6. É. Ya. Zandberg, U. Kh. Rasulev, and Sh. M. Khalikov, Zh. Org. Khim., 12, No. 6, 1143 (1976).
7. É. Ya. Zandberg and U. Kh. Rasulev, Zh. Tekh. Fiz., 38, No. 10, 1793 (1968).
8. É. Ya. Zandberg, É. G. Nazarov, and U. Kh. Rasulev, Zh. Tekh. Fiz., 50, No. 4, 796 (1980).
9. É. Ya. Zandberg and U. Kh. Rasulev, Teor. Éksp. Khim. 8, No. 5, 658 (1972).
10. J. H. Beynon, Mass Spectrometry and Its Applications to Organic Chemistry, Elsevier, Amsterdam (1960).
11. É. Ya. Zandberg. U. Kh. Rasulev, and Sh. M. Khalikov, Zh. Org. Khim., 10, No. 6, 1137 (1974).
12. É. Ya. Zandberg, U. Kh. Rasulev, and M. R. Sharapudinov, Teor. Éksp. Khim., 6, No. 3, 1137 (1970).

CYCLIZATION AND REARRANGEMENTS OF DITERPENOIDS.

VIII. PRODUCTS OF DEHYDRATION OF (1S,2S,7S,10R,11S,12S)-2,6,6,10,12-PENTAMETHYLTETRACYCLO[10.2.1.0^{1,10}.0^{2,7}]-PENTADECAN-11-OL BY PHOSPHORUS OXYCHLORIDE

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UDC 547.68(088.8)

On the dehydration of (1S, 2S, 7S, 10R, 11S, 12S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0^{1,10}.0^{2,7}]pentadecan-11-ol by phosphorus oxychloride in pyridine a mixture of three hydrocarbons is formed: the known (1R, 2S, 7S, 10S, 11R, 12S, 13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0^{1,10}.0^{2,7}.0^{11,13}]pentadecane and the previously undescribed (1R, 2S, 7S, 10S, 11S)-2,6,6,10,12-pentamethyltetracyclo[9.2.2.0^{1,10}.0^{2,7}]pentadeca-12-ene and (1R, 2S, 7S, 10S, 11S)-2,6,6,10-tetramethyl-12-methylenetetracyclo[9.2.2.0^{1,10}.0^{2,7}]pentadecane, based on a new carbon skeleton.

We have previously [1] investigated the products of the dehydration of (1R, 2S, 7S, 10S, 12S, 13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0^{1,10}.0^{2,7}]pentadecan-13-ol (I) – one of the two alcohols formed on the electrophilic cyclization of a number of labdane diterpenoids. Continuing this work, in the present communication we give information on the products of the dehydration of (1S, 2S, 7S, 10R, 11S, 12S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0^{1,10}.0^{2,7}]-pentadecan-11-ol (II) – an isomer of the alcohol (I) – by phosphorus oxychloride.

In this case, the reaction gave with fairly high yield a mixture of only three hydrocarbons, which were separated by chromatography on silica gel impregnated with silver nitrate and by crystallization. The least polar hydrocarbon proved to be (1R, 2S, 7S, 10S, 11R, 12S,13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.0^{1,10}.0^{2,7}.0^{11,13}]pentadecane (III), which is also formed in the dehydration of alcohol (I) [1]. The product next in polarity, containing a trisubstituted double bond, was, judging from its IR and PMR spectra and chromatographic behavior, identical with hydrocarbon A obtained in the dehydration of alcohol (I), the structure of which has remained unelucidated [1]. The most polar substance eluted from the column, having a hemicyclic double bond was identical with hydrocarbon B – another product of the dehydration of alcohol (I) [1] with an undetermined structure.

On the basis of the proofs given below, it was established that hydrocarbon A is (1R, 2S, 7S, 10S, 11R)-2,6,6,10-12-pentamethyltetracyclo[9.2.2.0^{1,10}.0^{2,7}]pentadeca-12-ene (IV), with a new carbon skeleton. On ozonization it gave two products: (1R, 2S, 7S, 10S, 11R, 12R)-2,6,6,10,12-pentamethyltetracyclo[9.2.2.0^{1,10}.0^{2,7}]pentadecan-12-one (V) and (1S, 2S,

