

CYCLIZATION AND REARRANGEMENT OF DITERPENOIDES.

VI. PRODUCTS OF DEHYDRATION OF (1R,2S,7S,10S,12S,13S)-2,6,6,10,12-PENTAMETHYLTETRACYCLO[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]PENTADECAN-13-OL BY PHOSPHORUS OXYCHLORIDE

P. F. Vlad, N. D. Ungur, A. N. Barba,  
S. T. Malinovskii, Yu. A. Simonov,  
and T. I. Malinovskii

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It has been established that on the dehydration of (1R,2S,7S,10S,12S,13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadecan-13-ol with phosphorus oxychloride in pyridine a mixture of six substances is formed, from which three previously undescribed hydrocarbons have been isolated and identified: (1R,2S,7S,10S,11R,12S,13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>.0<sup>11,13</sup>]pentadecane, (1R,2S,7S,10S,12R)-2,6,6,10,13-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(14)-ene, and (1R,2S,7S,10S,12R)-2,6,6,10-tetramethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(16)-ene, these being based on two new carbon skeletons.

The electrophilic cyclization of a number of labdane compounds under the action of a mixture of concentrated sulfuric and formic acids leads to the formation of a complex mixture of products in which the ratio of hydrocarbon and oxygen-containing fractions ranges between 2:3 and 1:1. The latter fraction has been studied in detail; its main components are the tetracyclic alcohols (I) and (II) and their ethers [1]. The hydrocarbon fraction, consisting of a complex mixture of substances, has not been investigated. Since tetracyclic compounds are present in the oxygen-containing fraction of the cyclization product, their presence in the hydrocarbon fraction, as well, might be assumed, contrary to statements in the literature [2], since the carbocation precursors of alcohols (I) and (II) can also be stabilized as the result of the splitting out of protons. Also in favor of this suggestion is the fact that alcohols (I) and (II) on interacting with a mixture of concentrated sulfuric and formic acids under more severe conditions [3] are likewise converted into tetracyclic hydrocarbons.

In view of the fact that the separation of complex mixtures of hydrocarbons is associated with great difficulties, to detect tetracyclic compounds in them we decided first to investigate the products of the dehydration of alcohols (I) and (II). As the dehydrating agent we selected phosphorus oxychloride in pyridine, since under these conditions the hydrocarbons formed do not undergo secondary isomerizations and, consequently, the composition of the dehydration product is predetermined by kinetic factors, and not by thermodynamic factors as when the reaction is performed in a mixture of concentrated sulfuric and anhydrous formic acids [3].

In the present communication we consider the products of the dehydration of (1R,2S,7S-10S,12S,13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadecan-13-ol (I) by phosphorus oxychloride in pyridine. It must be mentioned that the yield of reaction products was low, apparently because of the formation of water-soluble compounds. The reaction gave a mixture of six substances, which were separated by chromatography on a column containing silica gel impregnated with silver nitrate. The first substance eluted from the column was a crystalline hydrocarbon not, according to IR and PMR spectroscopy, containing ethylenic bonds, as was confirmed by its inertness with respect to peracids. Consequently it was pentacyclic. Its PMR spectrum contained the signals of five methyl groups at quaternary carbon atoms and, in the strong field at 0.57 and 0.75 ppm, a doublet of doublets of an

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Institute of Chemistry, Institute of Applied Physics, MSSR Academy of Sciences, Kishinev. Translated from *Khimiya Prirodnykh Soedinenii*, No. 2, pp. 203-211, March-April, 1988. Original article submitted July 3, 1987.

