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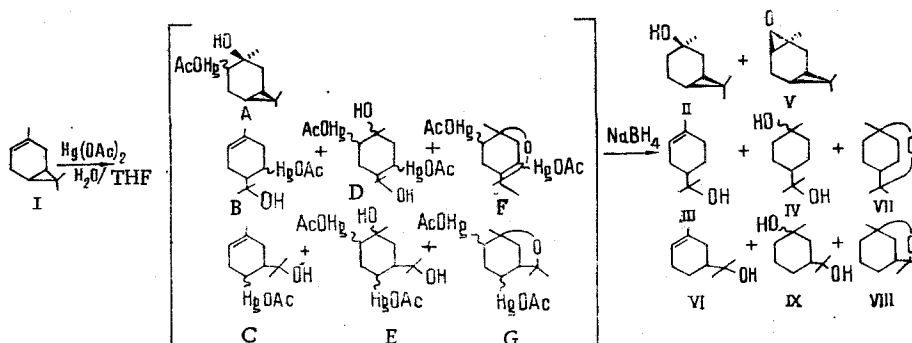
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The composition of the products of the oxymercuration-demercuration reaction of car-3-ene according to the degree of its transformation has been studied. It has been established that this reaction forms trans-caran-3-ol,  $\alpha$ -terpineol, m-menth-6-en-8-ol, 3,4-epoxy-trans-carane, p- and m-1,8-cineoles, p- and m-1,8-terpins, and terpene esters. It has been shown that the double bond of car-3-ene possesses a higher reactivity than the cyclopropane ring, and the opening of the latter takes place equally at both external bonds.

It is known [1] that the oxymercuration-demercuration of car-3-ene leads to the formation of trans-caran-3-ol and compounds of the p-menthane series —  $\alpha$ -terpineol and trans-1,8-terpin. These facts are not in harmony with the results obtained in the action of other electrophilic agents on car-3-ene, when products of both the p- and the m-series are formed [2].

We have studied the composition of the products of the oxymercuration-demercuration reaction of car-3-ene (I) and have shown that, in addition to trans-caran-3-ol (II),  $\alpha$ -terpineol (III), and trans-1,8-terpin (IV), this forms 3,4-epoxy-trans-carane (V), m-menth-6-en-8-ol (VI), p- and m-1,8-cineoles (VII and VIII), probably m-1,8-terpin (IX), and terpene esters (Table 1). Contrary to expectations, we did not find the acetates of the alcohols (II), (III), and (VI) in the reaction products.

Consequently, the oxymercuration-demercuration reaction of car-3-ene takes place similarly to its reactions with other electrophilic agents [2], i.e., the opening of the cyclopropane ring takes place at both its external bonds with the formation of compounds of the p- and m-menthane series.



As can be seen from Table 1 at the beginning of the reaction with a 10% conversion of the car-3-ene the main reaction product is the caranol (II). At a conversion of 54-57% the amount of this alcohol reaches a maximum (65%) and then it begins rapidly to fall. The amount of  $\alpha$ -terpineol and of m-menth-6-en-8-ol gradually rises and at a 64-73% conversion of the car-3-ene it may become the main reaction product. These results show the greater reactivity of the double bond in the reaction studied than of the cyclopropane ring.

The amount of the cineoles (VII and VIII) and of the terpins (IV) and (IX) in the reaction products also gradually rises, but it does not exceed 5.5% for each. At the same time, the ratio of the reaction products of the m- and the p- series shows that the opening of the

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TABLE 1. Change in the Composition of the Products of the Oxymercuration-Demercuration of Car-3-ene According to the Degree of Its Transformation