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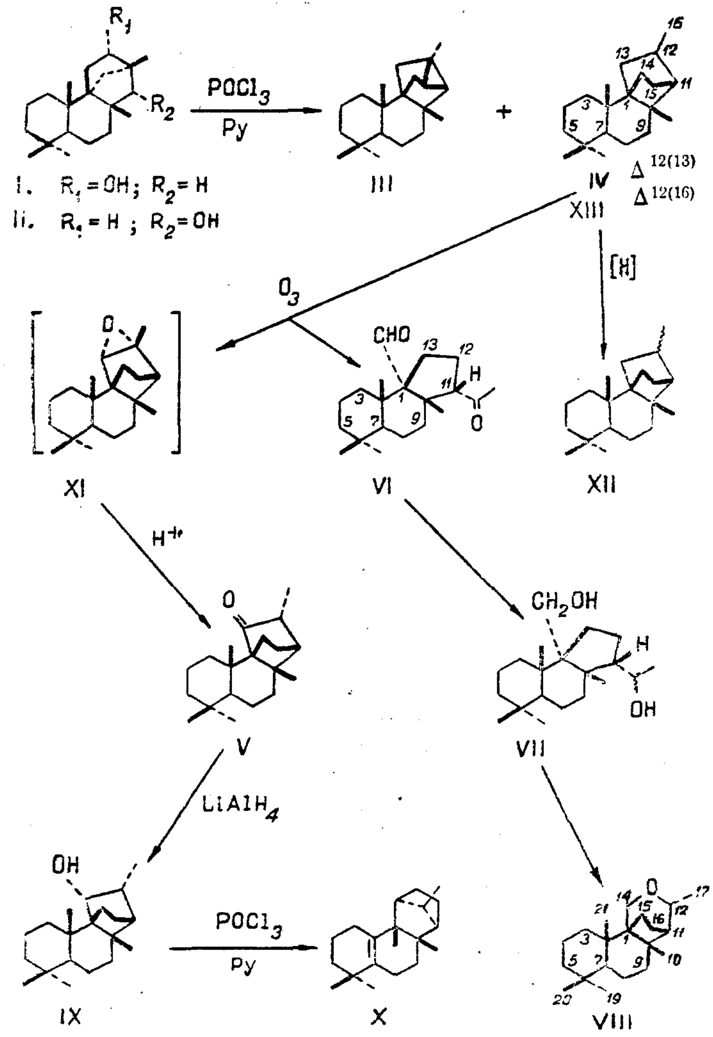
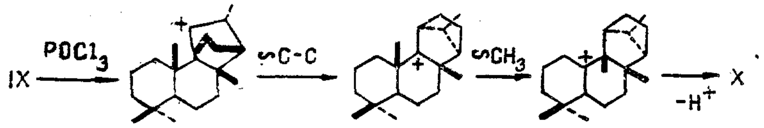
7S, 10S, 11S)-1-formyl-11-(1-hydroxyethyl)-2,6,6,10-tetramethyltricyclo[8.3.$0^{1,10}$.$0^{2,7}$]tridecane (VI). The IR spectrum of the latter contained the maxima characteristic for aldehyde and ketone groups and its PMR spectrum the signals of four methyl groups at quaternary atoms, of a methyl ketone group, and of an aldehydic proton. In the mass spectrum, the maximum peaks were those of ions with m/z 206 [M − ($CH_3COCH{=}CH_2$ + CO)] and m/z 191 (100%) (206 − CH_3). Attempts to perform the Baeyer–Villiger reaction with compounds (VI) were unsuccessful – a complex mixtures of substances was obtained from which it was impossible to isolate individual compounds. Reduction of the ketoaldehyde (VI) with lithium tetrahydroaluminate led to (1S, 2S, 7S, 10S, 11R)-11-(1-hydroxyethyl)-1-hydroxymethyl-2,6,6,10-tetramethyltricyclo[8.3.$0^{1,10}$.$0^{2,7}$]-tridecane (VII), which, on interaction with p-toluenesulfonic acid in benzene or with phosphorus oxychloride in pyridine, gave (1S, 2S, 7S, 10S, 11S, 12R)-2,6,6,10,12-pentamethyl-13-oxatetracyclo[9.3.2.$0^{1,10}$.$0^{2,7}$]hexadecane (VIII). The oxide nature of this compound followed from its IR spectrum: this contained bands at 1097 and 1106 cm^{-1} characteristic for a six-membered oxide ring. Its PMR spectrum contained the signals of four methyl groups at quaternary carbon atoms and one at a secondary carbon atom linked to oxide oxygen. Thus, on the dehydration of the diol (VII) no unsaturated alcohol with a $\Delta^{11(15)}$-double bond that would have permitted the further cleavage of the molecule, was formed. When however, the primary hydroxy group in diol (VII) was acetylated and the secondary hydroxy group was split out with phosphorus oxychloride in pyridine or with other water-abstracting reagents, a mixture of two dehydration products was obtained (GLC results) which it was impossible to separate. When the same mixture of substances was oxidized with potassium permanganate or osmium tetroxide a complex mixture of substances was formed from which it was impossible to isolate individual compounds. The ozonization of the same mixture of substances led to epoxidation at the double bond, and the opening of the epoxide ring with an acid again gave a complex mixture of substances.


