to the formation of 1,2-disubstituted ketones which correspond to a 1,5-hydride shift in the vinyl cationoid intermediate.

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CARBONYLATION OF TERPENES

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Terpene hydrocarbons are easily polymerized and become resinous during carbonylation in the presence of acid catalysts, and, as a result, carboxylic acids are formed in low yields and with low selectivity [1].

In this work the compositions of carboxylic acids formed during carbonylation of L-menthol in the presence of conc. H_2SO_4 [2] are studied in detail. The carbonylation of other terpenes is also studied: D,L-menthol, p-menthene-1, and 2,6-dimethyl-2,7-octadiene in the presence of BF_3-based catalysts: $CuO_2—2(BF_3 \cdot H_3PO_4) \cdot (BF_3 \cdot H_2O)$ (1:20) (K1), $BF_3 \cdot 2C_2H_5COOH$ (K2), $BF_3 \cdot 2CH_3COOH$ (K3), $BF_3 \cdot 2CH_2ClCOOH—BF_3 \cdot 2CH_3COOH$ (3:1) (K4), and $BF_3 \cdot 2CH_2ClCOOH$ (K5). BF_3-Based catalysts displayed high activity and selectivity during carbonylation of terpenes, and also during carbonylation of olefins and alcohols [3-5].

Carbonylation of L-menthol (L-M) (K1, 30°C, CO at atmospheric pressure) proceeds with a low yield of carboxylic acids (∼25%). In the presence of conc. H_2SO_4 (20°C, CO pressure at 80 atm), L-M is quantitatively converted to trans- and cis-p-menthane-1-carboxylic [trans- and cis-(I)], D,L-trans-p-menthane-3-carboxylic (II), trans- and cis-p-menthane-4-carboxylic [trans- and cis-(III)], trans- and cis-p-menthane-8-carboxylic [trans- and cis-(IV)], and 1,2,2,6-tetramethylcyclohexane-1-carboxylic (V) acids (Table 1). Tertiary carboxylic acids with the carboxylic group on C atoms in the 1, 4, and 8 positions are formed in preference, which indicates the rapid isomerization of the initially obtained secondary carbonium ions (a) into tertiary carbocations (B)-(E) by means of 1,2-migration of hydride ions (Scheme 1)

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TABLE 1. Carbonylation of L-Menthol, D,L-Menthol, p-Menthene-1, and 2,6-Dimethyl-2,7-octadiene (Diene)

Original terpene	Catalyst	Molar ratio of catalyst: terpene	T., °C	Pressure of CO, atm	Yield of acids, % of theor.	Comparative contents of acids, %							
						trans-(I)	cis-(I)	(II)	trans-(III)	cis-(III)	trans-(IV)	cis-(IV)	(V)
L-Menthol	H_2SO_4	8	20	80	94,8	23,9	18,2	3,1	14,5		34,4	4,9	1,0
	K5	5	80	90	88,2 *	17,7	12,6	1,7	13,3		33,3		–
DL-Menthol	H_2SO_4	8	20	80	82,2	54,5	7,8	0,6	2,2		24,1	4,7	6,1
	K4	2	80	80	99,0†	41,4	22,8	–	14,3		8,7	4,3	8,5
p-Menthene-1	K2	2	100	100	73,0†	47,7	27,3	–	–	7,2	12,0	5,7	–
»	K3	2	90	100	61,0	49,2	27,2	–	–	8,8	11,0	3,8	–
»	K5	2	80	100	60,2	48,7	25,2	–	–	7,4	12,4	6,3	–
Diene	K2	2	80	100	100,0†	–	–	–	–	3,3	12,4	–	74,3**
»	K2	2	85	100	98,3‡	–	–	–	–	6,8	13,2	–	70,0**
»	K2	2	90	100	91,2‡	–	–	–	–	8,3	17,4	–	65,0**

