# ORGANIC CHEMISTRY

# CARBONYLATION OF ALIPHATIC AND CYCLIC ALCOHOLS BY CARBON MONOXIDE IN THE PRESENCE OF COMPLEXES OF BF3

WITH ACETIC, PROPIONIC, OR MONOCHLOROACETIC ACID

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It was shown earlier [1, 2] that complexes of  $BF_3$  with  $CH_3COOH$ ,  $CH_3CH_2COOH$ , or  $CH_2CICOOH$ in a 2:1 mole ratio are highly active and stable catalysts of the carbonylation reaction of olefins and tertiary alcohols. The reaction proceeds easily at 80-100°C at a CO pressure of 100 atm with formation of  $\alpha, \alpha$ -dialkyl- and higher-branched alkane acids in yields close to 100%. These catalysts can be used repeatedly without a decrease in initial activity. Carbonylation of primary, secondary, and tertiary alcohols at a CO pressure of 100 atm and temperatures of from 25 to 150° was studied in this research.

It is seen from Table 1 that tertiary alcohols of aliphatic and cyclic structure are transformed easily and in high yields to carboxylic acids in the presence of all of the used catalysts:  $BF_3 \cdot 2CH_3CH_2COOH$  (C1),  $BF_3 \cdot 2CH_3COOH$  (C2), and the catalytic system (3:1)  $BF_3 \cdot 2CH_2$ -ClCOOH- $BF_3 \cdot 2CH_3COOH$  (C3). It should be noted that (I) reacted in the presence of C1 at 80°, being transformed to carboxylic acids in higher yields (average yield of acids 98.5% after 10-fold use of C1) then in the presence of C2 (average yield 81.1% after sixfold use of C2). In the presence of C3 (I) reacted at 70° with an 87.4% yield of acids. In the presence of C1 and C3 (I) was transformed with greater selectivity into trimethylacetic acid (63-64%) than in the presence of C2 (47.1%). In addition, from (I) were obtained dimeric C, acids: 2,2,4,4-tetramethylvaleric acid, 2-isopropyl-3,3-dimethylbutyric, 2-ethyl-2,3,3-trimethylbutyric, and C<sub>13</sub> acids, formed by carbonylation of 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 3,4,4-trimethyl-2-pentene, and triisobutylenes, respectively, C<sub>6</sub>, C<sub>7</sub>, and C<sub>8</sub> disproportionation acids.

In the presence of Cl, C2, and C3 at  $80-90^{\circ}$  (II) was transformed in yields of 94.7-98.9%into acids, which amounted to 45-55%  $\alpha,\alpha-dimethylbutyric, 17-18\%$   $\alpha,\alpha-dimethylvaleric and \alpha$  $methyl-<math>\alpha$ -ethylbutyric, 10-15\% trimethylacetic, and small amounts of  $C_8-C_{10}$  acids. Carbonylation of (II) was accompanied by disproportionation, the degree of which increased with increasing temperature (Table 2) and upon going from Cl (41.7\%) to C2 (45\%) and further to C3 (55\%). It is interesting to note that at 150° (II) in the presence of Cl was transformed in 93.8\% yield into acids, which consisted of 75\% 2,2,3,3-tetramethylvaleric acid, the formation of which evidently proceeds by the presented scheme. The structure of 2,2,3,3tetramethylvaleric acid was confirmed by elemental analysis data and PMR and mass spectroscopy