Scheme 1

In view of this, we obtained a single crystal of the oxide (VIII) and established its structure and relative configuration by x-ray structural analysis (Fig. 1). The configuration of the oxide (VIII) determined in this way is simultaneously the absolute configuration, since in its molecule the AB-bicyclic system with an angular methyl group of the initial alcohol (II) remained unchanged.

In ketone (V), the carbonyl group was, according to the IR spectrum, present in a six-membered ring. According to PMR spectroscopy there were five methyl groups in its molecule, four of which were located on quaternary atoms and a fifth on a secondary carbon atom. It was fairly inert chemically, it did not take part in the Baeyer—Villiger reaction and was reduced with difficulty by the Wolff—Kishner method. These facts show the powerful spatial screening of the carbonyl group of ketone (V). This ketone was reduced by lithium tetrahydroaluminate to the alcohol (IX). The exo orientation of its hydroxy group followed from its PMR spectrum: the proton at C-13 in it gave a signal at 3.28 ppm in the form of a doublet with J = 8.5 Hz, which is characteristic for endo-oriented carbonyl protons of norbornane systems (see, for example, the PMR spectrum of compound (I)) [2]. The dehydration of alcohol (IX) by phosphorus oxychloride in pyridine, contrary to what was expected, led not to the hydrocarbon (IV) but to a known substance with a rearranged carbon skeleton, (X) [3]. This rearrangement taking place in the manner shown in Scheme 2 made it possible to establish the configuration of the C12-methyl group in ring D of alcohol (IX) and all its precursors as far as the epoxide (XI), the rearrangement of which under the action of an acid should, as is known [4], take place stereospecifically with reversal of the configuration.

Scheme 2



In view of the facts mentioned and the structure of the initial substance (IV), the ketone under investigation was ascribed structure (V). The formation of this ketone can be explained by the epoxidation of the double bond of hydrocarbon (IV) by ozone which, as is known [5], is characteristic for polycyclic compounds with spatially screened double bonds, followed by the isomerization of the epoxide (XI) into the ketone (V) apparently taking place on the treatment of the ozonization product with acid.

Hydrocarbons B and (IV) are isomeric, since on hydrogenation they gave one and the same saturated hydrocarbon (XII). The first of them contained a hemicyclic double bond and was (1R, 2S, 7S, 10S, 11R)-2,6,6,10-tetramethyl-12-methylenetetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadecane (XII). On being heated with p-toluenesulfonic acid in benzene it isomerized into hydrocarbon (IV).

The conversion of alcohol (II) into the tetracyclic hydrocarbons (IV) and (XIII) apparently took place through the classical carbocations (XIV) and (XV), and into the pentacyclic hydrocarbon (III) via the nonclassical carbocation (XVI), and the conversion of alcohol (I) into compounds (IV) and (XIII) took place via the classical carbocation (XVII)→(XIV)→(XV) (Scheme 3).

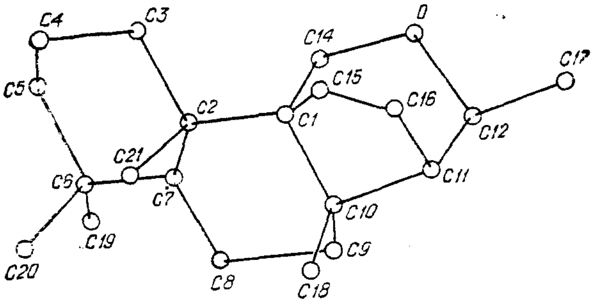
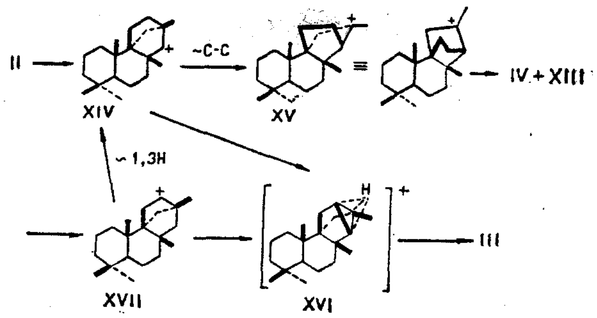


Fig. 1. Structure of (1S, 2S, 7S, 10S, 11S, 12R)-2,6,6,10,12-pentamethyl-13-oxatetracyclo[9.3.2.$0^{1,10}$.$0^{2,7}$]hexadecane (VIII).

Scheme 3



The difference in the composition of the products of the dehydration of alcohols (I) and (II) is apparently due to the fact that the back-isomerization of the carbocation (XIV) into the carbocation (XVII) does not take place under the reaction conditions and, consequently, is evidence in favor of the assumption that the conversion of these alcohols into tetracyclic hydrocarbons takes place via classical carbocations.