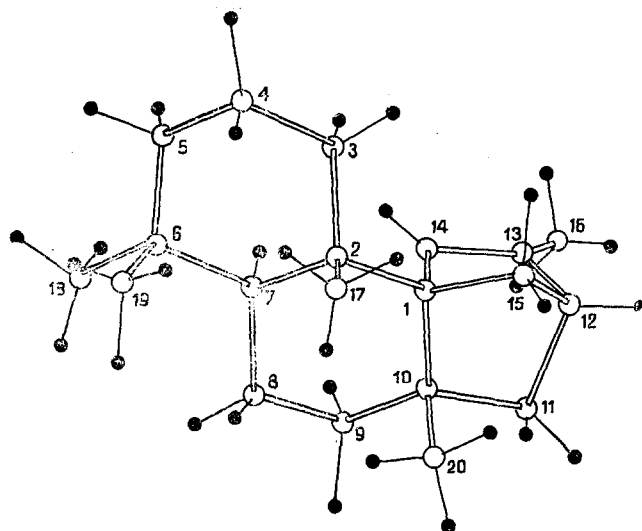
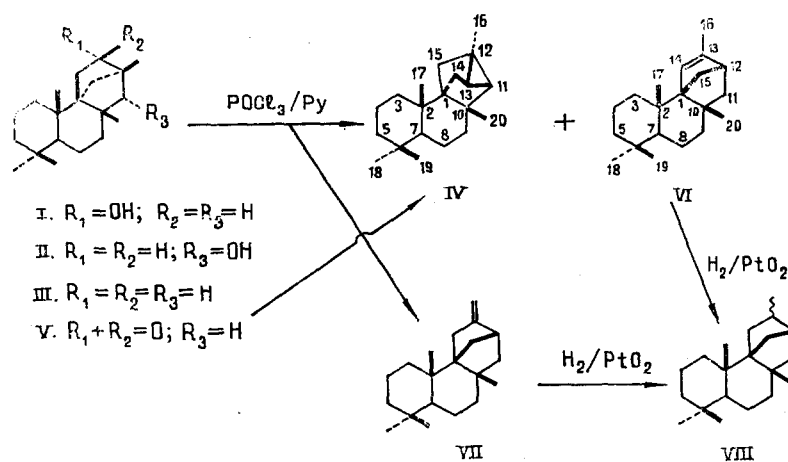


Fig. 1. Structure of (1R,2S,7S,10S,12R)-2,6,6,10,13-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>2,7]pentadec-13(14)-ene.

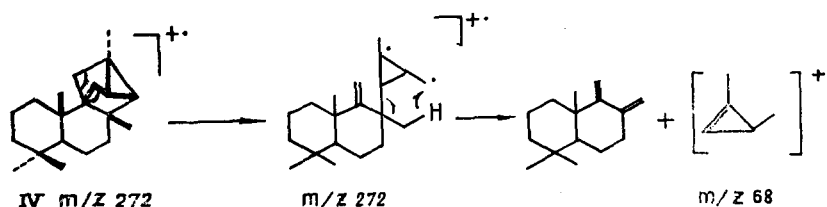
AB system of two vicinal protons attached to a cyclopropane ring. According to the <sup>13</sup>C NMR spectrum (see the Experimental part), the molecule of the compound under investigation contained five primary, seven secondary, three tertiary, and five quaternary carbon atoms. A comparison of this spectrum with the <sup>13</sup>C NMR spectrum of hydrocarbon (III) [1] showed that the basic difference between them consisted in the replacement of two secondary carbon atoms by tertiaries, which, again, was evidence in favor of the presence of an additional ring in the hydrocarbon under investigation. A strict analysis of the <sup>13</sup>C NMR spectrum of this hydrocarbon on the basis of the information available to us proved to be impossible, and the assignment of the signals given in the Experimental part is based solely on off-resonance results and a comparison with the <sup>13</sup>C NMR spectrum of hydrocarbon (III) (in the light of the structure of the first of them) and it cannot be regarded as definitive. The facts presented lead to the structure (1R,2S,7S,10S,11R,12S,13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.0<sup>1,10</sup>2,7.0<sup>11,13</sup>]pentadecane (IV) for the hydrocarbon under investigation.



Scheme 1.

The structure of this hydrocarbon was shown definitively through its synthesis by a known method [4] from the ketone (V) - the product of the oxidation of alcohol (I) [1]. When the tosylhydrazone of this ketone was heated with sodium monoethyleneglycolate in ethylene glycol, hydrocarbon (IV) proved to be the sole reaction product, its yield amounting to more than 80%.

The structure of hydrocarbon (IV) was also confirmed by its mass spectrum, in which the strongest peak was that of an ion with  $m/z$  68, a possible route for the formation of which is shown in scheme 2.



Scheme 2.

We may note that this hydrocarbon possesses a new carbon skeleton.

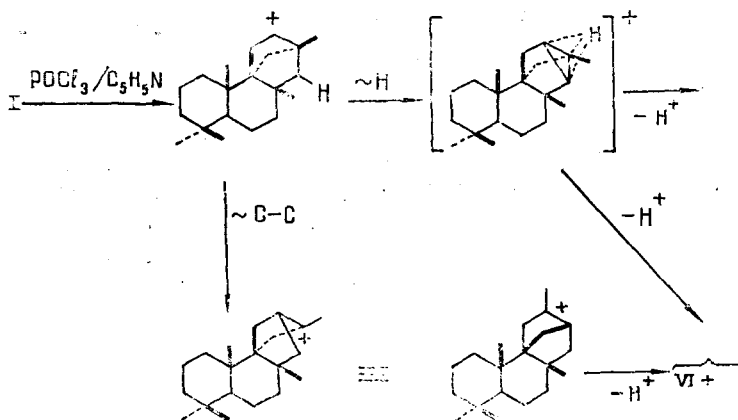
Rechromatography of the mother liquors from the crystallization of compound (IV) led to the isolation of crystalline hydrocarbon A, next in polarity; judging from IR and PMR spectra, its molecule contained a trisubstituted double bond, one of the substituents of which was a methyl group, and four methyl groups on quaternary carbon atoms. The structure of this new tetracyclic hydrocarbon has not yet been established.

