SUPERACID ISOMERIZATION OF PHYLLOCLADENE, ISOPHYLLOCLADENE, AND PHYLLOCLADANOL

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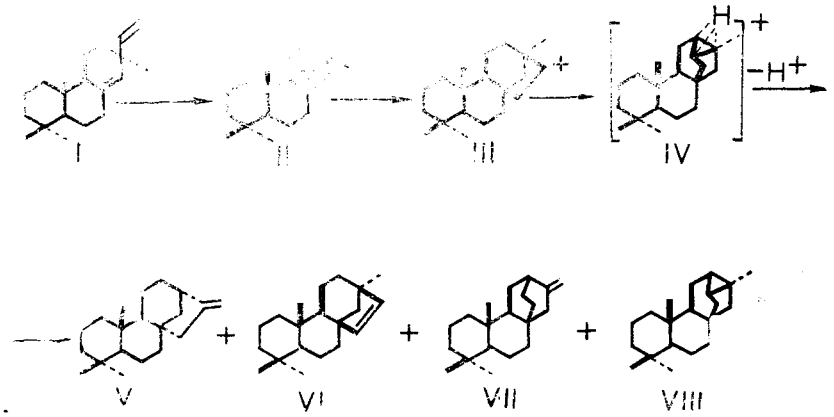
It has been established that, on interaction with a superacid, phyllocladene (XI), isophyllocladene (XV), and phyllocladan-16-ol (XIX) give identical mixtures of substances which include phyllocladene (XI), isophyllocladene (XV), neoisoatisene (XX), tetracyclic hydrocarbons with a new carbon skeleton (XXI) and (XXII), and a mixture of methyl ethers of alcohols formed as the result of the addition of methanol to the carbocations arising on the protonation of the above-mentioned hydrocarbons.

In 1955 Wenkert [1] put forward a hypothesis according to which, in the process of biogenesis, all tetracyclic diterpenoids (all those known at that time) are formed from a common tetracyclic nonclassical carbocation the precursor of which is pimara-8(14),15-diene with a pseudoaxial vinyl group at C-13 (I). As a result of the further development of these ideas (see, for example, [2-4]) in the light of new facts that have been accumulated, it has become clear that the tricyclic carbocation (II) (the product of the protonation of the 8(14)-double bond in the pimaradiene (I)) can in actual fact be the precursor only of kaurene (V), hibaene (VI), atisene (VII), and the pentacyclic hydrocarbon trachylobane (VIII) (see scheme 1). Another series of tetracyclic diterpenoids (namely phyllocladene (XI), isohibaene (XII), neoatisene (XIII), and the pentacyclic neotrachylobane (XIV)) must be formed from the carbocationic intermediate (IX), which is epimeric to the carbocation (II) at C-13, according to scheme 2. It is obvious that carbocations antipodal to the ions (II) and (IX) will lead to series of substances antipodal to those that are shown in schemes 1 and 2.



Scheme 1

The biogenetic interrelationships shown in scheme 1 have been confirmed by biochemical studies [3] and also by the interisomerization of compounds (V-VIII) under the action of acids [5].

Of substances with the carbon skeletons (XI-XIV) so far only phyllocladane compounds (structural type (XI)) [5, 6] and isohibaene (XII) [7] have been detected in natural sources.