EXPERIMENTAL

For the general part, see [1].

Dehydration of the Alcohol (II). With stirring at 0 to −2°C 16.7 g of cooled phosphorus oxychloride was added to a solution of 10 g of the alcohol (II) in 200 ml of dry pyridine, and then cooling was stopped and the reaction mixture was stirred until it reached room temperature and then for another 3 h at this temperature, after which it was boiled under reflux for 1 h. The cooled reaction mixture was treated with 200 ml of 10% sulfuric acid and was extracted three times with ether. The extract was washed with water, with sodium bicarbonate solution, and again with water and was dried and filtered and the solvent was distilled off. The residue (8.3 g) was chromatographed on a column containing 160 g of silica gel impregnated with silver nitrate. The results of chromatography are given in Table 1.

Hydrocarbon (IV). Chromatographic fraction 1 was recrystallized from methanol to give 0.82 g of (1R, 2S, 7S, 10S, 11R)-2,6,6,10,12-pentamethyltetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadeca-12-ene (IV), mp 36.5-37.5°C; $[\alpha]_D^{20}$ −21.5° (c 1.4). Its spectral characteristics were identical with those of hydrocarbon A (see [1]). When fraction 2 was recrystallized from methanol, 1.12 g of hydrocarbon (IV) was isolated.

Hydrocarbon (III). The mother liquor from the crystallization of fraction 1 was concentrated, and the product (0.87 g) was chromatographed on a column containing 38 g of silica gel impregnated with silver nitrate. Pentane eluted 92 mg of hydrocarbon (III) with mp 45.5-46.5°C (from methanol), which was identified by comparison with a sample obtained previously [1]. The same solvent then eluted from the column 0.27 g of a mixture of hydrocarbons (III) and (IV), and a mixture of pentane and benzene (49:1) eluted 0.43 g of hydrocarbon (IV).

Hydrocarbon (XIII). Fraction 3 (Table 1) was recrystallized from methanol to give 2.7 g of (1R, 2S, 7S, 10S, 11R)-2,6,6,10-tetramethyl-12-methylenetetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]-pentadecane (XIII) mp 54.5-56°C, $[\alpha]_D^{20}$ +49.7° (c 1.4), identical with the hydrocarbon B obtained previously [1].

TABLE 1. Chromatographic Separation of the Product of the Dehydration of Alcohol (II) by Phosphorus Oxychloride in Pyridine

Fraction No.	Solvent on the column	Weight of the fraction, g	Composition of the fraction according to GLC and to TLC on $SiO_2 \cdot AgNO_3$
1	Petroleum ether	1,76	Mixture of hydrocarbons (III) and (IV) (~1:5)
2	" "	1,82	Mixture of hydrocarbons (IV) and (XIII) (~9:1)
3	Petroleum ether—benzene (9:1)	3,95	Hydrocarbon (XIII)
4	Diethyl ether	0,61	The initial alcohol (II)

Ozonization of Hydrocarbon (IV). At −60 to −62°C, a current of a mixture of ozone and oxygen was passed through a solution of 9 g of hydrocarbon (IV) in 200 ml of CH_2Cl_2 and 4 ml of dry pyridine for 6 h, and then the solution was flushed with nitrogen, and 300 ml of ether was added. The resulting solution was washed with 10% sulfuric acid, with water, with saturated sodium bicarbonate solution, and with water again and was dried and filtered and the solvent was distilled off. The residue (9.3 g) was chromatographed on a column containing 180 g of silica gel. Petroleum ether eluted 0.72 g of the initial hydrocarbon (IV), and a mixture of petroleum ether and ethyl acetate (19:1) eluted 3.5 g of (1R, 2S, 7S, 10S, 11R)-2,6,6,10,12-pentamethyltetracyclo[9.2.2.$0^{1,10}$.$0^{2,7}$]pentadecan-13-one (V) with mp 124-125°C (from methanol), $[\alpha]_D^{20}$ −28.5° (c 1.0). IR spectrum (cm^{-1}): 1363, 1379 [$C(CH_3)_2$], 1725 (>C=O). PMR spectrum (δ, ppm): 0.76 (6H, s, CH_3-20 and CH_3-17), 0.83 (3H, s, CH_3 at C), 0.88 (3H, s, CH_3 at C-6), 1.02 (3H, d, J = 6.5 Hz, CH_3 at C-12). Found, %: C 83.32, H 11.25. $C_{20}H_{32}O$. Calculated, %: C 83.27; H 11.18.