Next from the column was eluted a crystalline product containing phosphorus but no halogen, which, on reduction with lithium tetrahydroaluminate, yielded the initial hydrocarbon (I). Its IR spectrum contained bands characteristic for P-O-C and P=O bonds ( $1220$  and  $1290\text{ cm}^{-1}$ , respectively). Thus, this substance was a phosphate of the alcohol (I). It was not investigated in detail.

Next to be eluted from the column was a crystalline tetracyclic hydrocarbon (B) with a semicyclic double bond (IR and PMR spectroscopic results) with four methyl groups on quaternary carbon atoms the structure of which has not yet been established.

The following substance eluted from the column was also a crystalline tetracyclic hydrocarbon, with a trisubstituted double bond, four methyl groups at quaternary carbon atoms and one at a double bond (IR and PMR spectroscopic results). The structure and stereochemistry of this compound were established by x-ray structural analysis and are represented by the formula (1R,2S,7S,10S,12R)-2,6,6,10,13-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(14)-ene (VI) (see Fig. 1).

The most polar of the products of the dehydration of alcohol (I) proved to be the crystalline tetracyclic hydrocarbon (1R,2S,7S,10S,12R)-2,6,6,10-tetramethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(16)-ene, formed in small yield (1.5%) and containing, according to IR and PMR spectra, a semicyclic ethylenic bond and four methyl groups at quaternary carbon atoms. Its structure and stereochemistry follow from the fact that the products of its hydrogenation and of the hydrogenation of compound (VI) were identical, i.e., these hydrocarbons are isomeric. They also possess a new carbon skeleton. The formation of hydrocarbons (IV), (VI), and (VII) from alcohol (I) can be represented by the scheme



Scheme 3.

The formation of hydrocarbons (VI) and (VII) may proceed through the classical isomeric carbonium ions (IX) and (X), although the route for their production via the nonclassical ion (XI) is not excluded, and that of the pentacyclic hydrocarbon (IX) may proceed through the nonclassical carbonium ion (XI).

#### EXPERIMENTAL

Melting points were determined on a Boetius stage. Specific rotations were measured on a Polamat S polarimeter in  $\text{CHCl}_3$ . IR spectra were taken in  $\text{CCl}_4$  on UR-20 and Specord IR 74 spectrometers, and PMR spectra in  $\text{CDCl}_3$  on Tesla BS 467 (60 MHz) and Bruker WP-200 SY (200 MHz) spectrometers with TMS as internal standard.  $^{13}\text{C}$  NMR spectra were also recorded on the second instrument (50.32 MHz). The signals are given on the  $\delta$  scale. Mass spectra were recorded on a MKh-1230 instrument with a glass sytem for the direct introduction of the sample into the ion source at an ionizing energy of 70 eV. GLC analysis was performed on a Chrom-5 chromatograph with a FID, using a 3 mm  $\times$  1.5 m glass column filled with 5% of SE-30 on Chromaton N-AW-DMCS (0.100-0.160 mm) at a column temperature of 180°C and an evaporator temperature of 230°C with helium as the carrier gas at  $V = 45$  ml/min. Silver-nitrate-impregnated silica gel was prepared by the method of Norin and Westfelt [5]. Solutions of substances in organic solvents were dried with anhydrous sodium sulfate.

Dehydration of the Alcohol (I). With stirring at 0 to  $-2^\circ\text{C}$ , 31.9 g of phosphorus oxychloride cooled to  $0^\circ\text{C}$  was added dropwise to a solution of 18.6 g of the alcohol (I) in 380 ml of dry pyridine cooled to  $-2^\circ\text{C}$ . With continued stirring, the temperature of the reaction mixture was raised to that of the room over 1 h, and then the mixture was boiled under reflux for 30 min. After cooling, 350 ml of 10% sulfuric acid was added to it and it 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 (10.1 g) was chromatographed on a column containing 220 g of  $\text{SiO}_2 \cdot \text{AgNO}_3$ . The results of the chromatographic separation of the product of the dehydration of alcohol (I) with phosphorus oxychloride in pyridine are given below:

	Solvent on the column	Wt of the fraction, g	Composition of the fraction to GLC and TLC on $\text{SiO}_2 \cdot \text{AgNO}_3$
1.	Petroleum ether	3.33	Mixture of hydrocarbons (VI) and A
2.	"	1.89	Phosphate of alcohol (I) contaminated with hydrocarbon B
	Petroleum ether-benzene		
3.	19:1	1.21	Hydrocarbon B contaminated with (VI)
4.	10:1	0.67	Hydrocarbon (VI)
5.	9:1	0.22	Hydrocarbon (VII)
6.	Diethyl ether	2.20	Initial alcohol
	Total	9.52	

Hydrocarbon (IV). Fraction 1 was recrystallized from methanol. This gave 1.85 g of (1R,2S,7S,10S,11R,12S,13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>.0<sup>11,13</sup>]-pentadecane (IV), mp 45.5-46°C,  $[\alpha]_D^{22} -10^\circ$  (c 3.3). IR spectrum ( $\text{cm}^{-1}$ ): 1366, 1380 [ $\text{C}(\text{CH}_3)_2$ ]. PMR spectrum (ppm): 0.80 (s, 3H), 0.83 (s, 3H), 0.91 (s, 6H), 1.12 (s, 3H,  $\text{CH}_3$ -12) (methyl groups at quaternary carbon atoms); 0.57 (1H, d,  $J = 6$  Hz, H-11); 0.75 (d, 1H,  $H = 6$  Hz, H-13) (AB system). Mass spectrum, (m/z, %): 272 ( $\text{M}^+$ , 37), 257(26), 229(4), 215(4), 189(11), 179(9), 163(13), 125(21), 119(37), 95(24), 68(100).  $^{13}\text{C}$  NMR spectrum (ppm) 54.86 (s, C-1); 49.90 (s, C-12), 49.90 (d, C-7), 45.11 (s, C-10), 42.56 (t, C-5), 40.36 (t, C-3), 36.60 (s, C-2), 35.78 (t, C-9), 34.05 (d, C-11), 33.29 (s, C-6), 33.11 (t, C-14), 32.91 (d, C-13), 30.30 (t, C-15), 21.78 (q, C-18), 21.44(q, C-19), 19.65 (q, C-20), 19.49 (q, C-17), 19.47 (q, C-16), 18.57 (t, C-8), 17.87 (t, C-4). Found %: C 87.99; H 11.99.  $\text{C}_{20}\text{H}_{32}$ . Calculated %: C 88.16; H 11.84.

Synthesis of Hydrocarbon (IV). In an atmosphere of argon, 80 mg of the tosylhydrazone of ketone (V) [1] was added to a freshly prepared solution of sodium monoethylenglycolate obtained from 80 mg of metallic sodium and 0.2 ml of ethylene glycol in 2 ml of diglyme [4], and the mixture was boiled with an air condenser for 2 h; after cooling, 15 ml of 10% sulfuric acid was added to it and it was extracted three times with ether. The usual working up of the ethereal extract yielded 43 mg of product, which was chromatographed on a column with 1 g of  $\text{SiO}_2 \cdot \text{AgNO}_3$ . Petroleum ether eluted 38.5 mg (80.7%) of hydrocarbon (IV), mp 45.5-46°C (from methanol), identical with the hydrocarbon obtained by the dehydration of alcohol (I).

Hydrocarbon A. The mother liquors from the crystallization of fraction 1 from methanol were chromatographed on a column with 65 g of  $\text{SiO}_2 \cdot \text{AgNO}_3$ . Petroleum ether eluted from the column 0.34 g of hydrocarbon (IV), 0.97 g of a mixture of it with the new hydrocarbon A, and then 54 mg of hydrocarbon A, mp 36-37.5°C (from methanol),  $[\alpha]_D^{20} -22.4^\circ$  (c 7.6).

IR spectrum ( $\text{cm}^{-1}$ ): 1650 ( $\text{>C=C<H}$ ), 1370, 1390 [ $\text{C}(\text{CH}_3)_2$ ]. PMR spectrum (ppm): singlets of 3H each at 0.83, 0.87, 0.90, and 0.93 (methyl groups at quaternary carbon atoms); 1.67 (d, 3H,  $J = 2$  Hz;  $\text{>C=C<CH}_3$ ), 5.56 (br. s 1H,  $\text{>C=C<H}$ ). Mass spectrum (m/z, %): 272 ( $\text{M}^+$ , 58), 257(9), 244(100), 229 (91), 134 (57), 121(41). Found %: C 88.20; H 11.84.  $\text{C}_{20}\text{H}_{32}$ . Calculated %: C 88.16; H 11.84.