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TABLE 1. Carbonylati cat:alcohol = 2:1, ra	on of Te te of ac	ertiary Idition	and Secon of alcoho	dary Alcohols in the Presence of BF <sub>3</sub> -Complex Catalysts (Cat) (mole ratio of 1 to cat 1 mole/mole of cat.h, $p_{CO}$ = 100 atm)
Alcohol	Cat	т., °с	Acid yield, %*	Acid (content, %)
tert-Butanol (I)	CI	80	98.5 <sup>a</sup>	Trimethylacetic (62.7), C <sub>6</sub> (1.0), C <sub>7</sub> (0.4), 2,2,4,4-tetramethylvaleric (13.6) 2-isopropyl-3,3-dimethylbutyric (12.3), 2-ethyl-2,3,3-trimethylbutyric (4.4),
(1)	C2	80	81.1 <sup>b</sup>	<pre>Cis (3:0) Trimethylacetic (47)1), Ce (1.7), C7 (1.3), 2,2,4,4-tetramethylvaleric (18.3), 2-isopropyl-3,3-dimethylbutyric (16.3), 2-ethyl-2,3,3-trimethylbutyric (3.0), C (12.3)</pre>
(1)	<b>C</b> 3	70	87.4	Trimethylacetic (64.0), C <sub>6</sub> (4.3), C <sub>7</sub> (4.8), 2,2,4,4-tetramethylvaleric (16.1),
2-Methy1-2-butano1	CJ	06	94.7+	<pre>z-isopropyi-3,3-aimetnyibutyric (0.0), uis (4.0) Trimethylacetic (23.5), α,α-dimethylbutyric (58.3), α,α-dimethylvaleric (7.8), ~-methyl-x-ethylbutyric (10.4)</pre>
	C2	06	98.9	Trimethylacetic (11.1), α, α-dimethylbutyric (55.5), α, α-dimethylvaleric (5.1), 
(11)	C3	80	96.5	u-metuyiru-etuyiyuutyiru (iz:+), cg (i:/), cg (iz:0), cig (z:2) Trimethylacetic (14.8), α, α-dimethylbutyric (44.3), α,α-dimethylvaleric (5.8),
2-Methyl-2-pentanol	C2	90.0	84.6	α-methyl=α-ethylputyric (10.4), Cg (0.4), Cg (1.74), Ci (1.7) Trimethylacetic (3.6), Cg (4.6), α,α-dimethylvaleric (52.5), α-methyl-α-ethyl- hutyric (24.6) α-ethylvaleric (5.4), α-methylcanroic (2.6), C. (6.7)
1Methyl-cyclohex-	C2	06,	63.7	l-Methylcyclohexane-l-carboxylic (100) (mp 39°, comp. [3])
anol-1 (IV)	: : : : : :	1 90	62.7	l-Methylcyclohexane-l-carboxylic (100) Trimsthulssontis (20-2) ≈_mothulturuis (20-2) f (41-6)
2-Heptanol (VI)	ទួ	06	85.0	a.α-Dimethylenanthic (31.9), α-methyl-α-ethylcaproic (38.2), α-methyl-α-propyl-
2-Hexanol (VII)	C3	100	91.3	<pre>valeric (21.3), α-ethylenanthic (5.0), α-methylcaproic (3.6) α,α-Dimethylvaleric (36.8), α-methyl-α-ethylbutyric (46.2), α-ethylvaleric</pre>
2-Octanol (VIII)	S	06	89.6 <sup>a</sup>	<pre>(14.1), C<sub>6</sub> (3.9) α.α-Dimethylenanthic (34.2). α-methyl-α-ethylcaproic (43.6). α-methyl-α-propyl-</pre>
	6		с со	valeric (11.1), $\alpha$ -ethylenanthic (5.8), $\alpha$ -methylcaprylic (5.3)
4-heptanol (LX)	5	20	0.20	α,α-Dimetnylenantnic (39.0), α-metnyl-α-etnylcaproic (30.0), α-metnyl-α-propyl- valeric (13.8), α-ethylenanthic (6.6), α-methylcaprylic (4.6)
Cyclopentanol (X)	CI	80	50.0	<pre>cis-Decalin-9-carboxylic (72.0) (mp 122°, comp. [14]), transdecalin-9-carboxylic (16 0) (mn 134 5° comm [41) unidentified decalincarboxylic (12.0)</pre>
(X)	C2	06	55.7	cis-Decaline-correction (60.0), trans-decalin-9-carboxylic (29.5), unidentified
(X)	<b>C</b> 3	60	76.0	cis-Decalin-9-carboxylic (18.5), trans-decalin-9-carboxylic (47.6), unidentified
				<pre>decalincarboxylic (4,4), cyclooctanecarboxylic (0.9), cycloheptanecarboxylic (2.1), cyclohexanecarboxylic (2.0), 1-methylcyclohexane-1-carboxylic (0.5), 1-ethylcyclohexane-1-carboxylic (1.3), cyclopentanecarboxylic (7.2), cyclo- butanecarboxylic (3.9), 1-methylcyclobutane-1-carboxylic (8.9), cyclopropane- carboxylic (1.5), 1-methylcyclonronona-1-carboxylic (1.2)</pre>
1-Propy1-1-cycla-	<b>c</b> 3	06	66.0	1-Propylcyclopentane-1-carboxylic (100) $[mp 132-137^{\circ} (760 mm), n_D^{2\circ} 1.4652]$
Cyclohexanol (XII)	C2 C3	06 80	54.5 69.5	<pre>1-Methylcyclopentane-1-carboxylic (49.2), cyclohexanecarboxylic (50.8) 1-Methylcyclopentane-1-carboxylic (61.5), cyclohexanecarboxylic (38.5)</pre>
*Average yield of aci +A mixture of acids ( atm in the presence o	ds after trimethy f Cl fro	r 10- (a /lacetic mn(II).	) and 6-f 20.8%, C	old (b) use of catalyst. , 4.0%, and 2,2,3,3-tetramethylvaleric 75.2%) was obtained at 150° and P <sub>CO</sub> = 100