A mixture of petroleum ether and ethyl acetate (9:1) eluted from the column 3.6 g (1R, 2S, 7S, 10S, 11R)-1-formyl-11-(1-hydroxyethyl)-2,6,6,10-tetramethyltricyclo[8.3.$0^{1,10}$.$0^{2,7}$]-tridecane (VI), mp 103-104°C (from acetonitrile), $[\alpha]_D^{20}$ +23.6° (c 1.5). IR spectrum (cm^{-1}): 1371, 1380 [$C(CH_3)_2$], 1704 (CHO and $COCH_3$), 2712 (CHO). PMR spectrum (δ, ppm): 0.83 [6H, s, $(CH_3)_2$ at C-6], 1.05 (3H, s, CH_3 at C-10), 1.27 (3H, s, CH_3 at C-2), 2.02 (3H, s, $COCH_3$). Mass spectrum, m/z (%): 304 (M^+, 9), 286(4), 276(12), 258(10), 206(44), 191(100), 163(28), 149(31), 135(26), 121(23). Found, %: C 78.76; H 10.62. $C_{20}H_{32}O_2$. Calculated, %: C 78.89; H 10.59.

The Glycol (VII). A solution of 3.6 g of ketoaldehyde (VI) in 150 ml of absolute ether cooled to 0 to +5°C was treated with 1 g of lithium tetrahydroaluminate in portions and the mixture was left at room temperature for 2 h. The excess of lithium tetrahydroaluminate was decomposed with ethyl acetate, and the solution was acidified with 10% sulfuric acid solution and was worked up in the usual way. The product was crystallized from petroleum ether, giving 2.3 g of the diol (VII) with mp 164-165°C, $[\alpha]_D^{20}$ −18° (c 2.7). IR spectrum (cm^{-1}): 1036, 3453, 3624 (OH). Found, %: C 77.95; H 11.87. $C_{20}H_{36}O_2$. Calculated, %: C 77.87; H 11.76.

The Oxide (VIII). A. With stirring, 0.2 ml of phosphorus oxychloride was added to a solution of 150 mg of the diol (VII) in 5 ml of dry pyridine at room temperature, and the solution was stirred at the ordinary temperature for 5 h. Then ice water was added to the reaction mixture and it was extracted with ether, and the extract was worked up in the usual way. This gave 110 mg of (1S, 2S, 7S, 10S, 11S, 12R)-2,6,6,10,12-pentamethyl-13-oxatetracyclo[9.3.2.$0^{1,10}$.$0^{2,7}$]hexadecane (VIII), mp 104-105°C (from petroleum ether). $[\alpha]_D^{20}$ −92° (c 1.1). IR spectrum (cm^{-1}): 1097, 1106 (C—O—C). PMR spectrum (δ, ppm): 0.86 (9H, s); 1.06 (3H, s) (methyl groups at C-2, C-6, and C-10); 1.04 (3H, d, J = 6.5 Hz, CH_3 at C-12); 3.50 and 4.22 (1H each, d, J = 11 Hz, AB system, CH_2-14); 3.90 (1H, q, J = 6.5 Hz, H-12). Found, %: C 82.89; H 11.68. $C_{20}H_{34}O$. Calculated, %: C 82.69; H 11.80.

B. A solution of 60 mg of the diol (VII) in 3 ml of dry benzene was boiled with 7 mg of p-toluenesulfonic acid in a Dean-Stark apparatus for 3.5 h. The solution was washed with 2% caustic potash and with water to neutrality and was dried and filtered, and the solvent was distilled off. The residue (53 mg) was chromatographed on a column containing 1.1 g of silica gel. A mixture of petroleum ether and ethyl acetate (9:1) eluted from the column 46 mg of a substance with mp 103.5-104.5°C (from petroleum ether) identical with the oxide (VIII) obtained in paragraph A.

The Alcohol (IX). At room temperature, 285 mg of lithium tetrahydroaluminate was added to a solution of 2.1 g of the ketone (V) in 50 ml of absolute ether. The mixture was kept at the same temperature for 2.5 h and was worked up in the usual way. The product (2.07 g) was crystallized from ethanol to give 1.27 g of the alcohol (IX), mp 85-86°C, $[\alpha]_D^{20}$ −58° (c 0.7). IR spectrum (cm^{-1}): 1365, 1381 [$C(CH_3)_2$], 3495, 3620 (OH). PMR spectrum (δ, ppm): 0.87 (6H, s, CH_3 at C-2 and CH_3 at C-6); 0.97 (3H, s, CH_3 at C-10), 1.01 (3H, d, J = 7 Hz, CH_3 at C-12), 1.04 (3H, s, CH_3 at C-6), 3.28 (1H, d, J = 8.5 Hz, H-13). Found, %: C 82.66; H 11.84. $C_{20}H_{34}O$. Calculated, %: 82.70; H 11.80.