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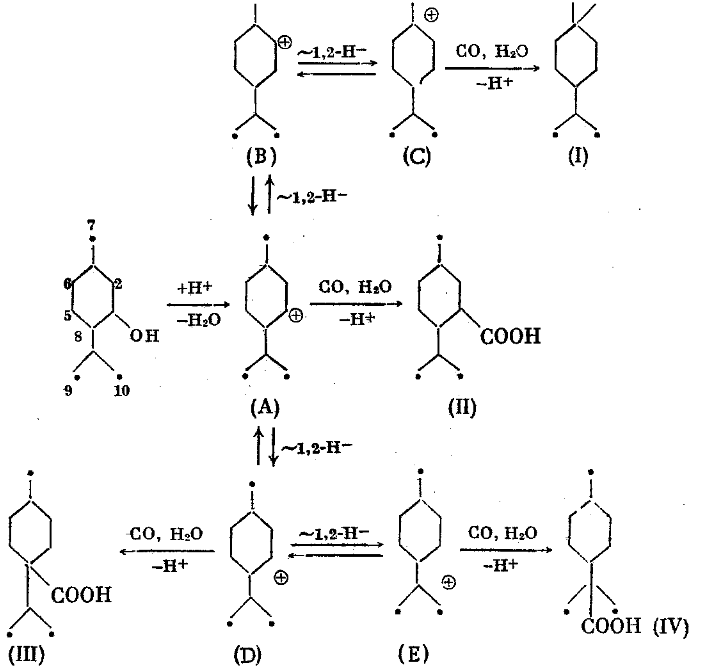
*21.4% of the acids in the acid mixture were of unestablished structure.

†The average yields of the acids after a 10-time use of the catalyst.

‡The average yields of the acids after a five-time use of the catalyst.

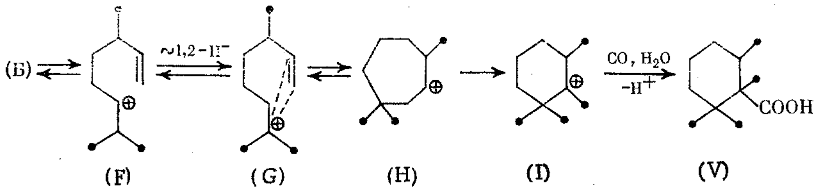
**The acid mixture in addition contained ∿10-12% 1,4,4-trimethylcycloheptane-1-carboxylic (VI) and 3,3,-7-trimethylcycloheptane-1-carboxylic (VII) acids in a 3:1 ratio.

Scheme 1



The formation of acid (V) from L-M evidently proceeds by means of β splitting of the C^3—C^4 bond in cation (B) with the formation of cation (F), which is isomerized to cation (G). The carbonium ion (G) is cyclized into cation (H), isomerizing further to cation (J), which also is carbonylated (Scheme 2).

Scheme 2



The spatial structure of trans-(I) and cis-(I) is established by ^{13}C NMR spectra of their amides and, in particular, by the γ effect [in the amide of cis-(I)] of the axial CH_3 group, causing a shift of the resonance signal of C atoms in the 3 and 5 positions in a strong field ∿5 ppm [6, 7]. The structure of trans-(I) is confirmed by the PMR spectrum of its methyl ester, and also by IR spectra of the amides of trans- and cis-(I). Moreover, the location of the $CONH_2$ group on C^1 in amides of trans- and cis-(I) follows from data of the deshielding of C atoms in position 1 (^{13}C NMR spectrum). The methyl ester of trans-(I) and amides of trans- and cis-(I) are not optically active, which agrees with the location of alkyl groups on C^1 and C^4 and a carboxyl group on C^1.

The location of the carboxyl group in trans-(IV) is established on the basis of the PMR spectrum of the methyl ester, in which the isopropyl group is shown in the form of a singlet ($\delta = 1.00$ ppm), indicating the substitution of a methine proton on the $COOCH_3$ group. The $(CH_3)_2C(COOCH_3)$ group in this ester has an equatorial orientation, judging by the preferable formation of trans-(IV) compared to cis-(IV) (see Table 1). This agrees with the energetic economy of the equatorial position of this group over the axial position by ∿5.5 kcal/mole [7].