Time, h	Degree of transformation, %	Composition of the reaction products, %								
		trans-caran-3-ol	3,4-epoxy-trans-carane	$\alpha$ -terpineol	p-1,8-cineole	p-and m-1,8-terpins	m-menth-6-en-8-ol	m-1,8-cineole	esters	residue after distillation
0,25	9,7	44,7	10,2	Tr.	—	Tr.	Tr.	—	41,5	3,6
0,50	19,8	58,2	4,2	3,4	—	0,3	3,2	—	25,1	5,6
2	44,0	59,3	3,5	3,3	Tr.	0,4	3,4	Tr.	17,3	12,8
4	54,4	65,5	2,6	3,5	0,1	0,3	3,6	0,2	10,9	13,3
6	57,5	65,0	1,4	3,9	0,3	0,4	4,0	0,3	10,4	14,3
10	58,3	36,9	0,5	17,0	0,6	0,4	17,5	0,7	10,9	15,5
20	64,2	11,8	0,6	19,2	4,6	2,4	20,4	4,0	19,0	18,0
30	73,5	4,0	0,5	18,8	5,5	4,7	19,2	4,8	22,3	20,2

cyclopropane ring takes place to equal extents at its two external bonds. 3,4-Epoxy-trans-carane is formed mainly at the beginning of the reaction and then its amount gradually decreases. The esters formed consist of a complex mixture the composition of which changes during the time of the reaction. The IR spectrum of the mixture contains, in addition to the absorption bands characteristic for reaction products (II), (III), and (VI) (Table 2), a "carbonyl band" in the  $1718\text{ cm}^{-1}$  region which is probably due to the AcO group, and a strong absorption band in the  $1170\text{ cm}^{-1}$  region which may belong to the stretching vibrations both of a C—O—C bond and of the C—O bond in an AcO group [3].

Reaction products (II-IX) are probably formed from the corresponding acetoxymercury derivatives (A-G) by their demercuration. The formation of 3,4-epoxy-trans-carane is not unexpected, since it is known that in the presence of bases  $\beta$ -hydroxyalkylmercury chlorides are converted into oxides [4].

#### EXPERIMENTAL

The IR spectra of the caranol (II) in a tablet of KBr and of the menthanols (III) and (VI) and of the mixture of esters in the form of thin layers were recorded on a UR-20 instrument.

GLC analysis was performed on a Khrom-4 instrument (flame-ionization detector) with two stationary liquid phases — diethyleneglycol adipate (DEGA) at  $125^\circ\text{C}$  — and the silicone elastomer E-301 with programming of the temperature from  $60$  to  $150^\circ\text{C}$  at the rate of  $2^\circ/\text{min}$ . Capillary columns 50 m long were used with He as the carrier gas.

The reaction products were identified by the addition during the GLC analysis of individual compounds obtained by independent synthesis. The relative retention times (RRTs) of the substances on DEGA were: (I) 0.06; (VII) 0.10; (VIII) 0.11; (V) 0.33; (II) 0.76; (VI) 0.96; (III) 1.00. The amount of the terpins (IV) and (IX) in the form of their mixtures was determined by GLC analysis on E-301.

Preparative GLC (PGLC) was performed on a PAKhV-04 instrument using as the stationary liquid phase didodecyl phthalate (25%) deposited on Chromaton N-AWDMCS (0.25–0.316 mm fraction) at a temperature of  $130^\circ\text{C}$  with a column 5 m long and He as the carrier gas.

Car-3-ene was isolated by the distillation of turpentine through a column with an efficiency of 80 theoretical plates (Table 2).

Oxymercuration-Demercuration of Car-3-ene (I). The reaction was performed by the method of Brown and Geohegan [5] at a ratio of car-3-ene to  $\text{Hg}(\text{OAc})_2$  of 1:2. The reaction products were extracted with ether, the extract was dried with  $\text{MgSO}_4$ , and the ether was distilled off. The residue was analyzed in a column containing E-301 and, after vacuum distillation (bp  $50$ – $120^\circ\text{C}$  at 3–5 mm Hg), on a column containing DEGA. The results are given in Table 1.

trans-Caran-3-ol (II). The caranol was isolated from the products of the reaction performed for 4 h by distillation by heating to  $80^\circ\text{C}$  (5–7 mm Hg) and was purified by recrystallization from gasoline (Table 2). Independent synthesis was performed by the method of Arbuzov et al. [6] followed by reduction of the 3,4-epoxy-trans-carane formed with  $\text{LiAlH}_4$ .

