*Russian Journal of Organic Chemistry, Vol. 37, No. 3, 2001, pp. 362–374. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 3, 2001, pp. 389–400.*


# Acid-Catalyzed Rearrangements of (–)-Thujopsene

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Received January 6, 2000

**Abstract**—The transformations of (–)-thujopsene in liquid ($HSO_3F$–$SO_2FCl$) and over solid ($TiO_2/SO_4^{2-}$) superacids, as well as by the action of peroxy acids, were studied. New tricyclic hydrocarbons were isolated. The experimental results were compared with the data of computer analysis of the most probable transformation pathways using molecular-mechanics and quantum-chemical methods.

The structure of thujopsene (**I**) was determined in the early 1960s. In its tricyclic molecule the cyclopropane ring is conjugated with the double bond, so that protonation of the molecule could give rise to cyclopropylcarbinyl cations whose further transformations could lead to various polycyclic structures. Thujopsene (**I**) attracted attention of a large number of organic chemists; its acid-catalyzed transformations were extensively studied in both aqueous [1] and nonaqueous [2, 3] solutions of common acids.

In the present work we examined rearrangements of thujopsene (**I**) in liquid superacid ($HSO_3F$–$SO_2FCl$) and over solid superacid ($TiO_2/SO_4^{2-}$). Dissolution of **I** in a $HSO_3F$–$SO_2FCl$ mixture (molar ratio $HSO_3F$ : **I** ~13 : 1, $SO_2FCl$ : $HSO_3F$ 4 : 1 by volume; –115°C) with subsequent quenching of the acid solution with methanol–diethyl ether gave a mixture of products which contained initial hydrocarbon **I** (6%, according to the GLC data), 4-methoxy-4,7,11,11-tetramethyltricyclo[5.4.0.$0^{1,3}$]undecane (**II**) (82%), and 4-methoxy-4,7,11,11-tetramethylbicyclo[5.4.0]undec-1-ene (**III**) (11%). Chromatographic separation of the mixture on a column charged with $Al_2O_3$ gave alkene **I** and a mixture of ethers **II** and **III** at a ratio of 6 : 1. When mixture **II**/**III** was passed through a column charged with silica gel, ether **II** was completely converted into initial thujopsene, whereas compound **III** remained intact. A similar result was obtained on storage of the same mixture. However, passing of mixture **II**/**III** through a layer of freshly calcined (140°C, 3 h) silica gel caused decomposition of the two ethers, and the major product was pseudowiddrene (**IV**) (65%, GLC). By column chromatography on silica gel impregnated with 20% of $AgNO_3$ we isolated pure compound **IV**.

A possible mechanism of formation of compounds **II**–**IV** from olefin **I** is shown in Scheme 1. According to this scheme, no profound skeletal rearrangements of **I** occurs under the given conditions. Protonation of thujopsene (**I**) gives α-cyclopropylcarbinyl cation **A** which reacts with nucleophile present in the reaction mixture (methanol) to afford either ether **II** or initial compound **I**. The formation of a small amount of ether **III** may be explained by the rearrangement sequence **A** → **B** → **C**. The transformations of ethers **II** and **III** over activated silica gel can be interpreted in terms of the rearrangement sequences **A** → **D** → **E** (ether **II**) and **C** → **B** → **A** → **D** → **E** (ether **III**), followed by quenching with methanol.

When compound **I** was dissolved in the system $HSO_3F$–$SO_2FCl$ at –60°C, the subsequent quenching with methanol–diethyl ether gave a mixture containing mainly (1*R*,2*S*,6*R*,7*S*)-1,2,7,9-tetramethyltricyclo-[5.2.2.$0^{2,6}$]undec-8-ene (**V**) (31%) and (1*S*,7*S*,8*S*,9*S*)-2,2,7,9-tetramethyltricyclo[6.2.1.$0^{1,6}$]undec-5-ene (**VI**) (19%) (Scheme 2). Pure hydrocarbons **V** and **VI** were isolated by successive chromatographic separations first on $Al_2O_3$ and then on $SiO_2$–20% $AgNO_3$.

Possible paths of carbocationic rearrangements of thujopsene **I** to compounds **V** and **VI** were simulated using ICAR program [4] and modified selection rules (see Experimental). The results of calculations showed that the shortest paths to compound **V** are nine-step rearrangements. The most acceptable of the four paths is shown in Scheme 3. Its acceptability was estimated by the ascent value (i.e., the difference $\Delta\Delta H_f^0$ between the least and most stable ions formed along the overall path, kcal/mol) and by the highest activation barrier.

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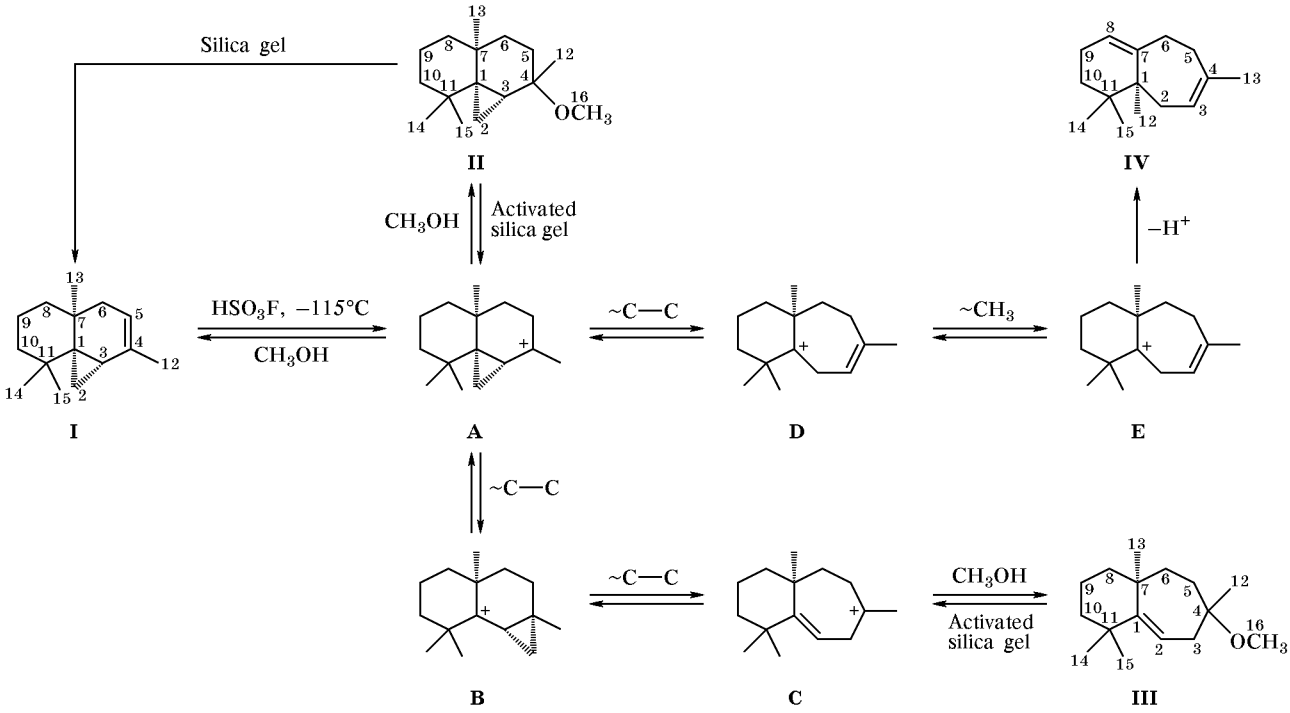
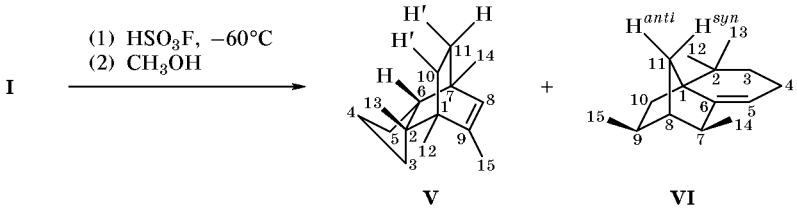
**Scheme 1.**