The possibility of the conversion of ion (E) into ion (C) is confirmed by the results of the carbonylation of (4-methylcyclohexyl-1)propan-2-ol in the presence of K4, mainly leading to the formation of acids containing a carboxyl group on C^1 and C^8, namely trans-(I), cis-(I), trans-(IV), and cis-(IV) in the ratio of 3:3:2:2.

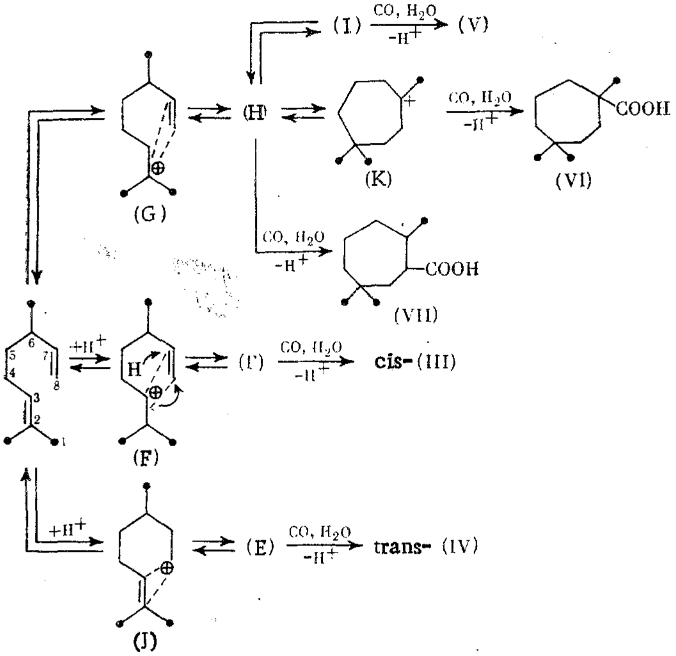
The conclusion about the structure of acid (V), obtained from L- and D,L-menthol, and also from the diene, is made on the basis of the mass and PMR spectra of (V) and its methyl ester, and the conclusion about the structure of acids (II), trans-(III), and cis-(III) is made from data of the GLC analysis of the corresponding alcohols, obtained by reduction of the esters with $LiAlH_4$. GLC analysis of stereoisomeric pairs in alcohol form guarantees a better separation; thus, stereoisomers with an axial orientation of the CH_2OH group are eluted from the chromatographic column first. The alcohol, corresponding to acid (II), gives one peak on the chromatogram, which allows the assumption that (II) is a racemic mixture of the D- and L-isomers. D,L-Menthol (D,L-M) during carbonylation in the presence of H_2SO_4 (20°C, CO pressure of 80 atm) proceeds analogously to L-M. K2 and K_3 at 80°C and a CO pressure of 100 atm catalyze this reaction very weakly, while K_4 causes complete conversion of D,L-M to trans-(I) and cis-(I). The preferred carbonylation of D,L-M at C^1 evidently is connected with the presence of a significant amount (∿35%) of neomenthol and isomenthol, in which the axial orientation of OH groups contributes to the preferred isomerization of the carbonium ions (A) originating from them to ion (C). p-Menthene-1 in the presence of K1 (30°C, CO at atmospheric pressure) is converted into acids only to 25%. K2, K3, and K5 appear significantly more active in this reaction; moreover, the activity of K2 is preserved almost unchanged after its 10th use (see Table 1).

The reaction of 2,6-dimethyl-2,7-octadiene (diene) with CO and H_2O in the presence of K1 (molar ratio of diene to K1 is 1:2, 30°C, CO at atmospheric pressure) leads to acid (V) (49.3% yield). In the reaction, catalyzed by K2 (80°C, CO pressure of 100 atm), the following acid are formed: (V) (74.3%), trans-(IV) (12.4%), and cis-(III) (3.3%). An increase in temperature to 85 and 90°C leads to a reduction of the total yield of acids and the relative yield of (V). Acid (V), according to ^{13}C NMR spectral data of its methyl ester, is a mixture of 2,2-cis- and 2,2-trans-1,6-tetramethylcyclohexane-1-carboxylic acids, probably with predominance of the energetically more favorable cis-isomer.