$\alpha$ -Terpineol (III) and m-Menth-6-en-8-ol (VI). The menthenols were isolated by the PGLC method from the products of the reaction performed for 20 h and were dried with  $\text{MgSO}_4$  and

TABLE 2. Properties of the Compounds and Features of Their IR Spectra

Compound num- ber	Puri- ty, %	bp, °C (mm Hg)	mp, °C	[α] <sub>D</sub> <sup>20</sup> , deg	d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	IR spectrum, ν, cm <sup>-1</sup>				
							CH <sub>3</sub>	gem-CH <sub>3</sub>	CH of a cyclo- propane ring	OH	C = CH
I	100	—	—	+17.5	0.8650	1.4727	1445	1374	975, 1036, 3075	—	787, 1685, 3050
	[11]	—	—	+15.6	—	1.4726	1439	1368	971, 1023, —	—	785, 1639
II	100	204 (740)	71–71.5	—	—	—	1450	1375, 1385	980, 1018, 3010	1116, 1125, 3320	—
	[12]	—	71.5	—	—	—	—	—	—	1116, 1125, 3190	—
III	96	217 (740)	35–36	–66	0.9477	1.4888	1457	1365, 1375	—	1130, 1160, 3190	802, 1645, 3045
	Us.	218 (760)	36.7	–23.6	0.9343	1.4818	1450	1355, 1365	—	1120, 1115, 3190	785, 1665, 3050
IV	90	203 (740)	—	+62.7	0.9390	1.4851	1450	1355, 1380	—	1132, 1155, 3400	790, 1675, 3045
	Us.	204 (760)	—	+108.4	0.9408	1.4834	1418	1365, 1380	—	1139, 1150, 3350	795, 1672, 3040
	[7]	—	—	—	—	—	—	—	—	—	—

distilled in vacuum (5-7 mm Hg (Table 2). The independent synthesis of the menthenol (VI) was carried out by the method of Bardyshev and Gorbacheva [7].

The Mixture of Esters. The mixture was isolated by the PGLC method from the products of the reaction performed for 20 h and were dried with  $MgSO_4$  and distilled in vacuum (5-7 mm Hg). The mixture had bp 180-190°C (740 mm Hg),  $[\alpha]_D^{20} -2.7^\circ$ ,  $d_4^{20} 1.0348$ ,  $n_D^{20} 1.4921$ , ester No. 90, and consisted according to the results of GLC analysis on DEGA, of 15 components (their RRTs were between 1.10 and 2.15). IR spectrum,  $\nu$ ,  $cm^{-1}$ : 1170 (C-O-C and C-O); 1718 (C=O); 960, 1010, 3030 (CH of a cyclopropane ring); 1365, 1375 (gem- $CH_3$ ); 1134, 3410 (OH); 790, 1640, 1350 (C-CH) [3].

The following compounds were obtained by the literature methods indicated: 3,4-epoxy-trans-carane (V), [6]; cis- and trans-p-terpins (IV) and also cis- and trans-m-terpins (IX), [8]; p- and m-cineoles (VII and VIII), [9], by the oxymercuration-demercuration of  $\alpha$ -terpinol and of m-menth-6-en-8-ol, respectively; and the acetates of the alcohols (II, III, VI), [10]. The RRTs of these acetates on DEGA were, respectively, 0.63, 0.98, and 0.92.

#### SUMMARY

It has been shown that the oxymercuration-demercuration of car-3-ene forms trans-caran-3-ol,  $\alpha$ -terpineol, m-menth-6-en-8-ol, 3,4-epoxy-trans-carane, p- and m-1,8-cineoles, p- and m-1,8-terpins, and terpene esters.

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