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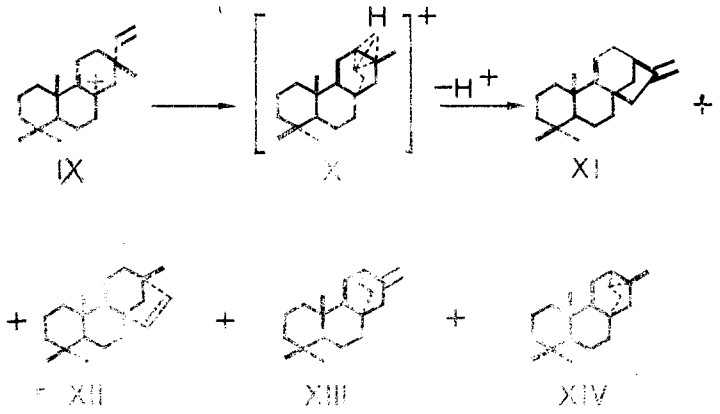
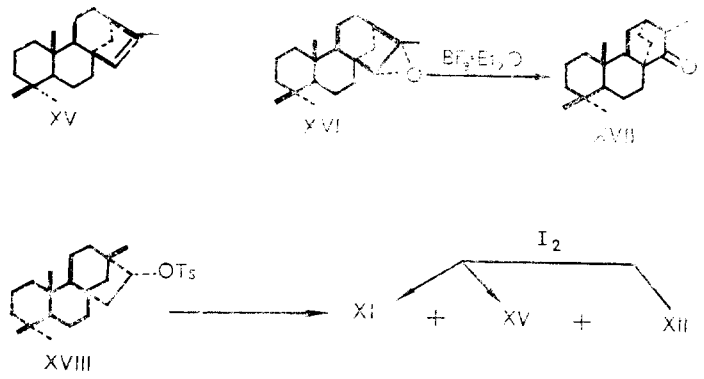


Scheme 2

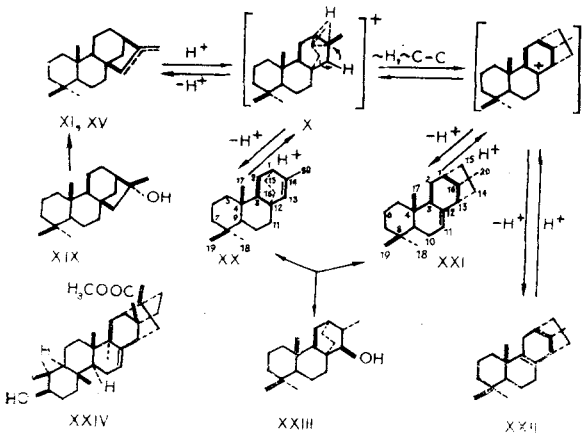
Neoatisene (XIII) has been obtained synthetically [8, 9]. There have been no biogenetic investigations on this group of substances. There is an extremely small number of publications devoted to their interisomerization in vitro. Under the action of iodine in boiling benzene, phyllocladene (XI) gives only an equilibrium mixture with isophyllocladene (XV) [6]. On the interaction of 15α,16α-epoxyphyllocladane (XVI) with boron trifluoride etherate, in addition to the usual products of the isomerization of the epoxide ring, neoisoatisan-14-one (XVII) is formed [10, 11]. On being boiled in collidine, isohiban-16-ol tosylate (XVIII) gives a mixture of phyllocladene (XI), isophyllocladene (XV), and isohibaene (XII). The latter is isomerized by iodine into a mixture of the phyllocladenes (XI) and (XV) [12].



Thus, at the present time by no means all the possible transformations reflected in scheme 2 have been realized in vitro. In view of this, and also of the fact that, with the exception of the phyllocladane diterpenoids, these compounds are difficultly accessible, it appeared of interest to investigate the behavior of phyllocladene (XI), isophyllocladene (XV), and phyllocladan-16-ol (XIX) in a superacid medium, since, as has been shown previously [13], superacids are capable of causing such transformations of diterpenoids as do not occur under the action of ordinary acids.

By dissolving isophyllocladene (XV) in the FSO_3H-SO_2FCl system at −120°C followed by "quenching" with methanol and diethyl ether (5:2), a mixture of products was obtained which, according to GLC, consisted of hydrocarbons and polar substances. The same result was obtained when the experiment was carried out with phyllocladene (XI) and phyllocladenol (XIX). By chromatography on silica gel impregnated with silver nitrate, the reaction mixtures were separated into hydrocarbon and oxygen-containing fractions. By the repeated chromatography of the hydrocarbon fractions on the same adsorbent, the olefins (XI), (XV), (XX), (XXI), and (XXII) were isolated in the individual state (scheme 3).