TABLE 2. Effect of Temperature on Carbonylation of Tertiary Alcohols in the Presence of  $BF_3$ -Complex Catalysts (Cat) (mole ratio of Cat:alcohol = 2:1, rate of addition of alcohol to Cat 1 mole/mole of Cat·h,  $p_{CO}$  = 100 atm)

tert-Butanol, C3													
		_											
T., °C	acid, %		trimeth ylacetic	C <sub>6</sub>	C7	C <sub>8</sub>	2,2,4,4 tetra- methyl valeric		2-iso- propyl- 3,3-di- methyl- butyric	2-ethyl- 2,3,3- trimeth- ylbutyric	· C <sub>13</sub>		
25 45 <b>70</b> 90 100	77 83 87 74 64	77,7         68,0           83,8         60,4           87,4         64,0           74,5         72,6           64.5         79,2		2,6 1,7 4,3 7,6 9,1	- 4,8 7,9 5,5	$\begin{vmatrix} -\\ -\\ -\\ 2,6\\ 1,8 \end{vmatrix}$	16,3 20,0 16,1 9,3 5,2		4,5 12,1 6,0 »	1,1 3,1 - -	7,5 2,7 4.8 -		
					2-N	Aethy1-2	-butano	1, (	C1		<u> </u>		
							conte	ent	of acids,	%			
т.,	°C	acid, %		trimeth acetic	y1-	α,α-din butyric	nethyl-	α, va	,α-dimeth lleric	yl- a-me ethyl	α-methyl-α- ethylbutyric		
30 45 60 70 80 90 105 115 125			80,0 85,2 91,0 90,7 91,7 94,7 88,0 73,5 62,5	15.8 17.5 18.3 20,6 22,5 23,5 25,2 25,2 28,5 32,0		67. 65. 62. 59. 58. 51. 53. <b>46</b> .	5 1 4 3 9 3 8 8 0		6,0 6,4 7,3 6,2 9,4 7,8 11,9 8,9 9,5		10,8 11,0 12,0 11,9 12,2 10,4 11,1 8,8 12,5		

Formation of 2,2,3,3-tetramethylvaleric acid proceeds by interaction of tert-dimethylethyl carbonium ion A with 2-methyl-2-butene, formed from (II), with intermediate formation of a labile (at 150°) bridge cyclopropenyl transition cation B, which under acidic conditions decomposes with cleavage of an ethyl cation and the more stable tert-carbonium ion C, which is carbonylated further. Dimerization of 2-methyl-2-butene occurs at lower temperatures (<150°) with formation of  $C_{10}$  olefins, which decompose into  $C_4$  and  $C_6$  olefins, being transformed further into trimethylacetic acid and  $C_7$  acids, respectively. Compound (II) underwent disproportionation to a small degree and at 90° in the presence of C2 was transformed in 84.6% yield to carboxylic acids containing 52.5%  $\alpha$ , $\alpha$ -dimethylvaleric, 24.6%  $\alpha$ -methyl- $\alpha$ -ethylbutyric, 5.4%  $\alpha$ -ethylvaleric, and 2.6%  $\alpha$ -methyl-caproic acids, and only 14.5% of total  $C_5$ ,  $C_6$ ,  $C_7$ , and  $C_8$  acids.

Compounds (IV) and (XI) were transformed selectively to 1-methylcyclohexane-1-carboxylic and 1-n-propylcyclopentane-1-carboxylic acids in yields of 62-66%. Compound (V) under optimum conditions (125°,  $p_{CO}$  = 100 atm) was transformed in the presence of C3 to carboxylic acids (70% yield) containing 29.0% trimethylacetic, 29.0%  $\alpha$ -methylbutyric, and 42.0% C9 acids. The method of preparative chromatography and PMR and mass spectroscopy demonstrated the structure of the C9 acids formed from (V), which were a mixture of 2,2,4-trimethylcapronic, 2-ethyl-2, 3-dimethylvaleric, 2,2,5-trimethylcapronic, 2,2,3,4-tetramethylvaleric, and 2-ethyl-2,4dimethylvaleric acids, with the first three acids being formed from 2-butylene dimers; 2,2,3,-4-tetramethylvaleric acid is formed from 2,3,4-trimethyl-2-pentene and 2-ethyl-2,4-dimethylvaleric acid is formed from the dimer of isobutylene and 2-butene.