Besides acids (V), 1,4,4-trimethyl- and 3,3,7-trimethylcycloheptane-1-carboxylic acids [(VI) and (VII), respectively] (3:1, total yield 10-12%) are formed upon carbonylation of the diene. Their structure is confirmed by sequential conversion to the methyl esters, alcohols, and aldehydes, and also by mass and PMR spectra and by data of elemental analysis.

Acid (V), evidently, is formed from the diene through carbonium-ions (G), (H), and (I), and acids (VI) and (VII) are formed through ions (L) and (H), respectively (Scheme 3)

Scheme 3



Cyclization of the diene with the formation of cycloheptane- and cyclohexylmethyl-carbonium ions was also observed in [8]. The conversion of the diene to the acid cis-(III) probably occurs by means of protonation of the diene at the C^2 atom with the formation of ion (F), which undergoes further cyclization to ion (D), and in the acid trans-(IV) by means of protonation of the diene at the C^7 atom with the formation of ion (K) and then cyclization to ion (E). The observed stereospecific formation of acids cis-(III) and trans-(IV) allows the assumption of the intermediate existence of bridge ions (F) and (J), corresponding to the indicated stereospecificity.

EXPERIMENTAL

Carbonylation in the presence of K1 was carried out at atmospheric pressure of CO and 30°C, and with the use of K2, K3, K4, and K5 the CO pressure was 80-100 atm and the temperature was 80-100°C according to the method of [3-5]. During repeated use of the catalyst the reaction products were isolated by extraction with n-hexane, and the separated catalyst was used again.

The p-menthene-1 used [bp 46-48°C (7 mm), n_D^{20} 1.4580] contained 62.9% p-menthene-1, 6.4% cis-pinane, 13.5% trans-pinane, 10.3% dipentene, and 6.9% of three unknown components; 2,6-dimethyl-2,7-octadiene [bp 41-42°C (10 mm), n_D^{20} 1.4418] contained 22.7% pinane; L-menthol (mp 41-42°C); D,L-menthol (mp 28°C) (synthetic) contained 65.0% of the basic substance, 20% neomenthol, and 15% isomenthol. D,L-Menthol was synthesized by hydrogenation of thymol, obtained by alkylation of m-creosol with propylene [9].

Gas—liquid chromatographic analyses of the acids, esters, and alcohols were performed on an LKhM-8-MD chromatograph in a stream of helium (50 ml/min) with the use of a flame-ionization detector with a column (2.5 m × 2 mm) of non-rusting steel and with 10% polyethylene glycol adipate and 3% H_3PO_4 on Chromosorb G. The analysis temperature of the esters was 150-160°C and of the alcohols 180-190°C. The relative times of retention of the methyl esters (ME) of the acids and the corresponding alcohols had the following values: trans-(III) 0.77, 0.55; cis-(III) 0.84, 0.66; (II) 0.68, 0.80; trans-(IV) 1.00, 1.00; cis-(IV) 1.09, 1.15; (V) 1.38; trans-(I) 1.23, 1.55; and cis-(I) 1.35, 1.67.

PMR spectra were taken on an XL-100 spectrometer; ^{13}C NMR spectra, on a "Bruker P-60" spectrometer with a frequency of 15.08 MHz. The separation of the esters was conducted on an LKhP-5A chromatograph constructed by the Special Design Office of the N. D. Zelinski Institute of Organic Chemistry of the Academy of Sciences of the USSR with a column 8 m × 20 mm with 15% carbon black of 20 mesh on Chromaton (0.25 mm).

From the mixture of carboxylic acids obtained by the carbonylation of p-menthene-1 in the presence of K2, K3, and K5, upon standing the acid trans-(I) crystallized out, mp 82.5°C (hexane) (Found: 71.8% C; 10.8% H. $C_{11}H_{20}O_2$. Calculated: 71.7% C; 10.9% H), the ME of trans-(I), bp 110-112°C (8 mm), n_D^{20} 1.4488, d_4^{20} 0.9341 (Found: 72.7% C; 11.0% H. $C_{12}H_{22}O_2$. Calculated: 72.7% C; 11.1% H), and the amide of trans-(I), mp 100.0°C (hexane) (Found: 72.0% C; 11.5% H; 8.6% N. $C_{11}H_{21}NO$. Calculated: 72.1% C; 11.5% H; 8.8% N). After removal of trans-(I) by vacuum distillation, a fraction was isolated with bp 145-150°C (9.5 mm), n_D^{20} 1.4652, from which the amide of acid cis-(I) was obtained, mp 136°C (hexane) (Found: 72.3% C; 11.6% H; 8.7% N. $C_{11}H_{21}NO$. Calculated: 72.1% C; 11.5% H; 8.8% N).