**Scheme 2.**



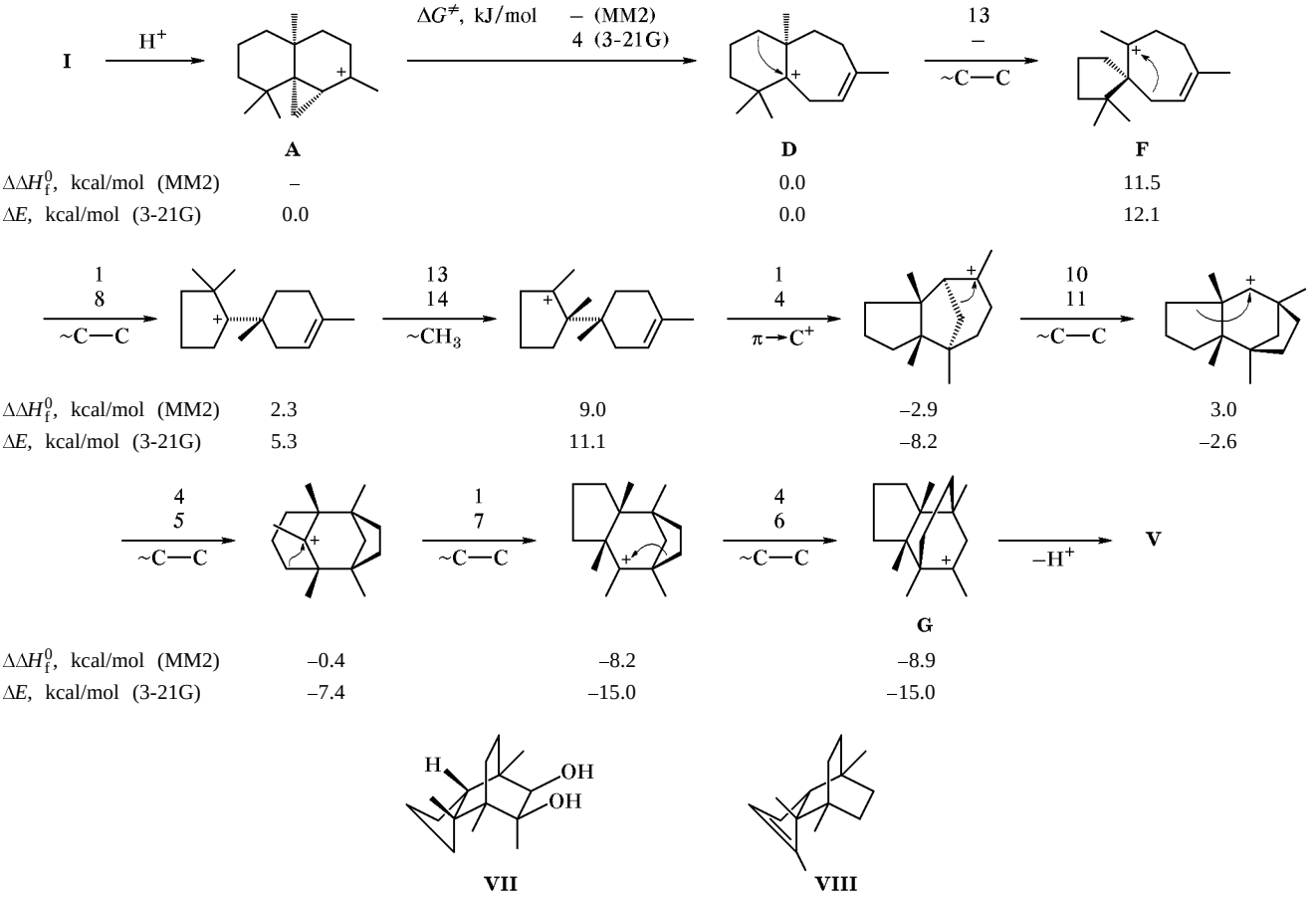

As follows from the data given in Scheme 3, the value of $\Delta\Delta H_f^0$ attains 12 kcal/mol, and the maximal barrier is equal to 15 (MM2) or 20 kcal/mol (3–21G).

The structure of compound **V** was established by $^1$H and $^{13}$C NMR spectroscopy, including two-dimensional techniques. Also, olefin **V** was hydroxylated with $OsO_4$ according to the procedure reported in [5]. The product was (1*R*,2*S*,6*R*,7*S*,8*S*,9*S*)-1,2,7,9-tetramethyltricyclo[5.2.2.0$^{2,6}$]undecane-8,9-diol (**VII**) whose structure (as racemate) was proved by X-ray analysis (see figure). The bond lengths in molecule **VII** approach standard values [6]. The bicyclo[2.2.2]-octane fragment adopts a *twist* conformation: the torsion angles $C^1C^2C^6C^7$, $C^7C^8C^9C^1$, and $C^1C^{10}C^{11}C^7$ are, respectively, 11.3(2), 19.1(2), and 13.3(2)°. In keeping with the Cambridge Structural Database [7], an analogous conformation was found for the 2-piperidinotricyclo[5.2.2.0$^{2,6}$]undecan-9-one molecule [8]. The five-membered ring has a $^4T_3$-*twist* conformation [8]. Molecules **VII** in crystal form infinite chains along the *c* axis via hydrogen bonds $O^1$–H···$O^2$ [H···$O^2$ 1.90(3), $O^1$···$O^2$ 2.757 Å, ∠$O^1HO^2$ 177(2)°]. The $O^2$–H hydroxy group is involved in intramolecular hydrogen bond $O^2$–H···$O^1$ with the following parameters: H···$O^1$ 1.90(2), $O^2$···$O^1$ 2.500(2) Å, ∠$O^2HO^1$ 127(2)°.

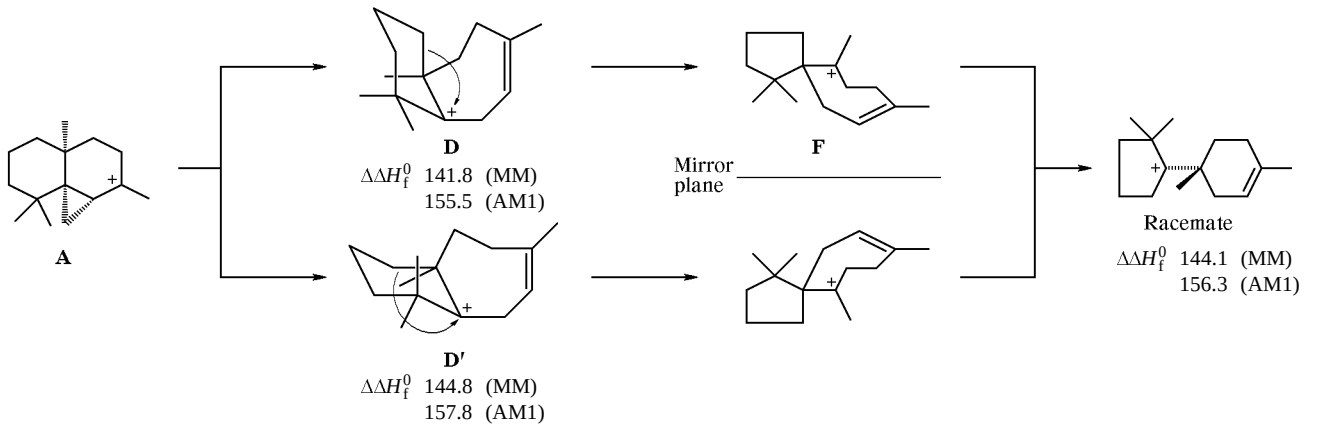
It should be noted that from optically active olefin **V**, $[\alpha]_{580}^{20}$ = –13.3 ($CHCl_3$, *c* = 14.07), we obtained racemic diol **VII**. This indicates partial racemization during the transformation **A** → **G**, presumably as a result of conformational transitions **D** ↔ **D′** shown in Scheme 4.

For compound **VI**, 7–9-step paths were simulated and analyzed. The $\Delta\Delta H_f^0$ values for the shortest paths exceeded 20 kcal/mol, whereas among 8–9-step paths the better was that presented in Scheme 5. It is characterized by a $\Delta\Delta H_f^0$ value of 16.7 kcal/mol (MM2),

**Scheme 3.**



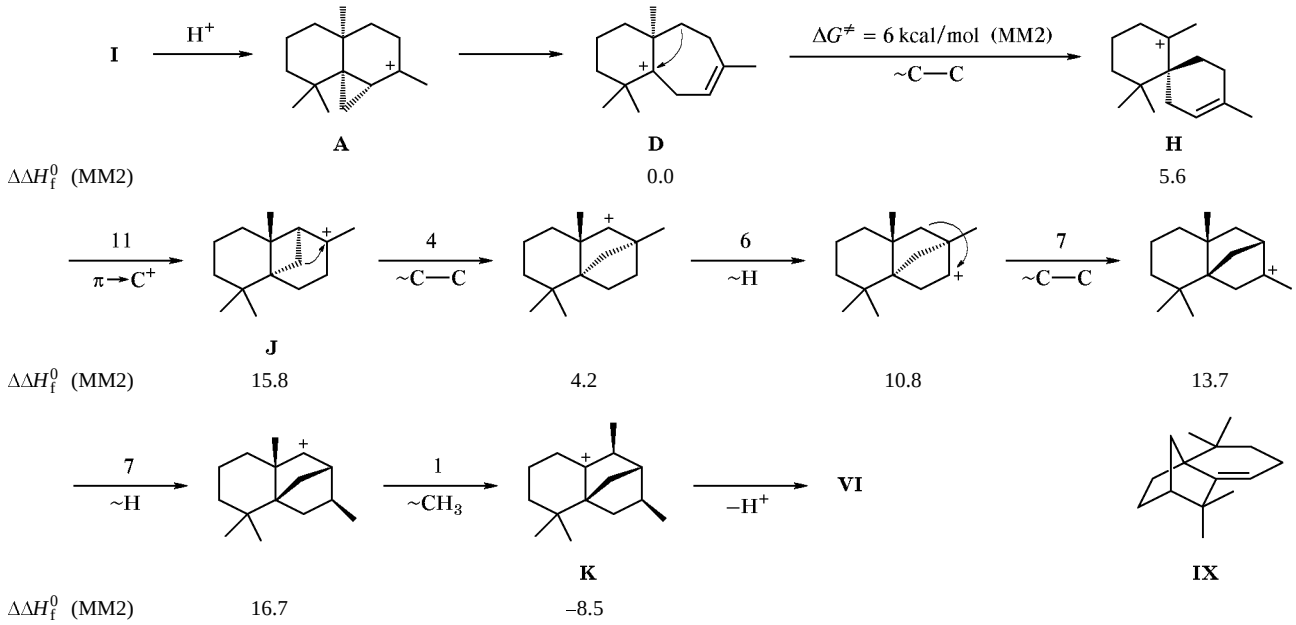

**Scheme 4.**




and the highest activation barrier was estimated at 21 kcal/mol. Both rearrangements do not occur at temperatures below –60°C, presumably because of high activation barriers.

