Decarbonylation of π -C₅H₅(CO)₂(PPh₃)WCOC₅H₄Mn(CO)₃ (VI). A solution of 0.20 g of (VI) in 15 ml of m-xylene was refluxed for 15 min, cooled, and chromatographed. The PPh3 was eluted with petroleum ether, while elution with C6H6 gave 0.14 g of a mixture of (III) and (V), which was separated on Al_2O_3 plates (using a 1:3 C_6H_6 -petroleum ether mixture as the mobile phase). We obtained 0.11 g (83%) of (III) and 0.03 g (15%) of (V), which in their melting points were identical with the above described specimens.

CONCLUSIONS

Some organotungsten σ -derivatives of cymantrene, π -C₅H₅(CO)₃WR and π -C₅H₅(CO)₂(PPh₃)WR $(R = C_5H_4Mn(CO)_3 \text{ and } COC_5H_4Mn(CO)_3).$

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CARBONYLATION OF OLEFINS AND ALCOHOLS WITH CARBON MONOXIDE IN

PRESENCE OF CATALYST SYSTEM: BF3•H2O-LIQUID SO2

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Previously it was shown [1] that olefins, with branching at the double bond, and tertiary alcohols in a mixture with methanol or ethanol are selectively carbonylated to esters under mild conditions (-70°C, atmospheric pressure) in the presence of the catalyst system: SbCl5-HCl-liquid SO2. The high selectivity of this system is due to the fact that HCl reacts with branched olefins or with tertiary alcohols to give the tertiary alkyl chloride, which with $SbCl_5$ gives the complex R_3C^{+} ($SbCl_6$)⁻, which by reaction with CO is converted to the acylium complex R₃CCO•SbCl₆, the subsequent reaction of which with an alcohol gives the ester of a branched acid. It is also possible that HCl reacts with SbCl5 to give the complex H⁺•SbCl₆, which then reacts with either the olefin or alcohol in a CO atmosphere to give the carbonium and acylium complexes. The existence of the acylium complex in SO2 solution was observed experimentally by the NMR method [2].

In the present paper it was shown that branched olefins and tertiary alcohols are easily carbonylated under mild conditions (-30°, atmospheric pressure) in the presence of the catalyst system: BF₃•H₂O-liquid SO₂. This catalyst system is active only in the carbonylation of branched olefins and tertiary alcohols, apparently due to the fact that the unstable BFa monohydrate gives a part of its water to the SO₂ by the following scheme:

 $BF_3 \cdot H_2O + SO_2 \rightleftharpoons H_2SO_3 + BF_3$

The free BF_3 in liquid SO_2 solution can form the complex $BF_3 \cdot SO_2$ [3]. Liquid SO_2 , as a solvent with a high dielectric constant [4], facilitates the formation of carbonium and acylium ions from olefins or alcohols and CO, and consequently also the progress of carbonylation

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TABLE 1. Carbonylation of Olefins and Alcohols with Carbon Monoxide in Presence of $BF_3 \cdot H_2O$ -Liquid SO_2 at Atmospheric Pressure and $-30^{\circ}C$ (mole ratio $BF_3 \cdot H_2O$:olefin = 2:1 $BF_3 \cdot H_2O$:alcohol = 4:1)

	ds,			Amo	unt of acids,	0 %	
Starting compound	Yield of aci	trimethy l- acetic	α, α-dia methylbuty- ric	α-ethyl- butyric	α, α -di- methylval- eric α -methylbu- tvric	C ⁹	C ₁₀
Isobutylene 2-Methyl-2-butene 2-Methyl-1-pentene 2-Methyl-2-pentene 2,4,4-Trimethyl-1-pentene Triisobutylene tert-Butanol Dimethylethylcarbinol Dimethylpropylcarbinol 1-Methyl-1-cyclohexene Propylene tetramers	40,5 65,9 79,0 76,5 93,6 95,0 76,5 79,8 87,4 100,0 * 100,0	$\begin{array}{c} 16,6\\ 10,6\\ 3,2\\ 2,5\\ 25,5\\ 12,3\\ 52,1\\ 9,9\\ 1,2\\ -\\ -\\ -\end{array}$	$\begin{array}{c} 12,2 \\ 62,9 \\ 5,4 \\ 10,0 \\ 9,2 \\ 7,4 \\ 4,5 \\ 62,7 \\ 3,7 \\ - \\ - \end{array}$	3,0 7,2 	$\begin{array}{c c c} 10,7 & 9,4 \\ 86,1 & - \\ 85,2 & - \\ 11,4 & - \\ 7,9 & 4,6 \\ 14.3 & 95,1 \\ - & - \\ - & - \end{array}$	28,3 8,1 4.3 2,3 39,2 23,4 12,7 6,1 - -	32,4 - - 14,7 49,0 26,0 - - 100,0