PMR spectrum of the ME of trans-(I) (δ, ppm): 0.775 d [$CH(C\underline{H}_3)_2$, J = 6.5 Hz], 1.08-1.30 m [$C\underline{H}(CH_3)_2$], 0.98 d [$H_{2,3}(a,a)—H_{5,6}(a,a)$, J = 6.5 Hz], 1.03 s [$C(C\underline{H}_3)(COOCH_3)$], 2.07 d [$H_2(e)—H_6(e)$, J = 9.5 Hz], 1.56 broad s [$H_3(e)—H_5(e)$ and $C\underline{H}(CH_2)_2$], 3.55 s ($COOCH_3$).

^{13}C NMR spectrum of the amide of trans-(I) (δ, ppm): 20.156 (C^9 and C^{10}), 27.866 (C^3 and C^5), 29.627 (C^7), 33.573 (C^8), 37.033 (C^2 and C^6), 43.894 (C^1), 44.683 (C^4), 182.316 ($\underline{C}ONH_2$); amide of cis-(I): 20.156 (C^9 and C^{10}), 22.645 (C^3 and C^5), 28.595 (C^7), 34.059 (C^8), 36.059 (C^2 and C^6), 46.564 (C^1), 47.597 (C^4), 194.398 ($\underline{C}ONH_2$). IR spectrum of the ME of trans-(I) (cm^{-1}): 1380 (ν_s, i-Pr), 1470 (ν_{as}, i-Pr), 1728 (ν C=O), amides of trans-(I) and cis-(I) ($CHCl_3$, cm^{-1}): 1450 (CH_2 cyclohexane ring), 1370 and 1390 ($\nu_{skeleton}$, i-Pr), 1660 and 1590 (ν C=O), 3460 and 3420 ($\nu_{N-H\ bond}$), 3540 and 3500 ($\nu_{free\ N-H}$).

Analysis of the pure ME of trans-(I) and solutions of the amides of trans-(I) and cis-(I) in $CHCl_3$ on a Spectropol-1 polarimeter in the 250-600 nm range showed the absence of optical activity.

By the carbonylation of L-menthol in the presence of H_2SO_4, acids were obtained which were separated by GLC in the form of their ME. The ME of trans-(I) has n_D^{20} 1.4488, the ME of cis-(I) has n_D^{20} 1.4530, the ME of trans-(IV) has n_D^{20} 1.4540, and the ME of cis-(IV) has n_D^{20} 1.4498. Carbonylation of p-menthene-1 in the presence of K2 produced acids whose ME were separated by an analogous method: the ME of trans-(IV) has n_D^{20} 1.4540 and the ME of trans-(I) has n_D^{20} 1.4488. PMR spectrum of the ME of trans-(IV) (δ, ppm): 0.8 d (3H, $C\underline{H}_3$

at C^1, J = 6.6 Hz), 1.00 s (6H, CH_3 at C^8), 0.75-1.2 m [4H, $H_{2,3}(a,a)$—$H_{5,6}(a,a)$], 1.45-1.85 m [6H, $H_4(a)$, $H_1(e)$ and $H_{2,3}(e,e)$—$H_{5,6}(e,e)$], 3.50 s (3H, OCH_3).