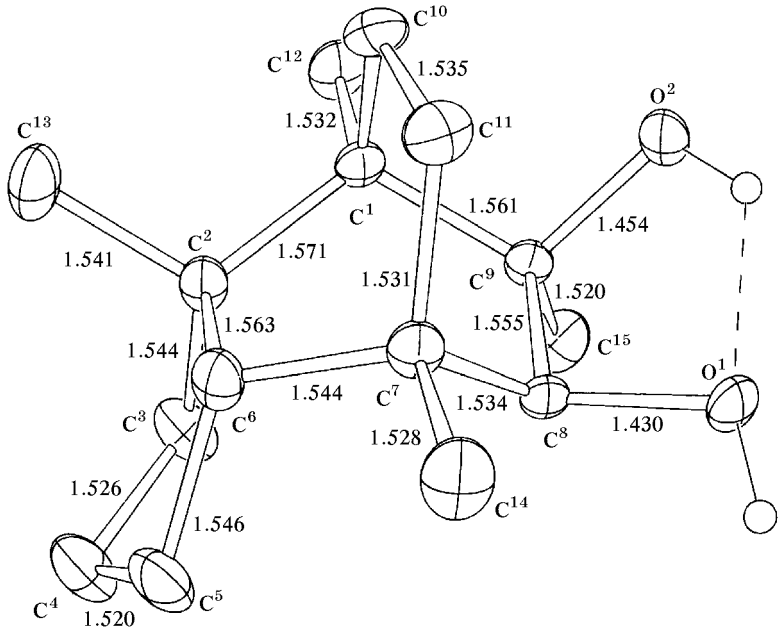
Analysis of Schemes 1, 3, and 5, as well as of published data, shows that all transformations of alkene **I** begin with the rearrangement of α-cyclopropylcarbinyl ion **A** into homoallyl ion **D**. The key stage in the formation of compounds **V** (Scheme 3) and **VI** (Scheme 5) is ring contraction in ion **D**. Scheme 3 shows contraction of the six-membered ring in **D** to give spiro[5.7]undecenyl cation **F** whose further transformations lead to ion **G** as precursor of **V**. The carbon skeleton of **V** is structurally related

**Scheme 5.**



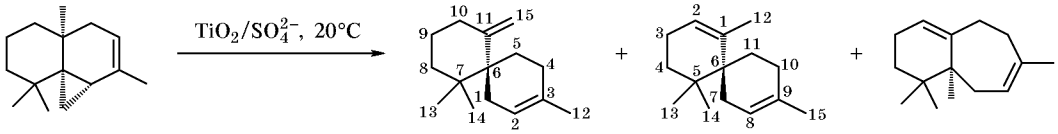

to the natural terpene cyclobasanene (**VIII**). The formation of alkene **VI** involves contraction of the seven-membered ring in **D** to give spiro[6.6]undecenyl cation **H** whose carbon skeleton is structurally similar to that of natural chamigrenes (Scheme 5). Transannular interaction in ion **H** leads to tricyclic cation **J**, and subsequent rearrangements of the latter yield ion **K** as a precursor of final alkene **VI**. Compound **VI** is structurally similar to isolongifolene (**IX**).

Reactions of terpenes with solid superacids almost were not studied previously [10]. For compound **I**, only the transformations over synthetic zeolites in the presence of water were reported [11]. According to [11], the main product was widdrol; also, pseudo-




Structure of the molecule of (1*R*,2*S*,6*R*,7*S*,8*S*,9*S*)-1,2,7,9-tetramethyltricyclo[5.2.2.0$^{2,6}$]undecane-8,9-diol (**VII**); the given bond lengths were determined with an accuracy of 0.002–0.003 Å.

**Scheme 6.**



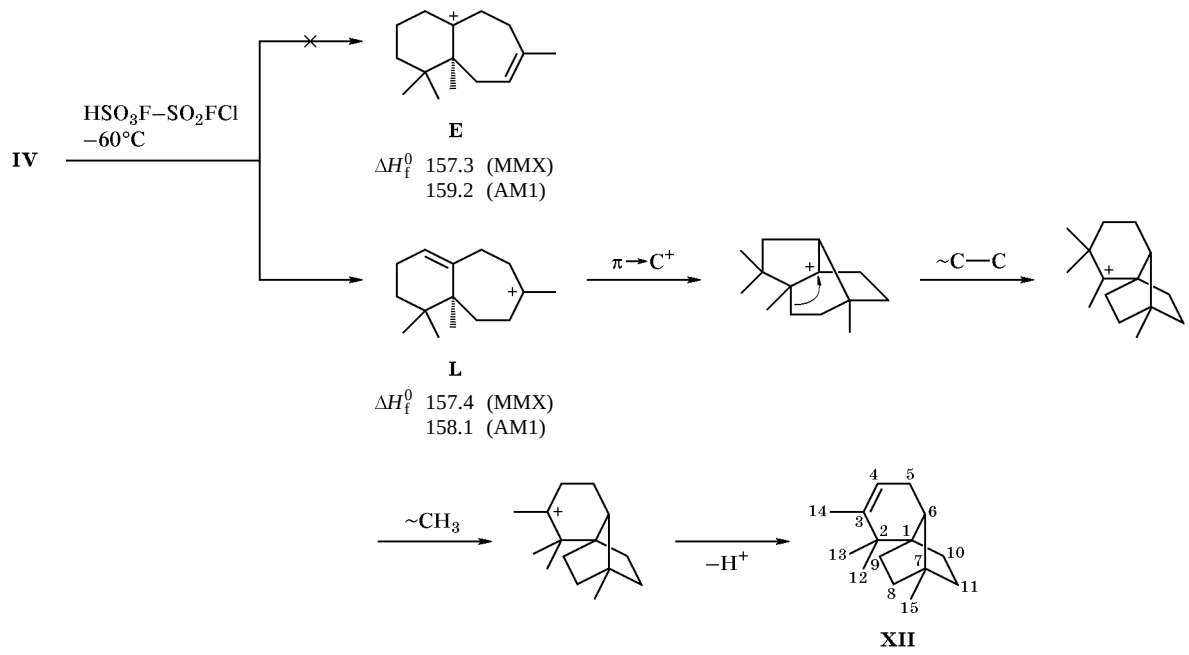

**I** **X** **XI** **IV**

widdrene (**IV**) and α-chamigrene (**XI**) were obtained in smaller amounts. The conversion of the initial hydrocarbon was as low as 33%, and the reaction conditions were fairly drastic (100°C, 100 h and more). We examined transformations of alkene **I** over the solid superacid $TiO_2/SO_4^{2-}$ in $CH_2Cl_2$ at 20°C. After 20 min, the mixture contained no initial olefin **I**, and the products were β-chamigrene (**X**) (37%), α-chamigrene (**XI**) (30%), and pseudowiddrene (**IV**) (25%) (Scheme 6). We succeeded in isolating pure hydrocarbons **IV**, **X**, and **XI** by chromatographic separation of the reaction mixture on silica gel containing 20% of $AgNO_3$. The formation of chamigrenes **X** and **XI** can be interpreted in terms of the following transformation sequence: **I** → **A** → **D** → **H** → **X** + **XI**; pseudowiddrene (**IV**) is likely to be formed as a result of the sequence **I** → **A** → **D** → **E** → **IV**.

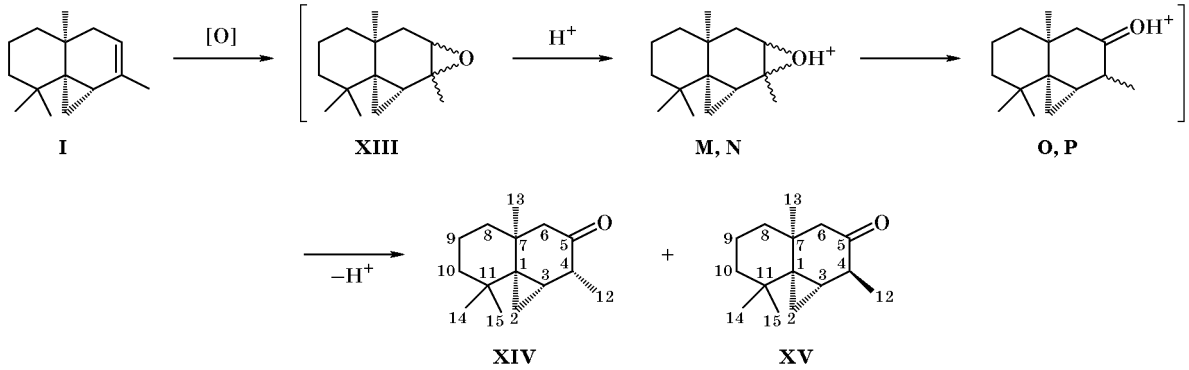
We also examined the behavior of alkene **IV** in the system $HSO_3F$–$SO_2FCl$ at –60°C. The major product of this reaction was 2,2,3,7-tetramethyltricyclo-[5.2.2.0$^{1,6}$]undec-3-ene (**XII**) (Scheme 7). Compound **XII** can be formed from **IV** through intermediate ion **L** which is absent in Schemes 3 and 5. In this case the protonation of olefin **IV** occurs at the $C^3-C^4$ bond rather than at the $C^7-C^8$ bond, and ion **E** is not formed. According to the calculations, the heats of formation of ions **E** and **L** are almost equal; therefore, their formatin is controlled by steric factors.