The structure of hydrocarbon (XX) was established with the aid of x-ray structural analysis (XSA) (Table 1) and was confirmed by its ^{13}C NMR spectrum (Table 2). This compound is (1R, 3R, 4S, 9S, 12S)-4,8,8,14-tetramethyltetracyclo[10.2.2.$0^{3,12}$.$0^{4,9}$]hexadec-13-ene, or isoneoatisene (XX) (Fig. 1). It has been obtained previously [8] by a 15-stage synthesis from maleopimaric acid. To prove its structure the authors concerned gave only its IR and PMR spectra.



Scheme 3

TABLE 1. Coordinates of the Nonhydrogen Atoms of the Olefin (XX) (in fractions of the cell, $\times 10^4$

Atom	x	y	z	Atom	x	y	z
C-1	2359(21)	6543(14)	7074(6)	C-2	2440(20)	5557(13)	7591(7)
C-3	0833(11)	5641(10)	8110(7)	C-4	1280(17)	5458(10)	8887(6)
C-5	2125(23)	4308(13)	8970(7)	C-6	2151(23)	3921(10)	9704(8)
C-7	0365(24)	3634(15)	10075(8)	C-8	−0625(20)	5085(13)	10340(7)
C-9	−0569(29)	5478(11)	9278(7)	C-10	−1487(21)	6611(15)	9172(8)
C-11	−1912(22)	6764(15)	8409(9)	C-12	−0209(18)	6645(15)	7924(8)
C-13	0032(23)	7675(12)	7010(6)	C-14	2288(21)	7590(11)	7475(7)
C-15	0565(26)	6373(15)	6645(8)	C-16	−1048(2)	6569(15)	7181(7)
C-17	2761(19)	6203(12)	9153(7)	C-18	0335(26)	5793(16)	10530(9)
C-19	−2634(25)	4807(17)	10281(9)	C-20	3719(23)	8156(15)	7353(9)

TABLE 2. ^{13}C NMR Spectra of the Neutral Compounds (XX-XXII)*

No. of carbon atom	Compound		
	XX	XXI	XXII
1	36,31 d	46, 5d[b]	41,7[illegible]d[b]
2	25,8[illegible] t	26[illegible]2 t	31,04 t
3	55,19 d[b]	50,82 d	42,89 s
4	37,51 s[c]	34,36 s	36,7[illegible] s
5	39,01 t	39,73 t	36,45 t
6	18,09 t	18,91 t	18,96 t
7	42,29 t	42,55 t	42,03 t
8	33 03 s	32,90 s	33,04 s
9	55,73 d[b]	44 66 d	51 50 d
10	19,56 t	2[illegible],21 t	19,32 t
11	28,21 t	115,75 d	32,86 t
12	37,94 s[c]	144,4[illegible] s	124,70 s
13	129,53 d	40,77 d	37,51 d[b]
14	139,62 s	32,92 t[c]	44,47 t[c]
15	37,91 t[d]	28,59 t[b]	34,36 t[c]
16	37,44 t[d]	50,85 t[b]	41,71 d[b]
17	14,99 q	17,71 q[d]	19,18 q
18	33,74 q	33,53 q	33,27 q
19	21,92 q	22,08 q	21,68 q[d]
20	20,[illegible]1 q	14,32 q[d]	22,98 q[d]

*Chemical shifts are given in ppm relative to $CHCl_3$. The values of the chemical shifts indicated by the same letters should possibly change places within a given column.

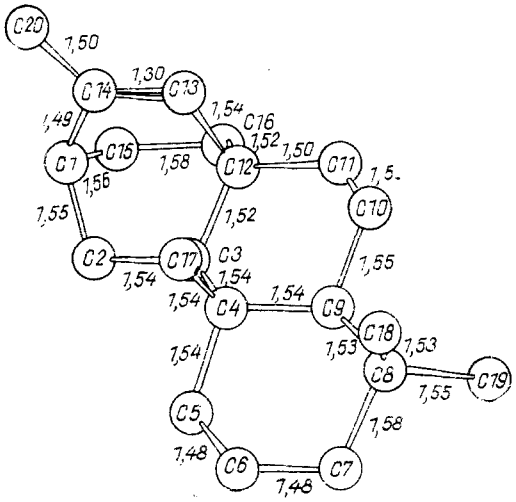


Fig. 1. Crystal structure of (1R, 3R, 4S, 9S, 12S)-4,8,8,14-tetramethyltetracyclo[10.2.2.0^{3,12}.0^{4,9}]hexadec-13-ene (XX).