* 1-Methyl-1-cyclohexanecarboxylic acid, mp 39°.

reactions. Liquid SO₂ apparently also has an effect on CO by facilitating its polarization and activity. H_2SO_3 is a weak acid and dissociates to give only a low H⁺ concentration. Due to this, only those olefins that directly give tertiary carbonium ions, i.e., branched olefins and tertiary alcohols, become involved in the reaction. The probability that equilibrium reaction exists between $BF_3 \cdot H_2O$ and SO_2 to give H_2SO_3 is confirmed by the fact that straight-chain olefins, as well as secondary and primary alcohols, do not enter into the carbonylation reaction, although $BF_3 \cdot H_2O$ is a stronger acid ($H_0 = -11.2$) than H_2SO_4 ($H_0 =$ -10.65) [5], which is also active in the carbonylation of straight-chain olefins at low temperatures [6].

From Table 1 it can be seen that the yield of the carboxylic acids increases with increase in the number of carbon atoms in the branched olefin or tertiary alcohol, along with an increase in the amount of monomeric acids in them and a decrease in the amount of disproportionation acids. In contrast to the di- and triisobutylenes, the propylene tetramer was carbonylated exclusively, in 98% yield, to the C¹³ acids. 1-Methyl-1-cyclohexene was converted quantitatively to 1-methyl-1-cyclohexanecarboxylic acid.

It is interesting to mention that, in the presence of $BF_3 \cdot H_2O$ -liquid SO₂, mixtures of C^5-C^{13} acids are formed from the di- and triisobutylenes. These mixtures also contain 2,2-dineopentylpropionic acid (I) (4-6%), which is not formed in the presence of $BF_3 \cdot 2CH_3CH_2$ -COOH or $BF_3 \cdot 2CH_3COOH$, which indicates that the found catalyst system has a milder effect (Table 2). The predominant formation of (I) could be expected when triisobutylene or diisobutylene, which is partially converted to triisobutylene, is used as the starting olefin. However, carbonium ion A is either slightly stable or completely unstable under the reaction conditions, and is isomerized to other carbonium ions with the formation of other C^{13} acids (see [7] for details).

 $(CH_3)_3CCH_2C(CH_3) = CHC(CH_3)_3 \longrightarrow [+H^+]_{-+} [(CH_3)_3CCH_2]_2^+ (CH_3) \xrightarrow{CO. H_2O}_{-H^+} \rightarrow [(CH_3)_3CCH_2]_2C(CH_3)COH (I)$

EXPERIMENTAL

We used olefins that were at least 99.7% pure, and also 2,4,4-trimethyl-1-pentene, bp $101.1-102.0^{\circ}$, $n_{D}^{2^{\circ}}$ 1.4089; triisobutylene (mixture of 1,1-dineopentylethylene and 2,2,4,6,6-pentamethyl-3-heptene in a 1:1 ratio), bp $177-178^{\circ}$ (760 mm), $n_{D}^{2^{\circ}}$ 1.4303; propylene tetramers, bp $60-95^{\circ}$ (9 mm), $n_{D}^{2^{\circ}}$ 1.4392; 1-methyl-1-cyclohexene, bp $102.3-102.6^{\circ}$ (760 mm), $n_{D}^{2^{\circ}}$ 1.4440; dimethylethylcarbinol, bp $102-103^{\circ}$ (760 mm), $n_{D}^{2^{\circ}}$ 1.4055, and dimethylpropylcarbinol, bp 122.5-123.5 (760 mm), $n_{D}^{2^{\circ}}$ 1.4121. The complex $BF_{3} \cdot H_{2}O$ (d₄^{2°} 1.778) was obtained by passing BF_{3} into water at $0-1^{\circ}$.