We thought it reasonable to compare the behaviors of thujopsene (**I**) in liquid superacid and over solid superacid with the results of transformation of the corresponding epoxy derivative. In other words, we tried to elucidate the effect of the mode of generation of cationic center on the results of tranformations. We found almost no published data on the synthesis and reactions of epoxy derivatives of thujopsene (**I**). Nomura *et al.* [12] described transformations of epoxy derivatives of **I** over acid-treated synthetic zeolites; however, no reference to preparation of the initial epoxy compound was given. We brought alkene **I** into reaction with monoperoxyphthalic acid following the procedure reported in [13], but instead of the expected epoxy derivatives **XIII** we obtained a mixture of isomeric thujopsanones **XIV** and **XV**

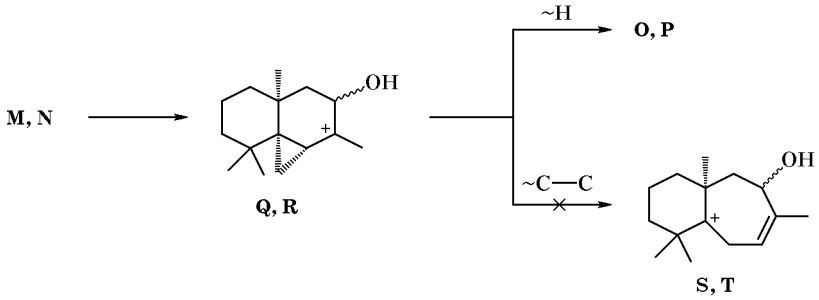
**Scheme 7.**



**Scheme 8.**



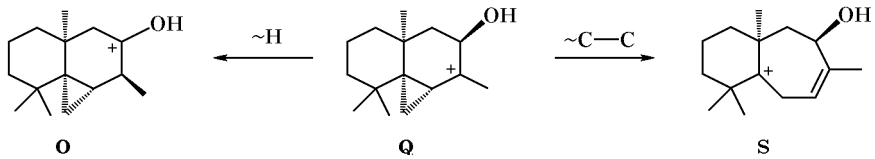

**Scheme 9.**



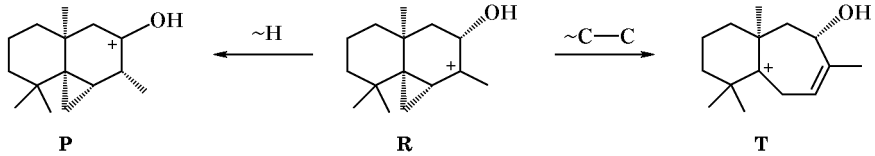

at a ratio of 7:1 (GLC). Pure compounds **XIV** and **XV** were isolated by column chromatography on silica gel. We also tried to oxidize thujopsene (**I**) with peroxyacetic and *m*-chloroperoxybenzoic acids, but the result was the same as above: a mixture of ketones **XIV** and **XV** was obtained. Presumably, the primary oxidation products, epoxy derivatives **XIII**, are quite unstable. They readily undergo protonation and subsequent cleavage (by a concerted mechanism) to form ketones **XIV** and **XV** (Scheme 8). A nonconcerted mechanism according to Scheme 9 is also possible. In this case ions **Q** and **R** do not rearrange into homoallyl ions **S** and **T** (like ion **A** is converted into **D**). On the other hand, ions **S** and **T** are more stable than **O** and **P** (Scheme 10). These data count in favor of the concerted mechanism of formation of ketones **XIV** and **XV**. Compounds **XIV** and **XV** undergo rearrangement neither in liquid superacid ($HSO_3F$–$SO_2FCl$ at –115°C or –60°C) nor over solid catalysts ($TiO_2/SO_4^{2-}$, HB-2 zeolite, askanite–bentonite clay at 20°C).

According to published data, acid-catalyzed transformations of olefin **I** [1–3] and epoxy derivatives

**Scheme 10.**

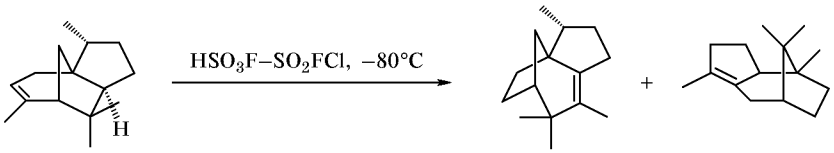



$\Delta\Delta H_f^0$ (AM1) 120.3 129.3 114.7



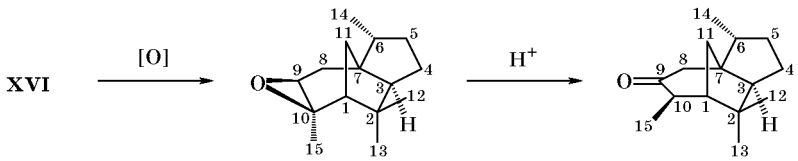

$\Delta\Delta H_f^0$ (AM1) 121.2 130.0 116.5

**Scheme 11.**




**XVI**

**Scheme 12.**




**XVII** **XVIII**

**XIII** [12] lead to different products. However, the reactions were carried out under different conditions; therefore, it is difficult to elucidate the role of the mode of generation of carbocationic center on the rearrangement pathway. Isofar as we failed to isolate compounds **XIII**, it was impossible to compare their behavior with the reactivity of olefin **I** toward liquid and solid superacids. Instead, we examined transformations of sesquiterpene α-cedrene (**XVI**) (which is isomeric to **I**) and its epoxy derivative **XVII**. The transformation of **XVI** in the system $HSO_3F$–$SO_2FCl$ was studied by us previously [14] (Scheme 11). Stable epoxy derivative **XVII** was synthesized from **XVI** by the standard procedure [13]. Compound **XVII** in liquid superacids (in $HSO_3F$–$SO_2FCl$ at –117 to –10°C and in $HSO_3F$ at 20–70°C) gives rise to only one product, cedranone (**XVIII**) (Scheme 12). We can conclude that in this case the mode of generation of cationic center exerts the determining effect on the direction of acid-catalyzed rearrangements.

Alkene **XVI** was stable to the action of various solid acid catalysts; no isomerization of **XVI** occurred even on boiling in formic acid (see Experimental). Epoxy derivative **XVII** over various solid catalysts ($TiO_2/SO_4^{2-}$, $ZrO_2/SO_4^{2-}$, β-zeolite, askanite–bentonite clay at 20°C) gives rise to ketone **XVIII** as the sole product. We previously found that conformationally labile 6,7- and 2,3-epoxy derivatives of α-humulene in liquid superacids at low temperature and over solid catalysts at room temperature [15] give rise to quite different products. This may be due to conformational control of the reaction. Presumably, rigid structure of epoxy derivative **XVII** makes it insensitive to the nature of acid medium.

The structure of all newly synthesized compounds was proved by $^1H$ and $^{13}C$ NMR spectroscopy. The $^1H$ NMR spectra of compounds **IV** [16], **XII** [3], and **XVII** [17] were reported previously; however, only a part of chemical shifts was given, and they were similar to those obtained by us. The $^1H$ and $^{13}C$ NMR spectra of **X** and **XI** were reported in [18] and [19], respectively, but the signals were not assigned: the chemical shifts were also consistent with our data. The $^1H$ and $^{13}C$ NMR spectra of **XIV** and **XVIII** were similar to the spectra reported in [20] and [17], respectively. Table 1 contains the $^{13}C$ NMR spectra of compounds **I**–**VI**, **X**–**XII**, **XIV**, and **XVII**.

We failed to observe the cyclopropane C–C bond in the two-dimensional 2D-INADEQUATE spectrum of **II** because of unfavorable selection with respect to $^1J_{C,C}$; also, the $C^1$–$C^{11}$ bond was not found because of similar chemical shifts of the corresponding atoms. The presence of the $C^1$–$C^{11}$ bond was proved by the LRJMD spectrum with decoupling from the $C^{14}H_3$ methyl protons (δ 0.39 ppm): apart from the expected signals of $C^{10}$, $C^{11}$, and $C^{15}$, we observed a weak singlet at $\delta_C$ 33.22 ppm. The $^1H$–$^1H$ double resonance spectra in combination with the two-dimensional $^{13}C$–$^1H$ COSY spectrum proved the presence of cyclopropane ring in the molecule.

The $^{13}C$–$^{13}C$ correlation spectrum of **V** did not display the $C^8$=$C^9$ double bond and also $C^1$–$C^2$, $C^1$–$C^9$, and $C^7$–$C^8$ bonds. However, signals from an olefinic proton in the $^1H$ NMR spectrum and from $sp^2$-carbon atoms in the $^{13}C$ NMR spectrum confirmed the presence of a double bond, and the other bonds were detected using the LRJMD spectra with decoupling from 8-H (δ 5.44 ppm) and 10′-H (δ 1.61 ppm). The orientations of the $C^6$–H and $C^2$–$C^{13}H_3$ bonds were assigned by analogy with the X-ray diffraction data obtained for diol **VII**.