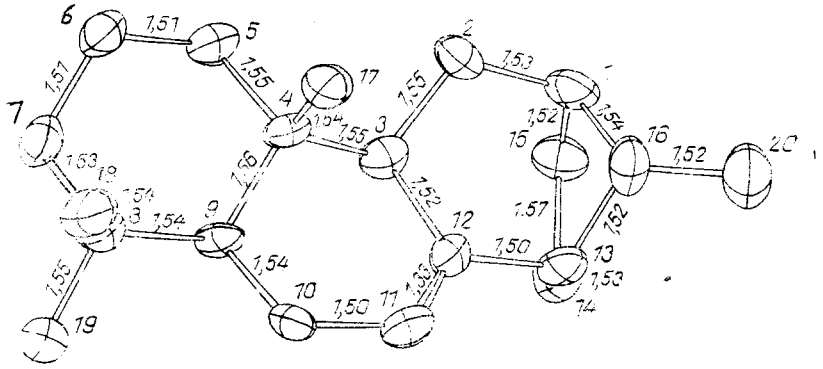


Fig. 2. Crystal structure of (1S, 3R, 4S, 9S, 13S, 16S)-4,8,8,16-tetramethyltetracyclo[11.2.1.0^{3,12}.0^{4,9}]hexadec-11-ene (XXI).

The structure of hydrocarbon (XXI) was also established with the aid of XSA (Table 3) and ^{13}C NMR (Table 2): this compound is (1S, 3R, 4S, 9S, 13S, 16S)-4,8,8,16-tetramethyltetracyclo[11.2.1.0^{3,12}.0^{4,9}]hexadec-11-ene (Fig. 2). Such a structure has previously been ascribed to the product of the dehydration of neoatisiran-14β-ol (XXIII) by phosphorus oxychloride [11] or thionyl chloride [10] on the basis solely of its IR, PMR, and mass spectra. In our opinion, the structures of compounds (X) and (XXI) were not reliably determined in the cited studies, since the spectral characteristics shown are insufficient for solving such a complex problem and, in essence, the choice of structures was based on chemical correlations with the initial compounds on the assumption of the absence of any far-reaching rearrangements whatever in the processes used.

TABLE 3. Coordinates of the Nonhydrogen Atoms of Hydrocarbon (XXI) (in fractions of the cell, ×10^4)

Atom	x	y	z	Atom	x	y	z
C-1	7279 (6)	0849 (17)	7224 (6)	C-2	5933 (6)	0513 (18)	6547 (7)
C-3	5134 (6)	1223 (0)	7247 (5)	C-4	3832 (6)	0300 (14)	6738 (5)
C-5	3215 (6)	1183 (18)	5459 (6)	C-6	1870 (6)	0886 (17)	4984 (6)
C-7	1297 (7)	2 27 (18)	5762 (6)	C-8	1771 (6)	1179 (18)	7036 (6)
C-9	3162 (5)	1243 (16)	7531 (5)	C-10	3728 (6)	0296 (18)	8792 (6)
C-11	5079 (6)	0348 (16)	9242 (6)	C-12	5724 (5)	0783 (14)	8559 (5)
C-13	7 72 (6)	1012 (16)	9075 (6)	C-14	7446 (6)	3336 (16)	8871 (6)
C-15	7556 (7)	3221 (16)	7619 (6)	C-16	7644 (6)	−0430 (17)	8401 (6)
C-17	3836 (7)	−2217 (16)	6733 (7)	C-18	1201 (7)	−1069 (17)	7098 (7)
C-19	1312 (7)	2777 (18)	7782 (7)	C-20	8998 (7)	−0734 (21)	8975 (8)

The absolute configurations of the olefins (XX) and (XXI) followed from the fact that on their formation from compounds (XI) and (XV) the configuration at C-10 remained unchanged.