The mixture of carboxylic acids, obtained by the carbonylation of the diene, was converted to a mixture of ME, from which the ME of acid (V) was separated, bp 68-69°C (4 mm), n_D^{20} 1.4508, d_4^{20} 0.9400. Found: 72.9% C; 11.2% H. $C_{12}H_{22}O_2$. Calculated: 72.7% C; 11.1% H. Acid (V) was obtained by saponification of the ME, bp 155-155.5°C (12 mm), n_D^{20} 1.4648, d_4^{20} 0.9736. PMR spectrum of the ME of (V) (δ, ppm): 0.675 s (6H, CH_3 at C^2), 0.75 d (3H, $C\underline{H}_3CH$, J = 4.5 Hz), 1.17 s (3H, CH_3 at C^1), 1.42-2.42 m (7H), 3.52 s (3H, OCH_3). NMR spectrum (V) (δ, ppm): 0.835 broad s (9H, CH_3 at C^1 and C^2), 1.07 d (CH_3 at C^6, J = 4.5 Hz), 0.98-2.30 m [7H, —$(CH_2)_3$— and $C\underline{H}(CH_3)$] and 12.0 s (1H, $COO\underline{H}$). Mass spectrum (V) (m/e): 184 (M^+), 139 (M^+ — COOH), 109 (139 — $2CH_3$), 83 [139 — $CH_2C(CH_3)_2$], 55 (83 — C_2H_4), $m_1^* = 49.65$ and $m_2^* = 36.5$. The transitions 139 — 56 → 83 and 83 — 28 → 55 characterize metastable ions.

The fraction [bp 70.5-77°C (4 mm), n_D^{20} 1.4550-1.4582] of a mixture of ME of acids (VI) and (VII) is separated during distillation of the ME of acids (270 g), which were obtained by carbonylation of the diene, on a fractionating column with an efficiency of 60 theoretical plates. Upon saponification of a portion of the ME of acids (VI) and (VII), a mixture of acids is obtained from which 1.8 g (VI) is separated by vacuum distillation, bp 135-140°C (19 mm), n_D^{20} 1.4608. Found: 71.8% C; 10.7% H. $C_{11}H_{20}O_2$. Calculated: 71.7% C; 10.9% H. Mass spectrum (m/e): 184 (M^+), 169 (M^+ — CH_3), 139 (M^+ — COOH), 111 (139 — C_2H_4), 109 (139 — $2CH_3$); and also 1.5 g (VII) is separated, bp 154-156°C (17 mm), n_D^{20} 1.4630. Found: 71.7% C; 11.2% H. $C_{11}H_{20}O_2$. Calculated: 71.7% C; 10.9% H. Mass spectrum (m/e): 184 (M^+), 169 (M^+ — CH_3), 139 (M^+ — COOH), 123 (139 — C_2H_3), 109 (M^+ — COOH — $2CH_3$).

By reduction of the fraction of ME of acids (VI) and (VII) with bp 70.5-77°C (4 mm), n_D^{20} 1.4577 with the help of $LiAlH_4$, a mixture of alcohols is obtained, which without separation is oxidized by $Na_2Cr_2O_7$ in AcOH to a mixture of aldehydes. Vacuum distillation of the aldehyde mixture gives 1,4,4-trimethylcycloheptanal, bp 135-138°C (19 mm), n_D^{20} 1.4572 [2,4-dinitrophenylhydrazone, mp 136°C (ethanol)]. PMR spectrum (δ, ppm): 0.84 s and 0.875 s (6H, CH_3 at C^4), 1.89 s (3H, CH_3 at C^1), 1.05-1.75 m [10H, —$(CH_2)_3$— and —$(CH_2)_2$—] and 9.8 s [H, $C\underline{H}O$] and 3,3,7-trimethyl-1-cycloheptanal, bp 113-114°C (13 mm), n_D^{20} 1.4588, d_4^{20} 0.9176 [2,4-dinitrophenylhydrazone, mp 137°C (ethanol)]. PMR spectrum (δ, ppm): 0.85 s (6H, $C\underline{H}_3$ at C^3), 1.12 d (3H, $C\underline{H}_3CH$, J = 5 Hz), 1.0-2.35 m [10H, —$(CH_2)_3$—, —(CH_2)—, and $C\underline{H}(CH_3)$ and $C\underline{H}CHO$], 7.9 s (H, $C\underline{H}O$).

