_3 at C-3, C-7, C-11, and C-15), 1.98 (s, 3H, $OCOCH_3$), 4.46 (d, J = 7 Hz, 2H, CH_2O–), 4.58 (br.s), 4.73 (br.s) (2h, >C=CH_2), 5.07 (m, 2H, 6-H, and 10-H), 5.27 (t, J = 7 Hz, 1H, 2-H). Calculated %: C 79.32; H 10.83. $C_{22}H_{36}O_2$. Found %: C 79.46; H 10.91.

b. By method B, 350 mg of 14-chloro-α-E,E,E-geranylgeranyl acetate (XVI) yielded 210 mg of a reaction product, which was chromatographed on a column containing 5 g of SiO_2. Petroleum ether–ethyl acetate (9:1) eluted 195 mg (61.5% yield) of α-E,E,E-geranylgeranyl acetate (VII).

α-E,E,E-Geranylgeraniol (IV). a) By method B, 210 mg of 14-chloro-α-E,E,E-geranylgeranyl acetate (XVI) yielded 161 mg of reaction product, which was chromatographed on a column containing 3 g of SiO_2. Petroleum ether–ethyl acetate (17:3) eluted 124 mg (74.6%) of α-E,E,E-geranyl geraniol (IV), a colorless viscous liquid. IR spectrum (cm^{-1}): 1010, 3467, 3605 (OH-group), 890, 1642 (>C=CH_2), 1661 (>C=C<$_H$). Calculated %: C 82.87; H 11.65. $C_{20}H_{34}O$. Found %: C 82.69; H 11.80.

b) As shown above, 185 mg of α-E,E,E-geranylgeranyl acetate (VII) gave 147 mg of a product which was chromatographed on a column containing 3.5 g of SiO_2. Petroleum ether–ethyl acetate (17:3) eluted 147 mg (91%) of α-E,E,E-geranylgeraniol (IV).

Superacid Cyclization of α-Geraniol (I). With stirring, a solution of 43 mg of α-geraniol (I) in 0.4 ml of 2-nitropropane cooled to −(78–80)°C was added to a solution of 140 mg of FSO_3H in 1.1 ml of 2-nitropropane cooled to the

same temperature, and the mixture was stirred for 5 min. Then 1 ml of a solution of Et_3N in petroleum ether (1:1) and 2 ml of 30% KOH solution was added to it and it was worked up in the usual way. The reaction product (42.2 mg) was chromatographed on a column containing 0.7 g of SiO_2. Petroleum ether eluted 3.3 mg (8.7%) of a mixture of hydrocarbons, which was not investigated, and petroleum ether–ethyl acetate (9:1) eluted 37.7 mg (87.8%) of α-cyclogeraniol (II). Compound (II) was identifed by a chromatographic and spectral comparison with a specimen that we had obtained previously [4].

Superacid Cyclization of α-Geranyl Acetate (V). With stirring, a solution of 50 mg of α-geranyl acetate (V) in 1.2 ml of 2-nitropropane cooled to −(78-80)°C was added to a solution of 245 mg of FSO_3H in 1.2 ml of 2-nitropropane cooled to the same temperature, and the mixture was stirred for 5 min. It was worked up as described above. The reaction product (48.7 mg) was chromatographed on a column containing 1.1 g of SiO_2. Petroleum ether eluted 2.3 mg (6.6%) of a mixture of hydrocarbons, which was not investigated, while petroleum ether–ethyl acetate (9:1) eluted 5.2 mg (9.5%) of the cis-hydroxyacetate (XVIII), and petroleum ether–ethyl acetate (17:3) eluted 41.7 mg (76.4%) of the trans-hydroxyacetate (XVII). Compounds (XVII) and (XVIII) were identified by chromatographic and spectral comparison with authentic specimens [4].

Superacid Cyclization of α-E,E-Farnesol (III). With stirring, a solution of 52 mg of α-E,E-farnesol (III) in 1.6 ml of 2-nitropropane cooled to −(80-85)°C was added to a solution of 235 mg of FSO_3H in 0.8 ml of 2-nitropropane cooled to the same temperature, and the mixture was stirred for 40 min. It was worked up as described above. The reaction product (53.2 mg) was chromatographed on a column containing 1.0 g of SiO_2. Petroleum ether eluted 4.4 mg (9.2%) of a mixture of hydrocarbons, which was not investigated, while petroleum ether–ethyl acetate (9:1) eluted 40.5 mg (77.9%) of (±)-drimenol (XIX). Compound (XIX) was identified by chromatographic and spectral comparison with a sample that we had obtained previously [2].

Superacid Cyclization of α-E,E-Farnesyl Acetate (VI). With stirring, a solution of 65 mg of α-E,E-farnesyl acetate (VI) in 1.6 ml of 2-nitropropane cooled to −(80-85)°C was added to a solution of 250 mg of FSO_3H in 1.2 ml of 2-nitropropane cooled to the same temperature, and the mixture was stirred for 30 min. It was worked up as described above. The reaction product (61.8 mg) was chromatographed on a column containing 1.1 g of SiO_2. Petroleum ether eluted 4.2 mg (8.4%) of a mixture of hydrocarbons, which was not investigated, while petroleum ether–ethyl acetate (4:1) eluted 57.1 mg (82.2%) of (±)-9αH-drimane-7α,11-diol 11-monoacetate (XX).

Superacid Cyclization of α-E,E,E-Geranylgeraniol (IV). With stirring, a solution of 55 mg of α-E,E,E-geranylgeraniol (IV) in 1.2 ml of 2-nitropropane cooled to −(78-80)°C was added to a solution of 190 mg of FSO_3H in 1.0 ml of 2-nitropropane cooled to the same temperature, and the mixture was stirred for 30 min. It was worked up as described above. The reaction product (53.2 mg) was chromatographed on a column containing 1.0 g of SiO_2. Petroleum ether eluted 4.6 mg (8.9%) of a mixture of hydrocarbons, which was not investigated, while petroleum ether–ethyl acetate (9:1) eluted 46.7 mg (84.9%) of (±)-14α-H-isoagath-12-en-15-ol (XXI). Compound (XXI) was identified by comparison with an authentic specimen.

Superacid Cyclization of α-E,E,E-Geranylgeranyl Acetate (VII). With stirring, a solution of 50 mg of α-E,E,E-geranylgeranyl acetate (VII) in 1.0 ml of 2-nitropropane cooled to −(78-80)°C was added to a solution of 150 mg of FSO_3H in 0.7 ml of 2-nitropropane cooled to the same temperature, and the mixture was stirred for 30 min. It was worked up as described above. This gave 47.8 mg of a reaction product, which was chromatographed on a column containing 0.9 g of SiO_2. Petroleum ether eluted 3.1 mg (7.6%) of a mixture of hydrocarbons, which was not investigated, while petroleum ether–ethyl acetate (17:3) eluted 39.6 mg (75.1%) of (±)-14αH-isoagathane-13α,15-diol 15-monoacetate (XXII). Compound (XXII) was identified by chromatographic and spectral comparison with a sample that we had obtained previously [1].

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