Hydrocarbon (XXII) was obtained from hydrocarbon (XXI) by boiling its solution in acetic acid. On the basis of this fact (see [11]) and the ^1H and ^{13}C NMR spectra (Table 2), compound (XXII) was ascribed the structure of (1S, 4S, 9S, 13S, 16S)-4,8,8,16-tetramethyltetracyclo-[11.2.1.$0^{3,12}$.$0^{4,9}$]hexadec-3(12)-ene.

Scheme 3 may be proposed to explain the isomerization of the phyllocladenes (XI) and (XV) and the phyllocladenol (XIX).

According to PMR spectra, the oxygen-containing fraction of the products of the superacid isomerization of compounds (XI), (XV), and (XIX) consisted of a mixture of methyl ethers. Attempts to separate it into individual compounds were unsuccessful. On interaction with chloromethylsilane and sodium iodide in acetonitrile [14], it gave a mixture of hydrocarbons identical in composition with the hydrocarbon fractions obtained on the superacid isomerization of compounds (XI, (XV), and (XIX).

Thus, in the present investigation we have realized the direct conversion of the phyllocladane diterpenoids (XI), (XV), and (XIX) into isomeric tetracyclic diterpenoids for the first time; there is no information in the literature on their isomerization into other tetracyclic compounds.

We have also shown that the interaction of the olefin (XX) with the FSO_3H–SO_2FCl system under the same conditions as were used for the isomerization of hydrocarbon (XI) leads to the formation of a mixture of products of complex composition (GLC results) consisting of the hydrocarbons (XV), (XX), (XXI), and (XXII) and methyl ethers. These facts show that the isomerization process is an equilibrium one, confirm the scheme for their transformations put forward above, and expand our knowledge of the interconversions of the tetracyclic diterpenes.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on Bruker WP 200SY and AC 200 instruments for 2-5% solutions in CCl_4–$CDCl_3$ (~1:1 by volume). In the PMR spectrum the signal of the $CHCl_3$ present in the $CDCl_3$ was used as the standard, δ 7.24 ppm; in the ^{13}C NMR spectrum the signal of $CDCl_3$ was used as standard, δ 76.90 ppm (δ scale). The assignment of the signals in ^{13}C NMR spectra was made in the light of available literature information for the individual fragments of the compounds studied and on the basis of the values of the residual splittings in spectra with selective and off-resonance irradiations of protons.

Phyllocladenol (XIX). From 3 g of a mixture of neutral diterpenoids obtained from the oleoresin of the Yeddo spruce was isolated a group of oxygen-containing compounds (2 g) which was separated on neutral Al_2O_3 (activity grade III, 1:50). Petroleum ether (bp 40-70°C)–benzene (1:1) eluted 0.7 g of the alcohol (XIX) with mp 181-181.5°C (methanol), $[\alpha]_D^{20}$ + 17.3° ($CHCl_3$, c 1.5). According to the literature: mp 182-185°C; $[\alpha]_D^{20}$ + 16.6° [15].

Production of Phyllocladene (XI) and Isophyllocladene (XV). A solution of 830 mg (2.86 mmole) of the phyllocladenol (XIX) in 20 ml of dry pyridine cooled to 0°C was treated dropwise with 1.31 ml (14.3 mmole) of phosphorus oxychloride. After 30 min, the reaction mixture was warmed to room temperature and was left for 62 h. The excess of phosphorus oxychloride was decomposed with ice, and then the mixture was treated with 10% H_2SO_4 solution to give an acid reaction and it was extracted with ether (3 × 10 ml). The ethereal layer was washed with water, with saturated sodium bicarbonate solution, and again with water and was dried over anhydrous Na_2SO_4, filtered, and evaporated in vacuum. The residue (766 mg) was chromatographed on a column containing 15 g of $SiO_2 \cdot AgNO_3$. Petroleum ether–benzene (7:3) eluted 265 mg of a mixture of phyllocladene (XI) and isophyllocladene (XV). Then the same mixture of solvents eluted 334 mg of isophyllocladene (XV). After this, petroleum ether–ethyl acetate (3:1) eluted 90 mg of the initial alcohol (XIX). Fraction 1 was rechromatographed on a column containing 8 g of $SiO_2 \cdot AgNO_3$. Petroleum ether–benzene (7:3) eluted 124 mg of phyllocladene (XI), mp 94-96.5°C (methanol), $[\alpha]_D^{20}$ + 12.8° (c 0.3; $CHCl_3$). According to the literature; mp 97-98°C; $[\alpha]_D$ + 15.6° [16]. This was followed by 43 mg of a mixture of compounds (XI) and (XV) and 85 mg of isophyllocladene (XV), mp 109-110°C (methanol); $[\alpha]_D^{20}$ + 25.4° (c 0.4; $CHCl_3$). According to the literature: mp 113-113.5°C; $[\alpha]_D$ + 24° [16].