Phosphate Ester of Alcohol (I). Chromatographic fraction 2 was recrystallized from petroleum ether, to give 1.15 g of a compound with mp 69.5-70°C,  $[\alpha]_D^{20} +74^\circ$  (c 1.1). A test for halogen was negative. The presence of phosphorus was shown by the test with ammonium molybdate [6]. IR spectrum ( $\text{cm}^{-1}$ ): 1220 (P—O—C), 1290 ( $\text{>P=O}$ ), 1370, 1390 [ $\text{C}(\text{CH}_3)_2$ ]. PMR spectrum (ppm): singlets of 3H each at 0.80, 0.85, 0.93, 1.03, and 1.10; 4.63 (m, 1, H  $\text{>CH-O}$ ). Found %: C 72.32; H 10.01.

Reduction of the Phosphate Ester with Lithium Tetrahydroaluminate. A solution in 1 ml of dry ether of 30 mg of the compound obtained above was treated with 30 mg of lithium tetrahydroaluminate, and the mixture was left at room temperature for 2.5 h. The excess of lithium tetrahydroaluminate was decomposed with ethyl acetate, the solution was acidified with 10% sulfuric acid and was extracted three times with ether, and the extract was worked up in the usual way. This gave 26.5 mg of alcohol (I), mp 159-160°C (from methanol), identified by a spectral and chromatographic comparison with an authentic sample.

Hydrocarbon B. Chromatographic fraction 3 was recrystallized from methanol, to give 0.47 g of hydrocarbon B, mp 55-56°C,  $[\alpha]_D^{21} +52^\circ$  (c 0.8). IR spectrum ( $\text{cm}^{-1}$ ): 880, 1675, 3083 ( $\text{>C=CH}_2$ ), 1375, 1390 [ $\text{C}(\text{CH}_3)_2$ ]. PMR spectrum (ppm): 0.86 (s, 6H), 0.94 (s, 3H), 0.96 (s, 3H) (methyl groups at quaternary carbon atoms); 2.75 (d, 1H,  $J = 16$  Hz), 4.51 (d, 1H,  $J = 2$  Hz), and 4.69 (d, 1H,  $J = 2$  Hz) ( $\text{>C=CH}_2$ ). Mass spectrum, (m/z, %): 272 ( $\text{M}^+$ , 55), 257(12), 229(3), 203(14), 163(11), 148(20), 134(100). Found %: C 87.97; H 11.69.  $\text{C}_{20}\text{H}_{32}$ . Calculated %: C 88.16; H 11.84.

Hydrocarbon (VI). Fraction 4 was recrystallized from methanol, to give (1R,2S,7S,10S,-12R)-2,6,6,10,13-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(14)-ene (VI), mp 63-64°C,  $[\alpha]_D^{19} -10.6^\circ$  (c 4.6). IR spectrum ( $\text{cm}^{-1}$ ): 1655, 3065 ( $\text{>C=C<H}$ ), 1370, 1390 [ $\text{C}(\text{CH}_3)_2$ ]. PMR spectrum (ppm): 0.85 (s, 6H,  $\text{CH}_3$ -2 and  $\text{CH}_3$ -6); 0.98 (s, 3H,  $\text{CH}_3$ -6), 1.25 (s, 3H,  $\text{CH}_3$ -10), 1.68 (d, 3H,  $J = 2$  Hz,  $\text{CH}_3$ -13), 5.61 (br. s, 1H, H-14). Found %: C 88.24; H 11.78.  $\text{C}_{20}\text{H}_{32}$ . Calculated %: C 88.16; H 11.84.

Hydrocarbon (VII). Fraction 5 was recrystallized from methanol, to give (1R,2S,7S,-10S,12R)-2,6,6,10-tetramethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(16)-ene (VII), mp 45.5-46.5°C,  $[\alpha]_D^{19} -81.5^\circ$  (c 0.5). IR spectrum ( $\text{cm}^{-1}$ ): 870, 1670 ( $\text{>C=CH}_2$ ), 1370, 1390 [ $\text{C}(\text{CH}_3)_2$ ]. PMR spectrum (ppm): 0.80 (s, 3H,  $\text{CH}_3$ -6), 0.83 (s, 3H,  $\text{CH}_3$ -6), 0.97 (s, 3H,  $\text{CH}_3$ -10), 1.15 (s, 3H,  $\text{CH}_3$ -2), 2.57 (br. s, 1H, H-12), 4.30 (s, 1H) and 4.52 (s, 1H) ( $\text{>C=CH}_2$ ). Found %: C 88.08; H 11.76.  $\text{C}_{20}\text{H}_{32}$ . Calculated %: C 88.16; H 11.84.