Dehydration of the Alcohol (IX). With stirring at 0°C, 0.6 ml of phosphorus oxychloride was added dropwise to a solution of 738 mg of the alcohol (IX) in 40 ml of dry pyridine. The reaction mixture was kept at room temperature for 30 min and was then boiled under reflux for 1 h. After cooling, it was worked up as described above. The reaction product (664 mg) was chromatographed on a column containing 20 g of silica gel. Petroleum ether eluted 585 mg of a liquid product identical, according to GLC and spectral characteristics, with hydrocarbon (X) that we had obtained previously [3]. A mixture of petroleum ether and ethyl acetate eluted 32 mg of the initial alcohol (IX).

Hydrogenation of the Hydrocarbon (IV). Hydrocarbon (IV) (38 mg) was dissolved in 6 ml of glacial acetic acid and, after the addition of 2.5 mg of platinum dioxide, it was hydrogenated to saturation under the usual conditions. The product was worked up in the usual way, giving 36 mg of the liquid hydrocarbon (XII), $[\alpha]_D^{20}$ −6.2° (c 1.1). IR spectrum (cm^{-1}): 1370, 1385 [$C(CH_3)_2$]. Mass spectrum, m/z (%): 274 (M^+, 43), 259 ($M - CH_3$, 100), 246(10), 232(14), 177(18), 163(16), 150(34), 136(47), 121(48), 107(53).

Hydrogenation of Hydrocarbon (XIII). Hydrocarbon (XIII) (22 mg) was hydrogenated in ethyl acetate (3 ml) in the presence of 2.5 mg of platinum dioxide as described above, giving 20 mg of a liquid product identical, from its chromatographic and spectral characteristics, with hydrocarbon (XII) obtained on the hydrogenation of hydrocarbon (IV).

Isomerization of Hydrocarbon (XIII). A solution of 6 g of hydrocarbon (XIII) in 100 ml of dry benzene was treated with 270 mg of p-toluenesulfonic acid, and the solution was boiled under reflux for 45 min. After the usual working up, 5.9 g of a reaction product was obtained which was chromatographed on a column containing 100 g of silica gel impregnated with silver nitrate. Petroleum ether eluted 4.2 g of hydrocarbon (IV), and a mixture of petroleum ether and ethyl acetate (49:1) eluted 1.6 g of the initial compound (XIII).

X-Ray Structural Results. The x-ray structural analysis of (VIII) was carried out on a DAR-UMB three-circle diffractometer controlled by a M-6000 computer, using MoK radiation by the $\theta - \theta/2\theta$ scanning method. To determine and refine the structure we used 788 reflections with $I > 3\sigma(I)$. The structure was solved by the direct method using the SHELX-86 program [6]. All the nonhydrogen atoms were revealed in Fourier syntheses. For the carbon and oxygen atoms, refinement was performed by the method of least squares in the anisotropic approximation and for the hydrogen atoms in the isotropic approximation (three hydrogen atoms being localized from difference Fourier syntheses). The final R-factor was 0.062.

Crystals of the oxide (VIII) belong to the monoclinic system with the following parameters of the elementary cells: a = 6.585(4); b = 8.397(3); c = 16.058(4) Å; γ = 78.1(1)°. Space group with symmetry $P2_1$, z = 2 at ρ_{calc} = 1.107 g/cm^3. The coordinates of the basal atoms are given in Table 2. The crystal structure of oxide (VIII) is shown in Fig. 1. Crystallographically independent molecules are present at distance greater than the van der Waals radii. The molecule consists of two carbocyclic (A and B) and one heterocyclic (C) saturated six-membered ring. The ethylene bridge fragment C15–C16 forms five- and seven-membered rings. The five-membered ring C1, C10, C11, C15, C16 has the envelope conformation with C10 being located in the flap of the envelope. The C1, C11, C15, and C16 atoms of the flat part are coplanar with an accuracy of 0.02 Å. The dihedral angle between the C1, C10, C11 and the C1, C11, C15, C16 planes deduced by the method of least squares is 51.1°. The seven-membered ring C1, C15, C16, C11, C12, O13, C14 is present in the boat conformation. Rings

TABLE 2. Coordinates of the Nonhydrogen Basal Atoms of the Oxide (VIII) ($\times 10^4$) with Their Standard Deviations

Atom	x/a	y/b	z/c
C1	3637(18)	6855(13)	2573(0)
C2	3660(19)	8085(15)	3265(14)
C3	2985(21)	7360(17)	4155(18)
C4	2611(20)	8763(16)	4877(16)
C5	905(19)	10174(19)	4619(11)
C6	1411(22)	10985(20)	3751(13)
C7	1962(24)	9650(21)	3062(14)
C8	2288(20)	10354(19)	2223(15)
C9	2411(19)	9032(18)	1475(14)
C10	3979(21)	7554(19)	1706(13)
C11	3986(22)	5982(17)	1110(16)
C12	1915(19)	5480(21)	1083(16)
C14	1583(20)	6251(19)	2580(14)
C15	5365(18)	5269(20)	2582(15)
C16	5534(24)	4698(18)	1684(17)
C17	1860(21)	3994(19)	500(17)
C18	6196(19)	7929(20)	1496(16)
C19	607(25)	12194(18)	3501(13)
C20	3019(20)	12080(19)	3902(17)
C21	5762(23)	8498(23)	3429(16)
O	1389(16)	5010(14)	1968(11)