Interaction of Isophyllocladene (XV) with Fluorosulfonic Acid. A solution of 0.30 g of the olefin (XV) in 2.0 ml of CH_2Cl_2 was added to a solution of 2.22 g of FSO_3H in 4.0 ml of SO_2FCl cooled to −120°C. The acid solution was neutralized with 30 ml of CH_3OH and 12 ml of $(C_2H_5)_2O$, and the subsequent workup was as described in [17]. The weight of crude product was 0.261 g. The experiments with the olefin (XI) and the alcohol (XIX) were carried out similarly.

The reaction mixture (530 mg) was chromatographed on a column containing 35 g of $SiO_2 \cdot AgNO_3$. Petroleum ether eluted 368 mg of a hydrocarbon fraction which was then rechromatographed on a column containing $SiO_2 \cdot AgNO_3$. Petroleum ether–ethyl acetate (19:1) eluted 157 mg of a mixture of methyl ethers (~1:2) according to GLC using a Chrom-5 chromatograph with a 3 mm × 1 m glass column containing 5% of SE-30 on chromaton N-AW-DMCS, 0.100-0.160 mm, with helium as the carrier gas at the rate of 45 ml/min, the temperature of the column being 190°C and that of the evaporator 250°C. Colorless viscous liquid. IR spectrum (CCl_4, cm^{-1}): 1356, 1368 [$C(CH_3)_2$], 1060, 1142 (C–O–C) and 2845 (OCH_3). PMR spectrum (CCl_4, δ, ppm): 0.81, 0.85, 0.91, and 1.18 (3 H each, s, signals of CH_3 groups), 3.07 (s, 3 H, OCH_3). Found, %: C 82.57; H 11.98. $C_{21}H_{36}O$. Calculated, %: C 82.83; H 11.92.

A solution of 30 mg (0.11 mmole) of the mixture of methyl ethers in 0.8 ml of dry acetonitrile was treated with 0.09 ml (0.71 mmole) of chlorotrimethylsilane and 106 mg (0.71 mmole) of dry NaI, and the mixture was boiled under reflux for 40 min. A saturated aqueous solution of $Na_2S_2O_3$ was added (until decolorization had been achieved) and the mixture was extracted with ether (3 × 5 ml). The ethereal layer was washed with water, with saturated $NaHCO_3$ solution, and with water again and was dried over anhydrous Na_2SO_4, filtered, and evaporated. This gave 23.6 mg (~88%) of a mixture of hydrocarbons identical in composition with the hydrocarbon fraction formed on the isomerization of the olefin (XV).

Chromatographic Separation of the Mixture of Hydrocarbons Obtained on the Isomerization of the Olefins (XI) and (XV) and also of the Alcohol (XIX). The chromatography of 780 mg of the mixture of hydrocarbons was carried out on a column containing 30 g of $SiO_2 \cdot AgNO_3$. The results are given below:

Fraction	Column Solvent	Weight of the fraction, mg	Composition of the fraction
1	Pentane	160	Hydrocarbon A (according to GLC, 3 components in a ratio of 3:9:1)
2	Pentane	335	Mixture of hydrocarbons A, B, and (XXII)
3	Pentane	92	Hydrocarbon (XXI)
4	Pentane–ethyl acetate (49:1)	183	Mixture of hydrocarbons (XI), (XV), and (XX)
		Total: 770	