Hydrogenation of Hydrocarbon (VI). A solution of 40 mg of hydrocarbon (VI) in 6 ml of glacial acetic acid was treated with 3 mg of  $\text{PtO}_2$  and was hydrogenated to saturation under the usual conditions. After the usual working up procedure, 38.4 mg of the liquid saturated hydrocarbon (VIII) was obtained. IR spectrum ( $\text{cm}^{-1}$ ): 1369, 1390 [ $\text{C}(\text{CH}_3)_3$ ]. PMR spectrum (ppm): 0.78 [s, 6H,  $2\text{CH}_3$ -6], 0.88 (d,  $J = 5$  Hz,  $\text{CH}_3$ -13), 0.90 (s, 3H,  $\text{CH}_3$ -10), 0.95 (s, 3H,  $\text{CH}_3$ -2). Mass spectrum (m/z, %): 274 ( $\text{M}^+$ , 14), 259(15), 231(9), 189(5), 161(14), 133(24), 81(70), 69(81), 55(97), 43(100).

Hydrogenation of Hydrocarbon (VII). Hydrocarbon (VII) (20 mg) was hydrogenated in ethyl acetate (3 ml) in the presence of 2.5 mg of  $\text{PtO}_2$  under the usual conditions. After the usual working-up procedure, 19.7 mg of hydrocarbon (VIII), identical with the product of the hydrogenation of hydrocarbon (VI), was obtained.

TABLE 1. Coordinates of the Basal Carbon Atoms of (VI) ( $\times 10^4$ ) with Their Standard Deviations

C atom	$x/a$	$y/b$	$z/c$
1	-900 (9)	2497 (8)	4234 (0)
2	480 (9)	4004 (8)	4478 (9)
3	-353 (10)	5269 (9)	4132 (12)
4	999 (13)	6760 (9)	4152 (14)
5	2533 (14)	6750 (10)	3370 (12)
6	3482 (16)	5543 (9)	3617 (10)
7	2062 (10)	4037 (8)	3654 (10)
8	2837 (10)	2707 (10)	3809 (12)
9	1430 (11)	1221 (11)	3629 (14)
10	-144 (11)	1100 (9)	4423 (11)
11	-1870 (12)	-206 (10)	4202 (12)
12	-3393 (16)	645 (9)	4130 (10)
13	-3143 (10)	1309 (9)	2988 (10)
14	1606 (16)	2391 (8)	3021 (10)
15	-2673 (11)	2013 (11)	4885 (10)
16	-4214 (11)	690 (10)	1973 (11)
17	979 (12)	4172 (16)	5728 (10)
18	4785 (17)	5481 (14)	2630 (12)
19	4650 (11)	5016 (10)	4683 (11)
20	450 (15)	818 (12)	5639 (13)

TABLE 2. Interatomic Distances (Å) and Valence Angles (degrees) in the Structure of Olefin (VI)

Atoms	Distances	Atoms	Valence angle	Atoms	Valence angle
C2C1	1,525 (9)	C2C1C10	113,8 (6)	C6C7C2	114,2 (8)
C10C1	1,536 (12)	C14C1C10	166,4 (6)	C8C7C2	111,3 (8)
C14C1	1,528 (11)	C15C1C14	101,1 (6)	C8C7C6	114,7 (6)
C15C1	1,512 (11)	C15C1C10	100,6 (6)	C9C8C7	113,7 (7)
C3C2	1,502 (13)	C7C2C1	104,4 (6)	C10C9C8	109,5 (10)
C7C2	1,538 (13)	C3C2C1	108,2 (6)	C9C10C1	107,6 (8)
C17C2	1,527 (16)	C7C2C3	106,6 (8)	C11C10C1	101,1 (7)
C4C3	1,481 (11)	C4C3C2	112,0 (7)	C11C10C9	116,7 (9)
C5C4	1,487 (18)	C5C4C3	109,7 (9)	C20C10C1	117,2 (9)
C6C5	1,483 (14)	C6C5C4	114,5 (10)	C20C10C9	109,7 (9)
C7C6	1,512 (9)	C7C6C5	108,2 (7)	C20C10C11	104,7 (8)
C18C6	1,531 (17)	C18C6C7	108,0 (8)	C12C11C10	102,4 (7)
C19C6	1,540 (16)	C18C6C5	108,7 (10)	C13C12C11	102,8 (9)
C8C7	1,470 (13)	C19C6C5	112,6 (8)	C15C12C11	102,8 (7)
C9C8	1,497 (11)	C19C6C7	113,9 (9)	C15C12C13	102,9 (7)
C11C10	1,547 (11)	C19C6C18	107,3 (8)	C14C13C12	106,0 (9)
C20C10	1,550 (20)	C16C13C14	126,9 (10)	C13C14C1	107,6 (9)
C12C11	1,544 (13)	C16C13C12	126,2 (7)	C12C15C1	92,6 (7)
C13C12	1,475 (16)				
C15C12	1,517 (14)				
C14C13	1,319 (9)				
C16C13	1,479 (16)				