The 2D-INADEQUATE spectrum of **VI** showed no $C^5=C^6$, $C^1-C^2$, and $C^1-C^6$ bonds. However, the other bonds imply only one mode of binding of the $C^1$, $C^2$, and $C^6$ atoms. In addition, the LRJMD spectra recorded with decoupling from the 5-H olefinic proton (δ 5.26 ppm) and $C^{12}H_3$ methyl protons (δ 0.87 ppm) indicated the presence of $C^1-C^6$ and $C^1-C^2$ bonds, respectively.

Ketone **XIV** showed in the $^1$H NMR spectrum *W*-coupling between 6-$H_{eq}$ and 4-H; this means that the 4-H proton occupies equatorial position.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM-400 spectrometer (400.13 MHz for $^1$H and 100.61 MHz for $^{13}$C) using $CDCl_3$ or $CDCl_3$–$CCl_4$ (1:1) as solvent and chloroform signals (δ 7.24 ppm, $\delta_C$ 76.90 ppm) as reference. The signals were assigned on the basis of $^1$H–$^1$H coupling constants in the double resonance spectra. The carbon signals were assigned using selective and off-resonance decoupling from protons, differential spectra modulated by long-range $^{13}$C–$^1$H coupling (LRJMD, the conditions were optimized for $J_{C,H}$ = 10 Hz), and two-dimensional $^{13}$C–$^1$H heteronuclear correlation spectra (COSY, $^1J_{C,H}$ = 134 Hz). The structure of compounds **II**, **V**, and **VI** was established on the basis of two-dimensional $^{13}$C–$^{13}$C correlation spectra (two-quantum coherence, 2D-INADEQUATE, the conditions were optimized for $^1J_{C,C}$ = 35 Hz).

The reaction mixtures were analyzed by GLC on a Biokhrom-1 chromatograph using the following columns: (1) 53000 × 0.26-mm glass capillary column, stationary phase XE-60; (2) 13000 × 0.22-mm quartz capillary column, stationary phase SE-54; and (3) 20000 × 0.27-mm quartz capillary column, stationary phase VS-30 (an analog of SE-30); flame-ionization detector, carrier gas helium. The products were separated by column chromatography on silica gel 40–100 μm (Czechia), silica gel impregnated with 20% of $AgNO_3$, and aluminum oxide (Brockmann activity grade II). The elemental compositions were determined from the high-resolution mass spectra which were run on a Finnigan MAT 8200 instrument. The specific rotations were measured on a Polamat A spectropolarimeter.

Twice distilled fluorosulfonic acid $HSO_3F$, bp 158–161°C, and $SbF_5$, bp 141–143°C, were used; $SO_2FCl$ was purified by passing through sulfuric acid. The reaction mixtures were prepared and quenched by the procedures described in [21]; A mixture of methanol with diethyl ether (5:2, by volume) was used as quencher. Titanium oxide sulfate ($TiO_2/SO_4^{2-}$) was prepared by the procedure reported in [22]. In addition, $ZrO_2/SO_4^{2-}$ [15], wide-pore HB-2 β-zeolite [23], and askanite–bentonite clay [22] were used as acid catalysts. (–)-Thujopsene, $[\alpha]_{580}^{20}$ = –109.2 ($CHCl_3$, *c* = 6.98), and (–)-α-cedrene, $[\alpha]_{580}^{20}$ = –88.1 ($CHCl_3$, *c* = 10) were purchased from Fluka. $^1$H NMR spectrum of **I**, δ, ppm (*J*, Hz): 0.61 s ($C^{14}H_3$), 0.66 d.d (2-H, $J_{2,3}$ = 9, $J_{2,2'}$ = 5), 0.70 d.d (2′-H, *J* = 5, $J_{2',3}$ = 5), 1.11 s ($C^{15}H_3$), 1.12 s ($C^{13}H_3$), 1.20 d.d.d (3-H, *J* = 9, 5, $J_{3,5}$ = 1.2), 1.40 m and 1.78 m (2H, 6-H), 1.80 br.s ($C^{12}H_3$); 1.09 m (1H), 1.23 d.d.d (1H, *J* = 13, 13, 4), 1.45–1.39 m (2H), 1.76 m (2H) (8-H, 9-H, 10-H), 4.99 d.m (5-H, $J_{5,6}$ = 7).

X-ray analysis of a single crystal of diol **VII** was performed on a Syntex $P2_1$ diffractometer (Cu$K_\alpha$ irradiation, graphite monochromator). Crystal habit 0.4 × 0.7 × 1.0 mm$^3$, $C_{15}H_{26}O_2$, *M* 238.36, tetragonal syngony; unit cell parameters: *a* = *b* = 16.534(4), *c* = 19.886(5) Å; *V* = 5436(2) Å$^3$; *Z* = 16; $d_{calc}$ = 1.165 g/cm$^3$; μ = 58 mm$^{-1}$; space group $I4_1/\alpha$. Intensities of 2525 independent reflections were measured by Θ/2Θ-scanning to 2Θ < 140°; corrections for absorption were introduced empirically (transmission 0.323–0.448). The structure was solved by the direct method using SHELXS-86 program and was refined by the least-squares procedure in full-matrix anisotropic approximation (for hydrogen atoms) using SHELXL-93 program; w$R_2$ = 0.1195, *S* = 1.09 (259 parameters) for all reflections (*R* = 0.0445 for 2098 reflections with $F > 4\sigma$). The positions of hydrogen atoms were determined from geometric considerations. The coordinates of non-hydrogen atoms are listed in Table 2. As follows from the space group found, diol **VII** is a racemate.

Modified selection criteria [24] were used to reduce the number of cationic intermediates generated by ICAR program [4]. These criteria were modified toward mitigation of inhibitions: the formation of tertiary cyclobutyl cations and 1,3-hydride shifts in the norbornane fragment were allowed. The gas-phase heats of formation $\Delta H_f^0$ (kcal/mol) were calculated by the MM2 molecular-mechanics method using Muller's parameters [25]; bridgehead carbocations were calculated by the MMX method [26]. Scheme 3 gives also the results of RHF/3-21G//3-21G calculations by GAMESS program [27]. The activation barriers $\Delta G^{\neq}$ were estimated by the procedure described in [28]; the barriers to β-fragmentation and the reverse process were estimated on the assumption that the transition state is similar to the transition state in the Wagner–Meerwein rearrangement. The values of $\Delta G^{\neq}$ for

**Table 1.** $^{13}C$ NMR spectra of compounds **I**–**VI**, **X**–**XII**, **XIV**, and **XVII**

| Atom no. | Chemical shifts $\delta_C$, ppm | | | | | |
|---|---|---|---|---|---|---|
| | **I**[a] | **II**[b] | **III**[b] | **IV**[b] | **V**[b] | **VI**[b] |
| 1 | 34.91 s | 33.22 s | 153.81 s | 44.86 s | 42.89 s | 55.41 s |
| 2 | 11.30 t | 9.23 t | 117.38 d | 31.02 t | 49.80 s | 30.84 s |
| 3 | 22.28 d | 26.37 d | 35.94 t | 122.09 d | 38.13 t | 33.86 t |
| 4 | 135.21 s | 71.21 s | 77.17 s | 134.19 s | 24.13 t | 23.05 t |
| 5 | 114.51 d | 31.73 t | 38.86 t | 36.08 t | 32.14 t | 113.63 d |
| 6 | 41.23 t | 33.67 t | 32.56 t | 29.87 t | 59.46 d | 150.76 s |
| 7 | 31.45 s | 31.68 s | 39.64 s | 144.13 s | 37.83 s | 43.32 d |
| 8 | 36.59 t | 35.74 t | 41.36 t | 119.53 s | 130.25 d | 48.46 d |
| 9 | 19.62 t | 18.40 t | 18.61 t | 21.66 t | 144.52 s | 36.78 d |
| 10 | 40.42 t | 40.43 t | 40.13 t | 32.50 t | 31.71 t | 39.25 t |
| 11 | 33.88 s | 33.11 s | 36.61 s | 34.16 s | 34.31 t | 31.29 t |
| 12 | 23.56 q | 26.97 q | 23.03 q | 23.50 q | 17.58 q | 24.00[c] q |
| 13 | 28.67 q | 28.97 q | 27.34 q | 24.52 q | 24.77 q | 26.88[c] q |
| 14 | 29.14 q | 28.92 q | 32.86[d] q | 24.25[e] q | 23.56 q | 19.66 q |
| 15 | 26.88 q | 26.65 q | 31.65[d] q | 24.05[e] q | 19.65 q | 22.27 q |
| 16 | | 48.68 q | 48.78 q | | | |

| Atom no. | Chemical shifts $\delta_C$, ppm | | | | |
|---|---|---|---|---|---|
| | **X**[a] | **XI**[a] | **XII**[a] | **XIV**[a] | **XVII**[b] |
| 1 | 29.02 t | 140.16 s | 52.84 s | 33.74[f] s | 53.58 d |
| 2 | 120.04 d | 122.94 d | 37.82 s | 6.50 t | 42.89 s |
| 3 | 132.48 s | 23.04 t | 139.38 s | 23.31 d | 60.84 d |
| 4 | 27.94 t | 32.96 t | 120.27 d | 40.03 d | 24.84 t |
| 5 | 26.00 t | 36.07 s | 23.48 t | 213.04 s | 35.67 t |
| 6 | 44.75 s | 40.60 s | 46.41 d | 52.34 t | 41.36 d |
| 7 | 37.30 s | 28.95 t | 45.70 s | 37.76 s | 51.86 s |
| 8 | 37.11 t | 122.55 d | 38.27[g] t | 38.52 t | 35.76 t |
| 9 | 23.84 t | 133.62 s | 31.94[h] t | 19.24 t | 58.09 d |
| 10 | 32.26 t | 29.15 t | 29.37[h] t | 40.31 t | 60.79 s |
| 11 | 148.62 s | 30.69 t | 35.24[g] t | 32.69[f] s | 36.62 t |
| 12 | 23.34 q | 23.58 q | 22.40[i] q | 17.04 q | 29.91 q |
| 13 | 23.15[j] q | 23.58[k] q | 26.16[i] q | 28.34 q | 27.32 q |
| 14 | 25.12[j] q | 25.28[k] q | 19.23 q | 29.50 q | 15.37 q |
| 15 | 110.85 t | 23.49 q | 18.89 q | 27.03 q | 23.53 q |

[a] In $CCl_4$–$CDCl_3$ (1 : 1).
[b] In $CDCl_3$.
[c–k] Alternative assignment is possible.