TABLE 3. Interatomic Distances (Å) and Valence Angles (deg) in the Structure of (VIII)

Atom	Distance	Atom	Valence angle	Atom	Valence angle
C1C2	1,52 (3)	C10C1C2	112 (1)	C6C7C2	118 (2)
C1C10	1,54 (3)	C15C1C2	118 (2)	C8C7C2	112 (1)
C1C15	1.57 (2)	C15C1C10	101 (2)	C8C7C6	112 (2)
C1C14	1,54 (1)	C14C1C2	110 (1)	C9C8C7	113 (1)
C2C3	1,65 (3)	C14C1C10	110 (2)	C10C9C8	108 (2)
C2C7	1.58 (2)	C14C1C13	105 (1)	C9C10C1	111 (2)
C2C21	1 52 (2)	C3C2C1	110 (1)	C11C10C9	115 (2)
C3C4	1,64 (3)	C7C2C1	108 (1)	C18C10C1	118 (2)
C4C5	1,52 (3)	C7C2C3	107 (2)	C18C10C9	107 (2)
C5C6	1.61 (3)	C21C2C1	105 (2)	C18C10C11	101 (1)
C6C7	1,56 (2)	C21C2C3	105 (2)	C16C11C10	96(2)
C6C19	1,56 (3)	C21C2C7	112 (1)	C12C11C10	113(2)
C6C20	1,55 (2)	C4C3C2	111 (2)	C12C11C16	108(2)
C6C17	1,55 (2)	C5C4C3	111 (2)	C15C12C11	110 (2)
C7C8	1,50 (3)	C6C5C4	113 (2)	C16C13C1	105 (2)
C8C9	1.63 (3)	C7C6C5	110 (1)	OC14C1	116 (1)
C9C10	1,49 (2)	C19C C5	106 (2)	C17C12C11	104 (2)
C10C11	1.63 (3)	C19C6C7	109 (2)	OC12C11	108 (2)
C10C18	1,59 (2)	C20C6C5	110 (2)	OC12C17	108 (2)
C11C16	1.62 (3)	C20C6C7	117 (2)	C12OC14	113 (1)
C11C12	1,51 (2)	C20C6C18	104 (2)	C11C16C1	101 (1)
C15C16	1,52 (3)				
C12C17	1,57 (3)				
OC14	1,46 (2)				
OC17	1,53 (2).				

A and B have the chair conformation and a trans-linkage. The flat fragments C2, C3, C5, C6, and C1, C7, C8, C10 are coplanar with accuracies of 0.014 and 0.002 Å. The departures of the C4 and C7 atoms from the plane fragment of A amount to 0.71 and −0.60 Å, respectively, and for the C2 and C9 atoms of ring B they are 0.70 and −0.66 Å. The six-membered rings B and C are cis-linked, and ring C has the chair conformation. The flat C1, C11, C15, C16 fragment is coplanar to within 0.02 Å, the O and C10 atoms departing from the plane by −0.60 and 0.82 Å, respectively. The dihedral angle between the planes of the fragments of the five-membered ring and the six-membered ring C is 73.1°. The C17 atom departs from the plane of ring C by 0.76 Å. The values of the torsion angles around ring A range from −52.1 to 59.4°, i.e., they have values characteristic for the chain conformation [7]. The torsion angles around ring B are −58.5 and 56.1°. The increased values of the torsion angles of ring C (−61.2 and 66.2°) are the consequence of the effect of the addition of the C15—C16 ethylene bridge to the C1 and C11 atoms. The increase in the C2—C3 and C3—C4 interatomic distances to 1.65 and 1.64 Å, respectively, is probably due to the strains arising on the linkage of the rings.

The interatomic distances and valence angles in the structure correspond to their hybrid state and are given in Table 3.

SUMMARY

It has been established that the dehydration of (1S, 2S, 7S, 10R, 11S, 12S)-2,6,6,10,12-pentamethyltetracyclo$[10.2.1.0^{1,10}.0^{2,7}]$pentadecan-11-ol by phosphorus oxychloride in pyridine forms a mixture of three hydrocarbons: the known (1R, 2S, 7S, 10S, 11R, 12S, 13S)-2,6,6,10,12-pentamethylpentacyclo$[10.2.1.0^{1,10}.0^{2,7}.0^{11,13}]$pentadecane and the previously unknown (1R, 2S, 7S, 10S, 11S)-2,6,6,10,12-pentamethyltetracyclo$[9.2.2.0^{1,10}.0^{2,7}]$pentadeca-12-ene and (1R, 2S, 7S, 10S, 11S)-2,6,6,10-tetramethyl-12-methylenetetracyclo$[9.2.2.0^{1,10}.0^{2,7}]$-pentadecane, which are based on a new carbon skeleton.