It should be noted that secondary alcohols in the presence of Cl and C2 were transformed into carboxylic acids in insufficiently high yields. In the presence of C3 carbonylation of secondary alcohols proceeded with formation of acids in high yields. Thus, (VI) and (IX) were transformed in yields of 82-85% to C<sub>8</sub> acids and (VIII) upon 10-fold use of C3 formed C<sub>9</sub> acids in an average yield of 89.6%. Cyclic alcohols (X) and (XII) were transformed into cyclic acids in a yield of 50-76%, the composition of which depends on the used catalyst. Thus, carboxylic acids formed from (X) in the presence of C1 contained 72.0% cis-decalin-9carboxylic acid, 16% trans-decalin-9-carboxylic acid, and 12% unidentified decalincarboxylic acis. Acids formed from (X) in the presence of C2 had approximately the same composition. In the presence of C3 from (X) in addition to the indicated decalincarboxylic acids were formed cyclooctane-, cycloheptane-, cyclohexane-, cyclopentane-, cyclobutane-, and cyclo-



Fig. 1. Effect of temperature on the carbonylation of alcohols in the presence of Cl or C<sub>3</sub> at  $p_{CO} = 100$  atm and a mole ratio of Cat:alcohol = 2:1. Yields of carboxylic acids: 1) from tert-butanol, C3; 2) from 2-methyl-2butanol, C1; 3) from 1-hexanol, C3; 4) from 2-butanok, C3; 5) from 2-hexanol, C3; 6) from 2-octanol, C3.

propanecarboxylic acids, and also 1-methylcyclobutane-1-carboxylic 1-ethylcyclopentane-1carboxylic, 1-methylcyclobutane-1-carboxylic, and 1-methylcyclopropane-1-carboxylic acids in a total content of 29.5%. Carboxylic acids from (XII) consisted of 1-methylcyclopentane-1-carboxylic and cyclohexanecarboxylic acids in a 1:1 ratio in the presence of C2 (yield 54.5%) and in a 1.5:1 ratio in the presence of C3 (yield 69.5%).

It is seen from Fig. 1 and Table 2 that tertiary alcohols (I) and (II) were transformed correspondingly into carboxylic acids in high yields in the presence of C3 and C1 in a broad temperature range. Upon increasing the reaction temperature the yield of acids from (I) increased from 77.7% at 25° to 87.4% at 70° and then decreased to 64.5% at 100°; in this case the content of trimethylacetic acid increased in the acid mixture from 68.0 to 79.2%, the content of C<sub>9</sub> acids decreased from 21.8 to 5.2%, and the content of C<sub>13</sub> acids decreased from 7.5 to 0%. With an increase in temperature the content of C<sub>6</sub>-C<sub>8</sub> acids increased in the acid mixture from 0% at 25° to 19.4% at 100°. Upon increasing the temperature the yield of acids from (II) increased from 80.0% at 30° to 4.97% at 90° and then gradually decreased to 62.5% at 125°. In this case the content of  $\alpha, \alpha$ -dimethylbutyric acid in the acid mixture from 67.5% at 30° to 46.0% at 125°, the content of trimethylacetic acid increased from 15.8 to 32.0%, and the content of  $\alpha, \alpha$ -dimethylvaleric and  $\alpha$ -methyl- $\alpha$ -ethylbutyric acids in the mixture did not change and amounted to 19-23%.

It is seen from Fig. 1 and Tables 1 and 3 that the ease of transformatin of alcohols to carboxylic acids increases upon going from primary to secondary and then to tertiary alcohols and that the catalytic activity increases upon going from C1 to C2 and then C3. The most active and selective catalysts of carbonylation of tert-alcohols are C1 and C2. System C3 was found to be most appropriate for carbonylation of secondary alcohols. Optimal temperatures of the carbonylation reaction of secondary alcohols in the presence of C3 decreased with an increase in molecular weight of the alcohol and were equal to 125° for (V) (yield of acid 69.2%), 100° for (VII) (91.3%), and 90° for (VIII) (89.6%).