1,3-hydride shifts in the norbornane fragment were calculated using the data of Sorensen [29] with correction for the absence of degeneracy according to the Marcus equation.

**Transformations of (–)-thujopsene (I) in $HSO_3F$–$SO_2FCl$ at –115°C.** To a solution of 2.61 g of $HSO_3F$ in 6.0 ml of $SO_2FCl$ we added at –115°C 0.4 g of thujopsene (**I**) in 0.5 ml of $CH_2Cl_2$. The mixture was quenched with 60 ml of methanol–diethyl ether. We isolated 0.43 g of a crude product which contained (according to the GLC data) 6% of initial thujopsene (**I**), 82% of ether **II** and 11% of ether **III**. The crude product was subjected to column chromatography on $Al_2O_3$ (eluent hexane) to isolate 0.01 g

of **I** and 0.4 g of a mixture of ethers **II** and **III** at a ratio of 6:1 ($^1$H NMR).

**4-Methoxy-4,7,11,11-tetramethyltricyclo-[5.4.0.0$^{1,3}$]undecane (II).** $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.28 d (2H, 2-H, $J_{2,3}$ = 8), 0.39 s ($C^{14}H_3$), 0.55 m (6-H), 0.86 s ($C^{15}H_3$), 0.90 s ($C^{13}H_3$), 0.90 t (3-H, *J* = 8), 0.98 d.m (8-H$_{eq}$, $J_{8\text{-}eq,8\text{-}ax}$ = 13), 1.01 d.d.d (10-H$_{ax}$, $J_{10\text{-}ax,10\text{-}eq}$ = 13, $J_{10\text{-}ax,9\text{-}ax}$ = 13, $J_{10\text{-}ax,9\text{-}eq}$ = 4), 1.12 s ($C^{12}H_3$), 1.17 m (6′-H), 1.18 m (2H, 5-H), 1.29 d.m (10-H$_{eq}$, *J* = 13), 1.31 d.m (9-H$_{eq}$, $J_{9\text{-}eq,9\text{-}ax}$ = 13), 1.42 d.d.d (8-H$_{ax}$, *J* = 13, $J_{8\text{-}ax,9\text{-}ax}$ = 13, $J_{8\text{-}ax,9\text{-}eq}$ = 4), 1.62 d.d.d.d.d (9-H$_{ax}$, *J* = 13, 13, 13, $J_{9\text{-}ax,8\text{-}eq}$ = 3.5, $J_{9\text{-}ax,10\text{-}eq}$ = 3.5), 3.04 s ($OCH_3$).

Ether mixture **II**/**III**, 0.065 g, was passed through a column charged with 2.7 g of activated silica gel (calcined for 3 h at 140°C). Using hexane as eluent, we isolated 0.046 g of a mixture containing ~65% of alkene **IV**. Subsequent chromatography on silica gel containing 20% of $AgNO_3$ gave 0.024 g of **IV**.

**1,4,11,11-Tetramethylbicyclo[5.4.0]undeca-3,7-diene (IV).** $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.85 s ($C^{14}H_3$, $C^{15}H_3$), 0.93 s ($C^{12}H_3$), 1.10 d.d.d.d (10-H$_{eq}$, $J_{10\text{-}eq,10\text{-}ax}$ = 13, $J_{10\text{-}eq,9'\text{-}ax}$ = 6.5, $J_{10\text{-}eq,9'\text{-}eq}$ = 2.5, $J_{10\text{-}eq,8}$ = 1), 1.58 br.s ($C^{13}H_3$), 1.64 d.d.d (10-H$_{ax}$, *J* = 13, $J_{10\text{-}ax,9'\text{-}ax}$ = 11, $J_{10\text{-}ax,9'\text{-}eq}$ = 6.5), 1.90 d.d.d.d.d (9′-H$_{eq}$, $J_{9'\text{-}eq,9'\text{-}ax}$ = 18, *J* = 6.5, $J_{9'\text{-}eq,8}$ = 4.5, *J* = 2.5, $J_{9'\text{-}eq,6}$ = 1.5), 2.00 br.d.d (2-H, $J_{2,2'}$ = 15, $J_{2,3}$ = 7.5), 2.17 d.d.q.d.d (2′-H, *J* = 15, $J_{2',3}$ = 6, $J_{2',13}$ = 2, $J_{2',5}$ = 2, $J_{2',5'}$ = 2), 2.23 br.d.m (5-H, $J_{5,5'}$ = 15), 1.96–2.28 m (5′-H, 6′-H, 9′-H$_{ax}$), 2.40 d.d.d.d.d (6-H, $J_{6,6'}$ = 13, $J_{6,5'}$ = 12, $J_{6,5}$ = 4.5, *J* = 1.5, $J_{6,8}$ = 0.5), 5.26 d.d.q.t (3-H, *J* = 7.5, 6, $J_{3,13}$ = 1.5, $J_{3,5}$ = 1.5), 5.32 d.d.d.d (8-H, *J* = 4.5, $J_{8,9'\text{-}ax}$ = 3, *J* = 1, *J* = 0.5).

On storage or on passing through a column charged with nonactivated silica gel, mixture **II**/**III** was converted into a mixture of olefin **I** and ether **III**, i.e., the latter is stable under these conditions. Mixture **I**/**III**, 0.022 g, was subjected to column chromatography on $Al_2O_3$ (eluent hexane) to isolate 0.016 g of thujopsene (**I**) and 0.003 g of ether **III**.

**4-Methoxy-4,7,11,11-tetramethylbicyclo[5.4.0]-undec-1-ene (III).** $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.05 s and 1.06 s ($C^{14}H_3$, $C^{15}H_3$), 1.11 d ($C^{12}H_3$, $J_{12,3'}$ = 1), 1.16 s ($C^{13}H_3$), 1.18 m (8-H$_{eq}$), 1.21 m (5-H), 1.23 m (10-H$_{ax}$), 1.40 m (10-H$_{eq}$), 1.41 m (6-H), 1.44 m (9-H), 1.46 d.d.d (8-H$_{ax}$, $J_{8\text{-}ax,8\text{-}eq}$ = 12.5, $J_{8\text{-}ax,9\text{-}ax}$ = 12.5, $J_{8\text{-}ax,9\text{-}eq}$ = 4), 1.66 m (6′-H), 1.70 m (9-H), 1.73 m (5′-H), 1.92 d.d.d (3-H, $J_{3,3'}$ = 13.5, $J_{3,2}$ = 9, $J_{3,5'}$ = 1.2), 2.44 d.d.q (3′-H, *J* = 13.5, $J_{3',2}$ = 6, *J* = 1), 3.16 s ($OCH_3$), 5.47 d.d (2-H, *J* = 9, 6).

**Table 2.** Coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å$^2 \times 10^3$) of non-hydrogen atoms in molecule **VII**

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | $U_{eq}$ |
|---|---|---|---|---|
| $C^1$ | 2622 (1) | 7060 (1) | 264 (1) | 32 (1) |
| $C^2$ | 2992 (1) | 7788 (1) | –139 (1) | 35 (1) |
| $C^3$ | 3919 (1) | 7810 (1) | –230 (1) | 53 (1) |
| $C^4$ | 4049 (2) | 8299 (2) | –872 (1) | 62 (1) |
| $C^5$ | 3397 (2) | 7968 (1) | –1335 (1) | 56 (1) |
| $C^6$ | 2670 (1) | 7761 (1) | –878 (1) | 37 (1) |
| $C^7$ | 2237 (1) | 6953 (1) | –1024 (1) | 33 (1) |
| $C^8$ | 2798 (1) | 6261 (1) | –810 (1) | 30 (1) |
| $C^9$ | 2885 (1) | 6225 (1) | –32 (1) | 32 (1) |
| $C^{10}$ | 1699 (1) | 7108 (1) | 156 (1) | 43 (1) |
| $C^{11}$ | 1481 (1) | 6930 (1) | –580 (1) | 44 (1) |
| $C^{12}$ | 2820 (2) | 7103 (1) | 1015 (1) | 49 (1) |
| $C^{13}$ | 2756 (2) | 8600 (1) | 186 (1) | 57 (1) |
| $C^{14}$ | 2009 (2) | 6880 (1) | –1766 (1) | 50 (1) |
| $C^{15}$ | 3702 (1) | 5892 (1) | 183 (1) | 51 (1) |
| $O^1$ | 2511 (1) | 5487 (1) | –1023 (1) | 44 (1) |
| $O^2$ | 2300 (1) | 5639 (1) | 215 (1) | 46 (1) |

**Transformations of thujopsene (I) in $HSO_3F$–$SO_2FCl$ at –60°C.** To a solution of 6.1 g of $HSO_3F$ in 14 ml of $SO_2FCl$ we added at –60°C 0.64 g of compound **I** in 0.5 ml of $CH_2Cl_2$. The mixture was quenched by adding 100 ml of methanol–diethyl ether. We isolated 0.58 g of a crude product which contained (GLC) 31% of compound **V**, 19% of **VI**, and 18% of methyl ether. By repeated chromatographic separations on $Al_2O_3$ (eluent hexane) and $SiO_2$–20% $AgNO_3$ (eluent hexane) we isolated 0.058 g of compound **V** and 0.035 g of **VI**.