LITERATURE CITED

1. P. F. Vlad, N. D. Ungur, A. N. Barba, S. T. Malinovskii, Yu. A. Simonov, and T. I. Malinovskii, Khim. Prir. Soedin., 203 (1988).
2. P. F. Vlad, N. D. Ungur, and M. N. Koltsa, Tetrahedron, 39, 3947 (1983).
3. P. F. Vlad, N. D. Ungur, A. N. Barba, D. V. Korchagina, I. Yu. Bagryanskaya, Yu. V. Gatilov, V. P. Gatilova, and V. A. Barkhash, Khim. Prir. Soedin., 198 (1988).
4. D. N. Kirk, Chem. Ind. (London), No. 3, 109 (1973).
5. P. S. Bailey, Ozonation in Organic Chemistry, Academic Press, New York (1978), Vol. 1, p. 272.

6. J. Sheldrik, SHELX-86, University of Göttingen, FRG (1986), p. 49.
7. R. Bucourt, Topics Stereochem., 8, 351 (1974).

CYCLIZATION AND REARRANGEMENTS OF DITERPENOIDS.

IX. ISOMERIZATION OF (1R,2S,7S,10S,11R,12S,13S)-2,6,6,10,12-PENTAMETHYLPENTACYCLO[10.2.1.$0^{1,10}$.$0^{2,7}$.$0^{11,13}$]PENTADECANE BY FLUOROSULFONIC ACID

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It has been shown that the opening of the cyclopropane ring in (1R, 2S, 7S, 10S, 11R, 12S, 13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.$0^{1,10}$.$0^{2,7}$.$0^{11,13}$]pentadecane takes place under the action of fluorosulfonic acid at all three carbon–carbon bonds, but at low temperatures the main isomerization product is (1R, 2S, 7S, 10S, 12S, 13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadecan-13-ol, and at the ordinary temperature the main products are (1R, 2S, 7S, 11S, 12R, 13R)-2,6,6,11,13-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadeca-9-ene and (1S, 2R, 11S, 12R, 15R)-2,7,7,11,15-pentamethyltetracyclo[10.2.1.$0^{2,11}$.$0^{3,8}$]pentadeca-3(8)-ene.

In an investigation of the dehydration by phosphorus oxychloride in pyridine of (1R, 2S, 7S, 10S, 12S, 13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.$0^{1,10}$.$0^{2,7}$]pentadecan-13-ol (I) and its isomer (II) that are formed on the electrophilic cyclization of a number of labdane alcohols, we have established that one of the products is the pentacyclic hydrocarbon (1R, 2S, 7S, 10S, 11R, 12S, 13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.$0^{1,10}$.$0^{2,7}$.$0^{11,13}$]pentadecane (III) [1, 2]. This hydrocarbon, containing a cyclopropane ring, is an analogue of trachylobane (IV) [3, 4]. As is known [3-5], under the action of acid, trachylobane and its derivatives isomerize into derivatives of ent-kaurane, ent-atisane, and ent-hibane, i.e., after the protonation of the cyclopropane ring each of the three of its C–C bonds undergoes cleavage.

In view of the accessibility of hydrocarbon (III) [1, 2], it appeared of interest to study its interaction with acids with the aim of obtaining tetracyclic substances with rearranged carbon skeletons.

In the present paper we give the results of the isomerization of hydrocarbon (III) by fluorosulfonic acid in 2-nitropropane at various temperatures. Isomerization was carried out for 5 min at a equimolar ratio of substrate and isomerizing agent.

When the reaction was performed at −100°C, the only reaction product was the alcohol (I) [6], the yield of which, with allowance for the initial compound (III) recovered, was 91%. Under these conditions only the cleavage of the C-11–C-13 bond of hydrocarbon (III) took place. At −75°C, the alcohol (I) was partially dehydrated with the formation of a small amount (∿13%) of the ether (V). At this temperature the formation of polymers also became more appreciable. The structure of ether (V) followed from its elementary and spectral analysis. Its molecular formula is $C_{40}H_{66}O$. In the IR spectrum there were maxima characteristic for C–O–C bonds at 1073 and 1091 cm^{-1}, and in its PMR spectra the signals of ten methyl groups at quaternary carbon atoms and of a proton at a carbon atom linked to ethereal oxygen. The structure of compound (V) was established definitively by independent synthesis from alcohol (I) by a known method [7].

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