By reduction of the ME of trans-(I) with $LiAlH_4$, 1-hydroxymethyl-trans-p-menthane (VIII) is obtained, mp 32.5°C (hexane). Found: 77.5% C; 12.7% H. $C_{11}H_{22}O$. Calculated: 77.6% C; 12.9% H. Analogously, reduction of the ME of (V) produces 1,2,2,6-tetramethyl-1-hydroxymethylcyclohexane, bp 118-120.5°C (17 mm), n_D^{20} 1.4700 (Found: 77.5% C; 12.8% H. $C_{11}H_{22}O$. Calculated: 77.6% C; 12.9% H), $Na_2Cr_2O_7$ (in AcOH) oxidation of which leads to 1,2,2,6-tetramethyl-1-cyclohexanal, bp 100-102°C (20 mm), n_D^{20} 1.4560, d_4^{20} 0.9024 [2,4-dinitrophenylhydrazone, mp 137.5°C (ethanol)]. Found: 58.8% C; 7.0% H; 15.8% N. $C_{17}H_{24}N_4O_4$. Calculated: 58.6% C; 6.9% H; 16.1% N.

By carbonylation of (4-methylcyclohexyl-1)propan-2-ol, obtained by hydrogenation of α-terpineol according to [11], in the presence of K4 (90°C, CO pressure of 100 atm) a mixture of the acids trans-(I), cis-(I), trans-(IV), and cis-(IV) in the ratio of 3:3:2:2 is obtained. This acid mixture is converted to a mixture of the ME [bp 110-116°C (20 mm), n_D^{20} 1.4510], which is converted to a mixture of alcohols by means of $LiAlH_4$ [bp 120-124°C (23 mm), n_D^{20} 1.4660]. A mixture of alcohols [bp 91.5-92.5°C (6 mm), n_D^{20} 1.4642, d_4^{20} 0.9048] is obtained by $LiAlH_4$ reduction of a mixture of the ME of acids formed during carbonylation of L-menthol in the presence of H_2SO_4. The alcohol of (VIII) possesses a floral odor. Esters of the acid trans-(I) possess favorable perfumery properties, namely the methyl ester [bp 110-112°C (8 mm), n_D^{20} 1.4510], the ethyl ester [bp 118-120°C (12 mm), n_D^{20} 1.4472], the isopropyl ester [bp 140-142°C (42 mm), n_D^{20} 1.4433], the n-butyl ester [bp 143-145°C (17 mm), n_D^{20} 1.4500], the isoamyl ester [bp 153-158°C (23 mm), n_D^{20} 1.4508], the neopentyl ester [bp 154-160°C (34 mm), n_D^{20} 1.4475], and the benzyl ester [bp 191-195°C (19 mm), n_D^{20} 1.4547]; as well as the ester of the alcohol of (VIII) and propionic acid [bp 134-137°C (4 mm), n_D^{20} 1.4528, d_4^{20} 0.9230].

CONCLUSIONS

1. The most active and selective catalysts for carbonylation of L-menthol, D,L-menthol, p-menthene, and 2,6-dimethyl-2,7-octadiene are $BF_3 \cdot 2C_2H_5COOH$, $BF_3 \cdot 2CH_3COOH$, $BF_3 \cdot 2CH_2ClCOOH$, $BF_3 \cdot 2CH_2ClCOOH$, and $BF_3 \cdot 2CH_2ClCOOH-BF_3 \cdot 2CH_3COOH$ (3:1).

2. The primary products of the carbonylation of L-menthol, D,L-menthol, and p-menthene-1 are trans- and cis-p-menthane-1-carboxylic and trans-p-menthane-8-carboxylic acids.

3. The carbonylation of 2,6-dimethyl-2,7-octadiene in the presence of BF_3-complex catalysts proceeds by cyclization to cyclohexyl and cycloheptyl carbonium ions, reacting with CO and H_2O with the formation of 1,2,2,6-tetramethylcyclohexane-1-carboxylic acid (70-75%), a mixture (3:1) of 1,4,4-trimethyl- and 3,3,7-trimethylcycloheptane-1-carboxylic acids (10-12%), and also a mixture of cis-p-menthane-4-carboxylic and trans-p-menthane-8-carboxylic acids (15-20%).

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