It is seen from Table 3 that the composition of acids obtained from (XIII), (VII), and (VIII) changed insignificantly with an increase in temperature. An increase in reaction temperature during carbonylation of (V) led to an increase in content of dimeric C<sub>9</sub> acids from 17.4% at 90° to 41.0% at 125° and to a further decrease in their content from 5% at 135°. In this case the content of trimethylacetic acid decreased from 35.5% at 90° to 27.5% at 135° and the content of  $\alpha$ -methylbutyric acid increased correspondingly from 47.1% at 90° to 59.6% at 135°. It should be noted that a large portion of C<sub>9</sub> dimeric acids consisted of a mixture of 2,2,4-trimethylcaproic, 2-ethyl-2,3-dimethylvaleric, and 2,2,5-trimethylcaproic acids, i.e., acids formed from 2-butene dimers, while the content of 2,2,3,4-tetramethyl- and 2-ethyl-2,4-dimethylvaleric acids formed from 2,3,4-trimethyl-2-pentene and from the dimer of

TABLE 3. Effect of Temperature on Carbonylation of Primary and Secondary Alcohols in the Presence of the Catalytic System  $3BF_3 \cdot 2CH_2C1C00H_BF_3 \cdot 2CH_3C00H$  (C3) (mole ratio of Cat:alcohol = 2:1, rate of addition of alcohol to the Cat 1 mole/mole of Cat.h,  $p_{CO} = 100$  atm)

1-Hexanol																
acid content, %																
Т., °С	yie aci	1d of .d, %	trimeth- ylacetic		C <sub>6</sub>		α,α met vale	-di- hyl- eric	i- α-me yl- yl-α- c ethyl butyri		α-ethyl valeric		α-met ylcapro	h- oic	C <sub>13</sub>	
80 90 100 110		7,2 27,7 45,8 30,2		  1,4 3,0	$     \begin{array}{c}            $		4 4 3 3	4,0 2,0 8,5 5,0	34,2 33,6 34,8 31,8		13,5 14,6 15,8 15,2		2,7 2,9 2,5 4,5		5,6 6,9 3,8 6,0	
		<u></u>				2-E	Butar	nol (V	)		·					
			1					acid	cor	ntent,	%					
т., °С	yie] acio	ld of 1, %	trin ylad	neth- cetic	α-r ylb	neth- utyric	2,2, trin yl cap	4- neth- roic	2-e 2,3 mei val	thyl- -di- thyl- eric	2,2,5- trimethy- yl caproic		2,2,3,4- tetra- methyl- valeric		2-ethy1- 2,4-di- methy1- valeric	
90 100 125 135		48,3 35,0 39,2 43,2 *	3 3 2 2	5,5 1,9 9,2 7,5	47,1 49,0 29,2 59,6		1	4,4 4,7 0,6 2,8	$\begin{array}{c} 6,0\\ 6,4\\ 11,9\\ 2,2\end{array}$		3,5 4,5 6,3 –		1,7 1,9 2,8		1,8 1,6 -	
	·		·			2-	Hex	anol (	VII)		·				<u> </u>	
								acio	d co	ntent,	%					
Т., °(	C	yield o: acid, %	<b>f</b>	trime ylace	th- tic	Co		α,α- meth valer	di- yl- ic	α-me yl-α ethyl butyr	th- - ic	α-eth valer	thyl- eric		α-methyl- caproic	
80 90 100 110	) ) )	67,0 89,5 91,3 82,5		2,0 4,3	) 1,6 4,8 3,9 6,5			32,( 38,( 36,8 43,5	5 5 5 2	49,7 41,0 45,2 37,2		12,8 14,0 14,1 5,1		3,3  3,7		
Octanol-2 (VIII)																
acic content $\eta_0$											.1 1					
T., °C		acid, 9	I 2	trim acet	nethyl-α tic c		-methyl- c-ethyl- aproic		α-ethylenanthic		-	α-me α-pro valeri	ic α		methyl- proic	
60 70 80 90 100		62,7 79,2 85,0 89,6 † 82,3			37,6 28,0 41,9 34,2 31,2		36 44 37 43 31	36.8 44,5 37,3 43,6 31,8		8,3 8,4 6,1 5,8 6,2		1: 1: 11 11 11	13,2 15,4 1,4 1,1 1,1		4,1 3,6 3,3 5,3 15,1	

\*The mixture also contained 7.9% C7 acids.

†Average yield of acids after 10-fold use of the catalyst. ‡The mixture contained 4.6% total  $C_5$ ,  $C_6$ , and  $C_8$  acids.

isobutylene with 2-butene, respectively, were insignificant (1.7-2.8%) in the mixture of acids.