Olefin (XXII) Fraction 2 (335 mg) was rechromatographed on a column containing 14 g of $SiO_2 \cdot AgNO_3$. Petroleum ether eluted 73 mg of hydrocarbon A (a mixture of components, see above). Then the same solvent eluted 67 mg of a mixture of hydrocarbons A and B, followed by 175 mg of the crystalline hydrocarbon (XXII): mp 57-58.5°C (methanol), $[\alpha]_D^{25}$ + 43.2° (c 1.3; $CHCl_3$). IR spectrum (CCl_4, cm^{-1}): 1367, 1381 [$C(CH_3)_2$]. PMR spectrum (δ, ppm): 0.792 s, 0.839 s, 0.869 s, (3 CH_3); 0.919 d (C^{20}–3H); 0.98-2.05 m (remaining protons).

Olefin (XXI). Fraction 3 (92 mg) was recrystallized from methanol: mp 98-99.5°C, $[\alpha]_D^{25}$ + 8.6° (c 1.4; $CHCl_3$), IR spectrum (CCl_4, cm^{-1}): 1360, 1376 [$C(CH_3)_2$]. PMR spectrum (δ, ppm): 0.757 s, 0.846 s, and 0.885 s (3 CH_3); 0.787 d (J = 7 Hz, C^{20}–3H); 5.13 m (H^{11}); 0.95-2.23 (remaining protons). Found, %: C 88.07; H 11.82. $C_{20}H_{32}$. Calculated, %: C 88.16; H 11.84.

Isomerization of the Olefin (XXI) (by the procedure of [11]). A mixture of 43 mg of the hydrocarbon (XXI) and 10 ml of glacial acetic acid was boiled under reflux for 32 h. It was then worked up in the usual way. This gave 37 mg of reaction product. According to TLC ($SiO_2 \cdot AgNO_3$) and GLC, an equilibrium mixture of hydrocarbons (XXI) and (XXII) had been formed. GLC conditions: Chrom-5; flame-ionization detector, 3 mm × 1.5 m glass

column; 5% of SE-30 on Chromaton N-AW-DMCS (0.10-0.16 mm); helium, 45 ml/min; column temperature 180°C; evaporator temperature 230°C.

Rechromatography of Fraction 4. Fraction 4 (183 mg) (see above) was chromatographed on a column containing 10 g of $SiO_2 \cdot AgNO_3$. Petroleum ether eluted 76 mg of the hydrocarbon (XX); mp 75-77°C (methanol), $[\alpha]_D^{25}$ + 41.5° (c 1,4; $CHCl_3$). According to the literature: mp 76.5-77.5°C, $[\alpha]_D^{20}$ + 40.56 ($CHCl_3$) [11]. IR spectrum (CCl_4, cm^{-1}): 1360, 1378 [$C(CH_3)_2$]. PMR spectrum (δ, ppm): 0.525 s, 0.773 s, 0.843 s (3 CH_3); 1.708 d (J = 1.5 Hz, $C^{20}H_3$); 2.22 m (H^1); 5.44 m (H^{13}); 0.95-1.85 m (remaining protons). Found, %: C 88.24; H 11.78. $C_{20}H_{32}$. Calculated, %: C 88.16; H 11.84.

Then petroleum ether–ethyl acetate (49:1) eluted 47 mg of a crystalline hydrocarbon with mp 94-97°C (methanol), $[\alpha]_D^{24}$ + 12.3° (c 1.1; $CHCl_3$), identical according to chromatographic characteristics (TLC, GLC) with the olefin (XI).

A mixture of the same solvents (97:3) eluted 31 mg of a crystalline hydrocarbon with mp 109-111°C (methanol), $[\alpha]_D^{24}$ + 25.4° (c 1.3; $CHCl_3$), identical with the olefin (XV) according to its chromatographic characteristics (TLC, GLC).