**(1*R*,2*S*,6*R*,7*S*)-1,2,7,9-Tetramethyltricyclo-[5.2.2.0$^{2,6}$]undec-8-ene (V).** $[\alpha]_{580}^{20}$ = –13.3 ($CHCl_3$, *c* = 14.07). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.92 d ($C^{13}H_3$, *J* = 1), 0.97 m (10-H), 0.97 s ($C^{14}H_3$), 1.01 m (5-H), 1.01 s ($C^{12}H_3$), 1.03 m (3-H), 1.10 d.d.d (11-H, $J_{11,11'}$ = 12, $J_{11,10}$ = 12, $J_{11,10'}$ = 3), 1.20 d.d (6-H, $J_{6,5}$ = 10, $J_{6,5'}$ = 7.5), 1.24 m (3′-H, 11′-H), 1.28 m (4-H), 1.43 m (4′-H), 1.61 d.d.d (10′-H, $J_{10',10}$ = 13, $J_{10',11'}$ = 9, *J* = 3), 1.70 d ($C^{15}H_3$, $J_{15,8}$ = 2), 1.76 m (5′-H), 5.44 br.s (8-H).

**(1*S*,7*S*,8*S*,9*S*)-2,2,7,9-Tetramethyltricyclo-[6.2.1.0$^{1,6}$]undec-5-ene (VI).** $[\alpha]_{580}^{20}$ = +35.32 ($CHCl_3$,

$c$ = 12.06). $^1$H NMR spectrum, δ, ppm ($J$, Hz): 0.87 s and 0.96 s ($C^{12}H_3$, $C^{13}H_3$), 0.93 d ($C^{14}H_3$, $J_{14,7}$ = 7), 0.95 d ($C^{15}H_3$, $J_{15,9}$ = 7), 1.10 d.d (*exo*-10-H, $J_{exo\text{-}10,endo\text{-}10}$ = 12, $J_{exo\text{-}10,endo\text{-}9}$ = 5), 1.15 d.d.d.d (*syn*-11-H, $J_{syn\text{-}11,anti\text{-}11}$ = 10, $J_{syn\text{-}11,endo\text{-}10}$ = 2.5, $J_{syn\text{-}11,8}$ = 1.5, $J_{syn\text{-}11,endo\text{-}9}$ = 1.5), 1.20 d.d.d.d (3-$H_{eq}$, $J_{3\text{-}eq,3\text{-}ax}$ = 13, $J_{3\text{-}eq,4'\text{-}ax}$ = 5, $J_{3\text{-}eq,4'\text{-}eq}$ = 3, $J_{3\text{-}eq,5}$ = 1), 1.34 d.d.d.d (*anti*-11-H, $J$ = 10, $J_{anti\text{-}11,endo\text{-}7}$ = 2, $J_{anti\text{-}11,8}$ = 1.5, $J_{anti\text{-}11,5}$ = 0.5), 1.45 d.d.d (3-$H_{ax}$, $J$ = 13, $J_{3\text{-}ax,4'\text{-}ax}$ = 11, $J_{3\text{-}ax,4'\text{-}eq}$ = 7), 1.47 d.d.d (*endo*-10-H, $J$ = 12, $J_{endo\text{-}10,endo\text{-}9}$ = 8, $J$ = 2.5), 1.55 d.d.d (8-H, $J$ = 1.5, $J$ = 1.5, $J_{8,endo\text{-}7}$ = 0.5), 1.63 d.q.d.d (*endo*-9-H, $J$ = 8, 7, 5, 1.5), 1.98 m (2H, 4-H), 2.11 q.d.d.d.d (*endo*-7-H, $J$ = 7, 2, $J_{endo\text{-}7,5}$ = 2, $J_{endo\text{-}7,4}$ = 2, $J$ = 0.5), 5.26 t.d.d.d (5-H, $J_{5,4}$ = 3.5, $J$ = 2, 1, 0.5).

**Diol VII** was synthesized by reaction of 0.062 g of alkene **V** with 0.08 g of $OsO_4$ in diethyl ether, following the procedure reported in [4]. Subsequent chromatography on a column charged with silica gel (gradient elution with hexane–diethyl ether, 10 to 30% of the latter) gave 0.045 g of diol **VII** with mp 145–147°C.

**Isomerization of alkene I over $TiO_2/SO_4^{2-}$.** Titanium oxide sulfate, 0.1 g, was calcined for 3 h at 400°C. After cooling, 1 ml of methylene chloride and a solution of 0.1 g of alkene **I** in 1 ml of $CH_2Cl_2$ were added in succession. The mixture was stirred for 30 min at 20°C, diluted with diethyl ether, and filtered. The filtrate was evaporated to leave 0.1 g of a crude product which was subjected to column chromatography on $Al_2O_3$ (eluent hexane) to obtain 0.089 g of a mixture containing (GLC), 37% of diene **X**, 30% of diene **XI**, and 25% of olefin **IV**. Subsequent column chromatography on $SiO_2$–20% $AgNO_3$ (gradient elution with hexane–diethyl ether, 0.3 to 1% of the latter) gave 0.024 g of diene **X**, $[\alpha]_{580}^{20}$ = –20.06 ($CHCl_3$, $c$ = 3.5); 0.019 g of diene **XI**, $[\alpha]_{580}^{20}$ = –46.9 ($CHCl_3$, $c$ = 11.0); and 0.016 g of compound **IV**, $[\alpha]_{580}^{20}$ = +69.3 ($CHCl_3$, $c$ = 4.0); overall yield 89%.

**3,7,7-Trimethyl-11-methylenespiro[5.5]undec-2-ene (X).** $^1$H NMR spectrum, δ, ppm ($J$, Hz): 0.82 s and 0.88 s ($C^{13}H_3$, $C^{14}H_3$), 1.16 d.d.d.d (8-$H_{eq}$, $J_{8\text{-}eq,8\text{-}ax}$ = 13, $J_{8\text{-}eq,9\text{-}ax}$ = 4, $J_{8\text{-}eq,9\text{-}eq}$ = 3, $J_{8\text{-}eq,10\text{-}eq}$ = 2), 1.47 d.d.d (5-$H_{ax}$, $J_{5\text{-}ax,5\text{-}eq}$ = 13, $J_{5\text{-}ax,4'\text{-}ax}$ = 13, $J_{5\text{-}ax,4'\text{-}eq}$ = 5.5), 1.54 d.d.d.d.d (9-$H_{ax}$, $J_{9\text{-}ax,9\text{-}eq}$ = 13, $J_{9\text{-}ax,8\text{-}ax}$ = 13, $J_{9\text{-}ax,10\text{-}ax}$ = 13, $J_{9\text{-}ax,8\text{-}eq}$ = 4, $J_{9\text{-}ax,10\text{-}eq}$ = 4), 1.56 br.s ($C^{12}H_3$), 1.54–1.79 m (4′-$H_{ax}$, 4′-$H_{eq}$, 9-$H_{eq}$), 1.77 d.d.d (8-$H_{ax}$, $J$ = 13, 13, $J_{8\text{-}ax,9\text{-}eq}$ = 4.5), 1.93 d.d.d.d (5-$H_{eq}$, $J$ = 13, $J_{5\text{-}eq,4'\text{-}ax}$ = 4.5, $J_{5\text{-}eq,4'\text{-}eq}$ = 2, $J_{5\text{-}eq,1'\text{-}eq}$ = 2), 1.97 br.d (1-H, $J_{1,1'}$ = 18), 2.07 br.d (10-$H_{eq}$, $J_{10\text{-}eq,10\text{-}ax}$ = 13), 2.11 m (1′-H), 2.23 d.d.d.d.d (10-$H_{ax}$, $J$ = 13, 13, $J_{10\text{-}ax,9\text{-}eq}$ = 6, $J_{10\text{-}ax,15}$ = 2, $J_{10\text{-}ax,15'}$ = 1), 4.50 d.d (15′-H, $J_{15',15}$ = 2, $J$ = 1), 4.85 d.d (15-H, $J$ = 2, 2), 5.26 d.m (2-H, $J_{2,1}$ = 5).