Thus, it can be concluded on the basis of the obtained data that complex catalysts C1, C2, and C3 are highly active and stable in the carbonylation reaction of tertiary and secondary alcohols and can be used repeatedly without a decrease in their activity. Primary alcohols in the presence of these catalysts were transformed in low yield into carboxylic acids.

#### EXPERIMENTAL

Carbonylation of alcohols under a CO pressure was carried out in a 0.3-liter stainlesssteel reactor having a shielded motor with addition of the alcohol to the catalyst over 20-30 min. In contrast to carbonylation of olefins, carbonylation of alcohols was carried out without addition of equimolar amounts of water to the catalyst. Carboxylic acids formed from alcohols during the reaction were separated from the homogeneous reaction mixture by extraction with n-hexane (4  $\times$  50 ml). After one use of the catalyst the carboxylic acids were separated by dilution of the reaction mixture with water.

The catalysts were prepared by the earlier described method [1, 2]. The obtained complexes had the following specific weights at 20°:  $BF_3 \cdot 2CH_3COOH 1.366$ ;  $BF_3 \cdot 2CH_3CH_2COOH 1.250$ ;  $3BF_3 \cdot 2CH_2ClCOOH\_BF_3 \cdot 2CH_3COOH 1.538$ . Alcohols with a purity 98.0% were used in the reaction.

The acid composition was determined on an LKhM-8MD chromatograph with a stainless-steel column, 2.5 m × 2 mm (at 186°), containing a stationary phase of 10% polyethylene glycol adipate and 3% H<sub>3</sub>PO<sub>4</sub> (of weight of support) on Chromosorb G with a flame-ionization detector and He as the carrier gas [1, 2, 5]. The carboxylic acids obtained by carbonylation of (I) were transformed into methyl esters and separated on an LKhP-5A preparative chromatograph of SKB KOKh AN SSSR construction on an 8 m × 20 mm column containing a stationary phase of 15% Carbowax 20M on Chromaton (0.25 mm); at 155° methyl 2-ethyl-2,3,3-trimethylbutyrate  $C_{10}H_{20}O_2$  was separated, bp 188.9-190.3° (760 mm),  $n_{D}^{\circ}$  1.4370. PMR spectrum ( $\delta$ , ppm): 0.845 s [9H, (CH<sub>3</sub>)<sub>3</sub> C]; 1.03 s [3H, (CH<sub>3</sub>)C(CH<sub>2</sub>CH<sub>3</sub>, J = 4.5 Hz); 3.50 s (3H, COOCH<sub>3</sub>). Mass-spectral data: 172 (M<sup>+</sup>), 157 (M<sup>+</sup> - CH<sub>3</sub>), 116 (M<sup>+</sup> - C<sub>4</sub>H<sub>8</sub>), 115 (M<sup>+</sup> - (CH<sub>3</sub>)<sub>3</sub>C), 113 (M<sup>+</sup> - COOCH<sub>3</sub>), 101 (M<sup>+</sup> - CH<sub>3</sub> + (CH<sub>3</sub>)<sub>3</sub>C, 57 (CH<sub>3</sub>)<sub>3</sub>C, 29 (C<sub>2</sub>H<sub>5</sub>).

From the mixture of carboxylic acids obtained from (II) in the presence of Cl at 150° and a CO pressure of 100 atm by rectification was separated 2,2,3,3-tetramethylvaleric acid [Found: C 68.55; H 11.36%. C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>. Calculated: C 68.4; H 11.4%; bp 130-135° (15 mm),  $n_D^{2°}$  1.4347], which by reaction with SOCl<sub>2</sub> was transformed into its acid chloride and then to methyl 2,2,3,3-tetramethylvalerate C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>, bp 188.5-189.1° (760 mm),  $n_D^{2°}$  1.4218,  $d_4^{2°}$  0.8783. PMR spectrum upon addition of a shift reagent (FOD)<sub>3</sub>Eu ( $\delta$ , ppm): 1.16 and 1.25, 2 g [12H, C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub> · COOCH<sub>3</sub>]; 0.83 distorted t (3H, CH<sub>2</sub>CH<sub>3</sub>, J = 6.5 Hz); 1.42-1.75 q (2H, CH<sub>2</sub>CH<sub>3</sub>, J = 6.5 Hz); 3.82 s (3H, COOCH<sub>3</sub>). Mass-spectral data: 172 (M<sup>+</sup>), 144 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 116 (M<sup>+</sup> - C<sub>4</sub>H<sub>8</sub>), 113 (M<sup>+</sup> -COOCH<sub>3</sub>), 102 (M<sup>+</sup> - C<sub>5</sub>H<sub>10</sub>), 101 (M<sup>+</sup> - C<sub>5</sub>H<sub>11</sub>), 71 (C<sub>5</sub>H<sub>11</sub>), 59 (COOCH<sub>3</sub>); 57 (C<sub>4</sub>H<sub>9</sub>).