X-Ray Structural Results. a) Olefin (XX). The x-ray structural experiment was performed on a SYNTEX $P2_1$ diffractometer using Mo radiation with a graphite monochromator and a sample with dimensions of 0.09 × 0.15 × 0.6 mm^3. Crystallographic results: a = 7.300(2), b = 12.194(4), c = 19.085(7) Å; space group $P2_12_12_1$, z = 4, $C_{20}H_{32}$, d_{calc} = 1.06 g/cm^3. The intensities of 945 independent reflections were measured by the $2\theta/\omega$ scanning method in the interval of $2\theta < 40°$. The calculations were made with 645 reflections having $I > 2\sigma$ with allowance for the evaporation of the crystal, which amounted to about 6%. The structure was interpreted by the direct method using the MULTAN program and was refined by the method of least squares in the anisotropic-isotropic block-diagonal approximation to R = 0.087 and R_w = 0.096, where $W^{-1} = \sigma_F^2 + (0.025\ F)^2$. The positions of the hydrogen atoms were given geometrically. The coordinates of the nonhydrogen atoms obtained are given in Table 1.

The structure of the molecule of olefin (XX) is shown in Fig. 1. The bond lengths had the usual values within the 2σ limits. The conformations of the C^4–C^9 and C^3, C^4, C^9–C^{12} rings were also the usual chair-shaped. The geometry of the bicyclo[2.2.2]octene fragment was close to the experimental geometry for bicyclo[2.2.2]oct-2-ene [18]. On the whole, the spatial structure of the molecule is analogous to the structure of ent-1α-p-bromobenzoyloxy-(16S)-atis-13-en-2-one, which has the same backbone [19].

b) Olefin (XXI). The x-ray structural experiment was carried out at a temperature of −90°C on a SYNTEX $P2_1$ diffractometer using Mo radiation with a graphite monochromator. Crystals in the monoclinic system: a = 11.894(4), b = 6.099(4), c = 12.088(4) Å, β = 110.96(2)°, space group $P2_1$, z = 2, $C_{20}H_{32}$, d_{calc} = 1.11 g/cm^3. The intensities of 2254 reflections of a crystal with dimensions of 0.08 × 0.2 × 0.37 mm^3 were measured by the ω-scanning method in the $2\theta < 45°$ hemisphere. After the averaging of the intensities of the equivalent reflections (R = 0.027), 1186 independent values were obtained of which 999 were observable values ($I > 2\sigma$). Attempts to interpret the structure by the direct method using the MULTAN 78 and SHELX 86 programs with the usual parameters proved to be unsuccessful. Taking into account Gilmore and Brown's recommendations [20] enabled us to find the correct model with the aid of the SHELX 86 program. The structure was refined by the method of least squares in the full-matrix anisotropic-isotropic (for the H atoms) approxiamtion using a program of the SYNTEX-XTL system to R = 0.059 and R_2 = 0.055. The coordinates of the atoms so obtained are given in Table 3.

The molecular structure of hydrocarbon (XXI) is shown in Fig. 2. Search in the Cambridge Structural Database [21] for the tetracyclo[$11.2.1.0^{3,12}.0^{4,9}$]hexadecane fragment forming the carbocyclic backbone of (XXI) led only to the methyl ester of pfaffic acid (XXIV) [22]. On the whole, the structure of hydrocarbon (XXI) and the corresponding fragment of the ester (XXIV) are close to one another. Ring A of the (XXI) molecule has the chair form. Ring B possesses a conformation intermediate between a half-chair and a sofa [23]. The deviation from the plane of the double bond of the C^4 atom is +0.53 Å, and of the C^9 atom −0.31Å, while the analogous ring of the ester (XXIV) is completely in the sofa form. Ring C of hydrocarbon (XXI), as also of the ester (XXIV) is characterized by a chair-like conformation with flattening in the region of the C^3 atom. An envelope conformation with the deviation of the C^{16} atom from the plane of the ring was found for ring D of the (XXI) molecule. The

form of the corresponding ring of the ester (XXIV) differs greatly from the envelope form because of the additional ethylene bridge. The value of the C^1–C^{16}–C^{13} valence angle, 99.8 (6)° is somewhat smaller than the value of 102.8(1.6)° found by the electron-diffraction method for bicyclo[3.2.1]octane [24].

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