**X-Ray Structural Results.** The x-ray structural analysis for hydrocarbon (VI) was conducted on a DAR-UMB three-circle diffractometer (with a controlling M-6000 computer), using Mo-K $\alpha$  radiation, with the  $\theta$ - $2\theta$  method of scanning. For the calculation 1008 independent reflections with  $I > 3\sigma$  were used. Absorption in the crystal was not allowed for. The crystals of the olefin (VI) belonged to the monoclinic system with the following parameters of the elementary cell:  $a = 7.558(3)$ ,  $b = 9.097(4)$ ,  $c = 11.855(6)$  Å,  $\gamma = 104.7(1)^\circ$ . The (hkl) extinctions indicated two possible space groups:  $P2_1$  and  $P2_1/m$ . The composition of the cell,  $Z = 2$  at  $\rho_{\text{calc}} = 1.145$  g/cm $^3$ , permitted preference to be given to the  $P2_1$  group. Also in favor of this hypothesis is the optical activity of compound (VI).

The structure was solved by means of the YANX program and was refined in the anisotropic approximation for the carbon atoms and the isotropic approximation for the hydrogen atoms. The final R-factor was 0.065. The coordinates of the basal atoms of compound (VI) are given in Table 1.

The crystal structure of the molecule of hydrocarbon (VI) is shown in Fig. 1. The crystallographically independent molecules are located at distances exceeding the sums of the Van der Waals radii. The distances between the individual carbon atoms in the molecule correspond to their hybrid states and agree well with those given in the literature [7].

TABLE 3. Deviations of the Atoms (Å) from the Planes Passing through the Central Fragments of the Structure of (VI) (marked \*) and Their Equations

1.	$3,732x + 4,581y + 6,844z - 5,114 = 0$		
	$C_2 = -0,70$	$C_5 = -0,62$	
	$C_3^* = -0,02$	$C_6^* = 0,02$	
	$C_4^* = -0,02$	$C_7^* = -0,02$	
2.	$1,427x - 2,923y + 11,149z - 3,875 = 0$		
	$C_1^* = -0,02$	$C_8^* = -0,02$	
	$C_2^* = 0,02$	$C_9^* = 0,02$	
	$C_7 = -0,69$	$C_{10} = 0,71$	
3.	$-3,943x + 4,462y + 9,112z - 4,792 = 0$		
	$C_1^* = 0,53$	$C_{12}^* = 0,59$	
	$C_{10}^* = -0,22$	$C_{13}^* = -0,24$	
	$C_{11}^* = -0,32$	$C_{14}^* = -0,34$	
4.	$0,512x - 1,813y + 11,615z - 4,767 = 0$		
	$C_1^* = -0,35$	$C_{11}^* = 0,05$	$C_{15}^* = 0,40$
	$C_{10}^* = 0,16$	$C_{12}^* = -0,25$	
5.	$-5,577x + 7,638y - 0,282z - 2,550 = 0$		
	$C_1^* = -0,26$	$C_{13}^* = 0,12$	$C_{15}^* = 0,33$
	$C_{12}^* = -0,29$	$C_{14}^* = 0,09$	

The mean distances are 1.514 Å for C(sp<sup>3</sup>)-C(sp<sup>3</sup>), 1.503 Å for C(sp<sup>3</sup>)-C(sp<sup>2</sup>), and 1.319 Å for C(sp<sup>2</sup>)-C(sp<sup>2</sup>). The slight deviations from their standard values are connected with the stress caused by the C1, C15, C12 methylene bridge in the C1, C10, C11, C12, C13, C14 cyclohexane ring. The interatomic distances and the valence angles of the structure of olefin (VI) are given in Table 2. In the molecule of this compound the six-membered ring A has the chair conformation. The amounts by which the C2 and C5 atoms depart from the C3, C4, C6, C7 plane are -0.70 and 0.62 Å, respectively, while ring B adopts the chair conformation with the C7 and C10 atoms at distances of -0.69 and 0.71 Å from the plane of the ring. The norbornyl fragment has the usual form with deviations of the C15 atom from the C1, C10, C11, C12 and the C1, C12, C13, C14 planes of 0.40 and 0.38 Å, respectively.

The deviation of the atoms from the planes passing through the central fragments of the structure and the equations of these fragments are shown in Table 3.