The dimeric C, acids formed upon carbonylation of (V) were transformed into the methyl esters, from which by the method of preparative chromatography were separated esters of the acids (indicated in order of emergence from the analytical and preparative columns): 2,2,4-trimethylcaproic  $C_{10}H_{20}O_2$ , bp 181.8-181.9° (760 mm),  $n_D^2$ ° 1.4207; 2-ethyl-2,3-dimethylvaleric  $C_{10}H_{20}O_2$ , bp 183.4-183.6° (760 mm),  $n_D^2$ ° 1.4225; 2,2,5-trimethylcaproic  $C_{10}H_{20}O_2$ , bp 187-187.2° (760 mm),  $n_D^2$ ° 1.4270; 2,2,3,4-tetramethylvaleric  $C_{10}H_{20}O_2$ , bp 85-87° (33 mm),  $n_D^2$ ° 1.4342, d<sup>2</sup><sub>4</sub>° 0.9084, and 2-ethyl-2,4-dimethylvaleric  $C_{10}H_{20}O_2$ , bp 189.8-190.1° (760 mm),  $n_D^2$ ° 1.4287.

Reaction of a mixture (1:1) of (I) and (V) in the presence of 75% H<sub>2</sub>SO<sub>4</sub> by the known method [6] yielded 2,3,4-trimethy1-2-pentene, bp 116.1-116.5° (760 mm), n<sup>2°</sup><sub>D</sub> 1.4272, d<sup>2°</sup> 0.7446, the carbonylation of which in the presence of 82.5% H<sub>2</sub>SO<sub>4</sub> (molar ratio of H<sub>2</sub>SO<sub>4</sub>: olefin 3:1) at 10° and a CO pressure of 120 atm [7] or in the presence of C1 (80°, 100 atm of CO) yielded 2,2,3,4-tetramethylvaleric acid C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>, mp 97.7° (n-hexane). PMR spectrum of methyl 2,2,4-trimethylcaproate (8, ppm): 1.05 s [6H, C(CH<sub>3</sub>)<sub>2</sub>COOCH<sub>3</sub>): 0.50-0.93 combined t and d [6H, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)]; 1.12-1.72 m [5H, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>]; 3.55 s (3H, COOCH<sub>3</sub>). PMR spectrum of methyl 2-ethyl-2,3-dimethylvalerate (δ-ppm): 0.69-0.85 t [6H, CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)C(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>3</sub>), J = 4.55 Hz; 1.02-1.07 two s [6H, CH(CH<sub>3</sub>)C(CH<sub>3</sub>)]: 1.19-1.85 m [5H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)C(CH<sub>2</sub>CH<sub>3</sub>); 3.50 s (3H, COOCH<sub>3</sub>). Mass-spectral data:  $172 (M^+)$ , 144 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 116 (M<sup>+</sup> - C<sub>4</sub>H<sub>8</sub>), 113 (M<sup>+</sup> - (COOCH<sub>3</sub>)), 102 (M<sup>+</sup> - C<sub>5</sub>H<sub>10</sub>), 101 (M<sup>+</sup> - C<sub>5</sub>H<sub>11</sub>), 71 (C<sub>5</sub>H<sub>11</sub>), 59 (C<sub>4</sub>H<sub>9</sub>). PMR spectrum of methyl 2,2,5-trimethylcaproate (δ, ppm): 0.815 d [6H, (CH<sub>3</sub>)<sub>2</sub>CH]; 0.95 s [6H, C(CH<sub>3</sub>)<sub>2</sub>]; 1.11-1.98 m [5H, (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>); 3.48 s (3H, COOCH<sub>3</sub>). Mass-spectral data: 172 (M<sup>+</sup>), 116 (M<sup>+</sup> - $C_4H_8$ ), 113 (M<sup>+</sup>-COOCH<sub>3</sub>)), 102 (M<sup>+</sup>-C<sub>5</sub>H<sub>10</sub>) 101 (M<sup>+</sup>-C<sub>5</sub>H<sub>11</sub>), 87 (M<sup>+</sup>-C<sub>5</sub>H<sub>10</sub>+CH<sub>3</sub>)), 71 (C<sub>5</sub>H<sub>11</sub>), 57 (C<sub>4</sub>H<sub>9</sub>). In the mass spectrum were observed the metastable ions m<sub>1</sub>\* = 44.9 m<sub>2</sub>\* = 74.2, confirming the structure of the ester, namely the transitions 71<sup>-CH<sub>2</sub></sup> 57 and 102<sup>-CH<sub>3</sub></sup> 87, respectively. PMR spectrum of methyl 2,2,3,4-tetramethylvalerate ( $\delta$ , ppm): 0.835 and 0.99, the first s coincides with half d [10.5 H and 4.5 H,  $C(CH_3)_2$ ] and 1/2 d [( $CH_3$ )CHCH( $CH_3$ ), J = 7 Hz]; 1.45-2.29 m [2H, (CH<sub>3</sub>)<sub>2</sub>CHCH(CH<sub>3</sub>)]; 3.50 s (3H, COOCH<sub>3</sub>). Mass spectrum: 172 (M<sup>+</sup>), 116 (M<sup>+</sup> - $C_{4}H_{8}$ , 102 (M<sup>+</sup> -  $C_{5}H_{10}$ ), 87 (CH<sub>3</sub>-C<sup>+</sup> = C(OCH<sub>3</sub>)(OH)), 70 (C<sub>5</sub>H<sub>10</sub>), and a strong metastable ion  $m^* = 74.2$ , confirming the transition 102  $CH_3$  87. PMR spectrum of 2-ethyl-2,4-dimethylvalerate ( $\delta$ , ppm): 0.85 s [3H, (CH<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)COOCH<sub>3</sub>]; 0.92 d [6H, (CH<sub>3</sub>)<sub>2</sub>CH, J = 7 Hz); 0.69 t [3H, (CH<sub>3</sub>)- $C(CH_2CH_3)COOCH_3$ , J = 7 Hz]; 1.08-1.82 m [5H,  $(CH_3)_2CHCH_2C(CH_2CH_3)(CH_3)$ [; 3.50 s (3H, COOCH<sub>3</sub>). Mass-spectral data: 172 (M<sup>+</sup>), 144 (M<sup>+</sup> - C<sub>2</sub>H<sub>4</sub>), 143 (M<sup>+</sup> - C<sub>2</sub>H<sub>5</sub>), 116 (M<sup>+</sup> - (COOCH<sub>3</sub>)), 102  $(M^+ - C_6 H_{11}), 71 (C_5 H_{11}), 67 (C_4 H_9).$ 