**1,5,5,9-Tetramethylspiro[5.5]undeca-1,8-diene (XI).** $^1$H NMR spectrum, δ, ppm ($J$, Hz): 0.84 s and 0.89 s ($C^{13}H_3$, $C^{14}H_3$), 1.19 d.d.d.d (4-$H_{eq}$, $J_{4\text{-}eq,4\text{-}ax}$ = 13.5, $J_{4\text{-}eq,3'\text{-}ax}$ = 6, $J_{4\text{-}eq,3'\text{-}eq}$ = 4, $J_{4\text{-}eq,2}$ = 1), 1.64 m ($C^{12}H_3$, $C^{15}H_3$, $J$ = 1.5–2.5), 1.68 d.d.d (11-$H_{ax}$, $J_{11\text{-}ax,11\text{-}eq}$ = 12.5, $J_{11\text{-}ax,10'\text{-}ax}$ = 12.5, $J_{11\text{-}ax,10'\text{-}eq}$ = 6), 1.57–1.77 m (4-$H_{ax}$, 10-H), 1.85 br.d.d (7′-$H_{ax}$, $J_{7'\text{-}ax,7'\text{-}eq}$ = 18, $J_{7'\text{-}ax,8}$ = 5) 1.88–2.01 m (3-H, 10-H, 11-$H_{eq}$), 2.11 d.d.q.t (7′-$H_{eq}$, $J$ = 18, $J_{7'\text{-}eq,8}$ = 2.5, $J_{7'\text{-}eq,15}$ = 2.5, $J_{7'\text{-}eq,10}$ = 2.5), 5.29 t.q (2-H, $J_{2,3}$ = 3.5, $J_{2,12}$ = 1.5), 5.43 d.q.t (8-H, $J$ = 5, $J_{8,15}$ = 1.5, $J_{8,10}$ = 1.5).

**Transformations of alkene IV in the system $HSO_3F$–$SO_2FCl$.** To a solution of 0.52 g of $HSO_3F$ in 1.20 ml of $SO_2FCl$ we added at –60°C a solution of 0.025 g of alkene **IV** in 0.2 ml of $CH_2Cl_2$, and the mixture was poured into 5 ml of methanol–diethyl ether. According to the GLC data, the crude product contained 80% of compound **XII** which was purified by column chromatography on $SiO_2$–20% $AgNO_3$ (eluent hexane).

**2,2,3,7-Tetramethyltricyclo[5.2.2.0$^{1,6}$]undec-3-ene (XII).** $^1$H NMR spectrum, δ, ppm ($J$, Hz): 0.85 s and 1.00 s ($C^{12}H_3$, $C^{13}H_3$), 0.97 s ($C^{15}H_3$), 1.16 m and 1.61 m (2H, 9-H or 10-H), 1.27 d.d.d ($J$ = 12, 9, 5.5) and 1.69 m (10-H or 9-H), 1.40 m (2H, 8-H or 11-H), 1.21 m and 1.54 m (2H, 11-H or 8-H), 1.36 br.d.d (6-H, $J_{6,5}$ = 10, $J_{6,5'}$ = 8), 1.65 d.d.d ($C^{14}H_3$, $J_{14,5}$ = 2.5, $J_{14,4}$ = 2, $J_{14,5'}$ = 2), 1.70 d.d.q.d (5-H, $J_{5,5'}$ = 18, $J$ = 10, 2.5, $J_{5,4}$ = 2), 1.88 d.d.d.q (5′-H, $J$ = 18, 8, $J_{5',4}$ = 4.5, $J$ = 2), 5.21 d.d.q (4-H, $J$ = 4.5, 2, 2).

**Reaction of alkene I with monoperoxyphthalic acid.** Thujopsene (**I**), 0.2 g (0.001 mol), was added to 2.7 ml of a solution of monoperoxyphthalic acid (0.0012 mol) in ether. The mixture was kept for 5 days at 5°C and washed with a 5% solution of NaOH and with water. The ether solution was dried over anhydrous sodium sulfate. According to the GLC data, the crude product, 0.25 g, contained ketones **XIV** and **XV** at a ratio of 7 : 1. By column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0.5 to 3% of the latter) we isolated 0.095 g of ketone **XIV**, mp 44°C (published data [30]:

mp 45–46°C), and 0.048 g of ketone **XV**, mp 64°C (published data [30]: mp 67–68°C).

**4,7,11,11-Tetramethyltricyclo[5.4.0.0$^{1,3}$]undecan-5-one (XIV).** $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.39 d (2H, 2-H, $J_{2,3}$ = 8), 0.53 s ($C^{14}H_3$), 1.01 s ($C^{15}H_3$), 1.03 d ($C^{12}H_3$, $J_{12,4}$ = 7), 1.05 s ($C^{13}H_3$), 1.19 m (8-H$_{ax}$, 10-H$_{ax}$), 1.20 t.d (3-H, *J* = 8, $J_{3,4}$ = 6), 1.30 d.d.d.d (8-H$_{eq}$, $J_{8\text{-}eq,8\text{-}ax}$ = 13.5, $J_{8\text{-}eq,9\text{-}ax}$ = 3.5, $J_{8\text{-}eq,9\text{-}eq}$ = 3, $J_{8\text{-}eq,10\text{-}eq}$ = 2), 1.40 d.d.d.d (10-H$_{eq}$, $J_{10\text{-}eq,10\text{-}ax}$ = 13.5, $J_{10\text{-}eq,9\text{-}ax}$ = 3.5, $J_{10\text{-}eq,9\text{-}eq}$ = 3, *J* = 2), 1.44 d.d.d.d (9-H$_{eq}$, $J_{9\text{-}eq,9\text{-}ax}$ = 13.5, $J_{9\text{-}eq,10\text{-}ax}$ = 4, *J* = 3, 3), 1.58 d.d (6-H$_{eq}$, $J_{6\text{-}eq,6\text{-}ax}$ = 16.5, $J_{6\text{-}eq,4\text{-}eq}$ = 1.5), 1.68 d.d.d.d.d (9-H$_{ax}$, *J* = 13.5, $J_{9\text{-}ax,8\text{-}ax}$ = 13.5, $J_{9\text{-}ax,10\text{-}ax}$ = 13.5, *J* = 3.5, 3.5), 1.98 d (6-H$_{ax}$, *J* = 16.5), 2.48 q.d.d (4-H$_{eq}$, *J* = 7, 6, 1.5).

**Reaction of α-cedrene (XVI) with monoperoxyphthalic acid.** Alkene **XVI**, 0.3 g (0.0015 mol), was added to 3.4 ml of a solution of monoperoxyphthalic acid (0.0022 mol) in ether. The mixture was kept for 4 days at 5°C and was treated as described above for oxidation of compound **I**. We isolated 0.28 g of epoxy derivative **XVII**.

**9β,10β-Epoxy-2,2,6,10-tetramethyltricyclo-[5.3.1.0$^{3,7}$]undecane (XVII).** Yield 89%. $[\alpha]_{580}^{20}$ = –80.2 ($CHCl_3$, *c* = 8.7). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 0.76 d ($C^{14}H_3$, $J_{14,6}$ = 7), 0.95 s ($C^{13}H_3$), 1.14 s ($C^{12}H_3$), 1.20 d.d.d (*anti*-11-H, $J_{anti\text{-}11,syn\text{-}11}$ = 12, $J_{anti\text{-}11,1}$ = 4, $J_{anti\text{-}11,8\text{-}eq}$ = 2.5), 1.24 d.d.d.d (5-H, $J_{5,5'}$ = 12, $J_{5,4}$ = 6, $J_{5,4'}$ = 6, $J_{5,6}$ = 6), 1.36 s ($C^{15}H_3$), 1.37 d.d.d.d (4-H, $J_{4,4'}$ = 12, *J* = 6, $J_{4,3}$ = 6, $J_{4,5'}$ = 6), 1.54 d.d.d (8-H$_{eq}$, $J_{8\text{-}eq,8\text{-}ax}$ = 15, $J_{8\text{-}eq,9}$ = 4.5, *J* = 2.5), 1.55 m (4′-H), 1.57 q.d.d (6-H, *J* = 7, 6, $J_{6,5'}$ = 6), 1.63 br.d.d (*endo*-3-H, $J_{endo\text{-}3,4'}$ = 9, $J_{endo\text{-}3,4}$ = 6), 1.74 d (*syn*-11-H, *J* = 12), 1.76 d.d.d.d (5′-H, *J* = 12, 6, 6, $J_{5',4'}$ = 1.5), 1.81 br.d (1-H, *J* = 4), 1.88 d (8-H$_{ax}$, *J* = 15), 2.95 d.d (9-H, *J* = 4.5, $J_{9,1}$ = 1).

**Isomerization of epoxy derivative XVII over TiO$_2$/SO$_4^{2-}$.** To 0.05 g of $TiO_2/SO_4^{2-}$ in 1 ml of $CH_2Cl_2$ we added a solution of 0.05 g of compound **XVII** in 1 ml of $CH_2Cl_2$, and the mixture was stirred for 15 min at room temperature. After appropriate treatment, we isolated 0.05 g of a crude product containing 95% (GLC) of ketone **XVIII**. The product was purified by column chromatography on $Al_2O_3$. Yield 0.043 g (86%). Following a similar procedure, ketone **XVIII** was synthesized from compound **XVII** in the presence of HB-2 β-zeolite, askanite–bentonite clay, and solid superacid $ZrO_2/SO_4^{2-}$.

**Reaction of compound XVII with the system HSO$_3$F–SO$_2$FCl.** To a solution of 0.25 g of $HSO_3F$ in 1.2 ml of $SO_2FCl$ we addded at –117°C 0.02 g of compound **XVII** in 0.2 ml of $CH_2Cl_2$. The mixture was poured into 4 ml of methanol–diethyl ether. According to the GLC data, the product, 0.015 g, was ketone **XVIII**. The same product was obtained from epoxy derivative **XVII** when the reaction was carried out at –75, –40, and –10°C, as well as with the system 5% $SbF_5$–$HSO_3F$ at 20 and 50°C.

The authors are grateful to the Russian Foundation for Basic Research (project no. 96-07-89187) for providing access to the Cambridge Structural Database.

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