#### SUMMARY

1. The dehydration of (1R,2S,7S,10S,12S,13S)-2,6,6,10,12-pentamethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadecan-13-ol with phosphorus oxychloride in pyridine forms a mixture of five hydrocarbons and the phosphate ester of the initial alcohol.

2. The hydrocarbon fraction of the dehydration product includes (1R,2S,7S,10S,11R,12S,13S)-2,6,6,10,12-pentamethylpentacyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(14)-ene, and (1R,2S,7S,10S,12R)-2,6,6,10-tetramethyltetracyclo[10.2.1.0<sup>1,10</sup>.0<sup>2,7</sup>]pentadec-13(16)-ene - three hydrocarbons not previously described, based on two new carbon skeletons.

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#### GLYCOSYLATION OF TRITERPENE ALCOHOLS OF THE LUPANE SERIES

L. É. Odinokova, M. V. Denisenko,  
V. A. Denisenko, N. I. Uvarova

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The glycosylation of lupeol, allobetulin, 3 $\beta$ -28-dihydroxy-18-lupene, 3 $\beta$ -28-dihydroxy-18 $\beta$ ,19 $\beta$ -epoxylupane and of betulin monoacetates in acetonitrile with mercury cyanide has been studied. The 3- and 28-mono- and the 3,28-di-O- $\beta$ -D-glucopyranosides of 3 $\beta$ -28-dihydroxy-18-lupene and of 3 $\beta$ -28-dihydroxy-18 $\beta$ ,19 $\beta$ -epoxylupane have been synthesized for the first time. Preparative methods for the synthesis of glucosides of lupeol, of allobetulin, and of betulin 3- and 28-monoacetates are proposed.

Continuing a study of the glycosylation reaction of triterpenoids of the lupane series [1], we have performed the condensation of lupeol (I), allobetulin (XIII), betulin 28-monoacetate (IV), betulin 3-monoacetate (VI), 3 $\beta$ -28-dihydroxy-18-lupene (Xa), and 3 $\beta$ -28-dihydroxy-18 $\beta$ ,19 $\beta$ -epoxylupane (XIV) with  $\alpha$ -acetobromoglucose in acetonitrile in the presence of mercury cyanide [2] and also in toluene in the presence of cadmium carbonate for the alcohols (I), (VIII), (IV) and (VI). The results of the experiments are given in Table 1.

The use of mercury cyanide as catalyst led to high yield of glycosylation products and to low recoveries of the initial alcohols (Table 1, experiments 1-6).

On the basis of the results of the investigations by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, the products obtained were assigned the structures of, respectively, lupeol 3-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (III), allobetulin 3-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (IX), 28-O-acetylbetulin 3-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (V), 28-O-acetylbetulin 28-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (Va), 3-O-8-dihydroxyacetylbetulin 28-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (VII), 3 $\beta$ -28-dihydroxy-18-lupene 3-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (XI), 3 $\beta$ -28-dihydroxy-18-lupene 28-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (XII), 3 $\beta$ -28-dihydroxy-18-lupene 3,28-di-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (XIIa), 3 $\beta$ -28-dihydroxy-18 $\beta$ ,19 $\beta$ -epoxylupane 3-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (XV), 3 $\beta$ -28-dihydroxy-18 $\beta$ ,19 $\beta$ -epoxylupane 28-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (XVI), and 3 $\beta$ -28-dihydroxy-18 $\beta$ ,19 $\beta$ -epoxylupane 3,28-di-O-(2',3',4',6'-tetra-O-acetyl- $\beta$ -D-glucopyranoside) (XVII).

The  $\beta$ -glucoside acetates (IX), (V), (Va) and (VII) were identified by comparison with authentic samples [1].

In the  $^1\text{H}$  spectra of the 3-monoglucosides (III), (XI), (XV) and the diglucosides (XIIa) and (XVII) the doublet signal of the anomeric proton of the sugar component appeared at 4.50-4.53 ppm ( $J_{1',2'}$  = 7.8-8.0 Hz), and in the  $^1\text{H}$  spectra of the 28-monoglucosides (XII) and (XVI) and of the diglucosides (XIIa) and (XVII) at 4.45-4.48 ppm ( $J_{1',2'}$  = 8.0 Hz). For the monoglucosides, the presence of an acetylated sugar component was confirmed by the appearance in the  $^1\text{H}$  spectra of these compounds of the signals of the protons of four acetate groups in the 2.00-2.09 ppm region and the signal of six protons in the 3.39-5.33 ppm region, and, for the diglucosides, of the signals of the protons of eight acetate groups (2.00-2.09 ppm) and of 12 protons (3.39-5.34 ppm).

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