## CONCLUSIONS

The complexes  $BF_3 \cdot 2CH_3CH_2COOH$  and  $BF_3 \cdot 2CH_3COOH$  and the system  $3BF_3 \cdot 2CH_2C1COOH-BF_3 \cdot 2CH_3-COOH$  are active and stable catalysts of the carbonylation reaction (80-100°,  $P_{CO}$  = 100 atm) of tertiary and secondary alcohols of aliphatic and cyclic structure with formation of carboxylic acids in high yields and can be used repeatedly without a decrease in the initial activity.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

AND THEIR HYDROPOLYMERIZATION ON EXPOSURE TO CARBON MONOXIDE AND

### HYDROGEN.

55.\* HYDROPOLYMERIZATION OF LOWER OLEFINS IN THE

PRESENCE OF Co-ZrO2 AND Co-TiO2 CATALYSTS

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Precipitated Co-catalysts, including oxides of metals of Groups II and III of the periodic system, are active in hydropolymerization reactions of olefins initiated by CO [1-3]. The nature of the metal oxides used as supports of Co-catalysts, has a significant effect on their activity. It was of interest to study the behavior of oxides of metals of Group (IV)  $(ZrO_2 \text{ and } TiO_2)$  as supports of Co-catalysts of the hydropolymerization reaction of lower olefins initiated by CO, since these oxides are promoters of precipitated Co-MgO-kieselguhr catalysts in processes of ethylene hydropolymerization and synthesis of aliphatic hydrocarbons from CO and H<sub>2</sub> [4, 5].

#### EXPERIMENTAL

The apparatus and experimental method for hydropolymerization of olefins at atmospheric pressure were described in [1, 2]. Catalyst samples were loaded into a quartz reactor placed in an electric-heating oven. All catalysts were treated before experiments with H<sub>2</sub> by the

\*See [1] for Communication 54. †Deceased.

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