Into a 250-ml Erlenmeyer flask, equipped with a magnetic stirrer and placed in a glass beaker, containing a cooling mixture composed of acetone and dry ice, were charged 95 ml (2.2

	r~/]													ļ
								Amo	ount of aci	ids, %				
Catalyst)₀``£	CO pres-	Yield of acids, ϕ_b	trimeth- ylacetic			2,2,4,4- tetra- methyl- valeric	2-isopro- py1-3,3- dimeth- ylbuty- ric	2-ethyl- 2,3,3- trimeth- ylbuty- ric	2,2-di- neopen- tylpro- pionic	2-tert- buty1-3, 5,5-tri- methy1- caproic	2,2,4,4, 6,6-hexa methyl- heptano- ic	2-isopro- Py1-3,3,5, 5-tetra- methylca- proic	
			Mixture (of 2,4,4-tri	methy!	-1-pei	ntene and	2,4,4-tri	methyl-2-	-pentene (1,1)			1
BFa+2C2H5COOH	- 80	1 100	9'66	29,5	3,0	3,0	18,7	24,2	6,5	1	0'2 [3,9	4,2	
				2,	1,4-tri	methyl	i-1-pente	лe						
BFa+H2O - liquid	50 ₂ 30	Atm	0.00	25,5	2,6	11.4	25,0	10,0	4,2	5,9	2,3	2,9	4,2	
		Mixtur	e of 1,1-0	lineopentyl	ethyleı	ne and	2,2,4,6,6	i-pentame	ethy1-3-he	sptene (1:	1)			
BF ₁ -2CH ₅ COOH	180	100	87,8	34,8	2,2	1,7	18,1	20,1	4,4	1	1,0,1	5,1	7,5	
BFs - 2C2 II - COOIL	08	100		48,0	21	 	13,1	14,1	2,9	1	5.1	00 00 00 00 00 00	4,8	
BF ₃ ·H ₂ O - 11quia	$50_2 + -30$	Atm	0,46	1 12,4 1	7,4	1 6.7	14.2	0,0	3,2	1,5	20,9	12,0	13,0	

TABLE 2. Carbonylation of Di- and Triisobutylene in Presence of Complex BF₃ Catalysts (Ct) [Ct:olefin = 2:1 (mole ratio)]

moles) of liquid SO₂ and 24 ml (0.5 mole) of $BF_3 \cdot H_2O$. The system was blown with CO from a gas holder. The stopcock on the gas-outlet tube was closed, the stirrer was turned on, and 26.5 ml (0.25 mole) of 2-methyl-1-pentene was added from a dropping funnel in 1 h at -30°. Here 0.20-0.25 mole of CO was absorbed. After evaporating the SO₂ the reaction mixture was diluted with water. The upper organic layer was separated and combined with the benzene extracts of the aqueous layer. The benzene solution was treated with 20% NaOH solution and the alkaline solution was acidified with H₂SO₄ to give a mixture of acids in 79.0% yield. The mixture of acids was analyzed by GLC on an LKhM-8 MD chromatograph, using a 2.5 m × 2 mm stainless steel column packed with 15% poly(ethylene glycol adipate) and 3% H₃PO₄ deposited on Chromosorb G (60-80 mesh), at 186° [8].

The fractional distillation of the methyl esters of the mixed acids, obtained by the carbonylation of 2,4,4-trimethyl-1-pentene in the presence of $BF_3 \cdot H_2O$ -liquid SO_2 , led to the isolation of the previously unknown methyl ester of (I), $C_{14}H_{28}O_2$, bp 207.6-207.8° (760 mm), np^{2°} 1.4268, the saponification of which gave (I), bp 190-192° (15 mm). The structure of (I) and its methyl ester was confirmed by elemental analysis, and by the NMR and mass spectral data.

CONCLUSIONS

The carbonylation of olefins, with branching at the double bond, and of tertiary alcohols with CO at -30° and atmospheric pressure, in the presence of the catalyst system: BF₃• H₂O-liquid SO₂, leads to the formation of mixtures of α, α -dialkylalkanoic acids in 79-100% yield.

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REACTION OF TETRAKIS(TRIFLUOROMETHYL)ALLENE WITH [n⁵-C₅H₅Mo(CO)₃]

AND $[\eta^5 - C_5 H_5 W(CO)_3]^-$

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The gamut of the reactions of metal carbonyl anions with fluoroolefins, described in the literature, is restricted to olefins that contain a "vinylic" fluorine atom [1-4]. The σ -vinyl complexes of the metals are formed in these reactions when the anion has a sufficiently high nucleophilicity.

Previously we had shown [5-8] that the reaction of $[\eta^5-C_5H_5Fe(CO)_2]^{-1}$ and $[Re(CO)_5]^{-1}$ with tetrakis(trifluoromethyl)allene leads to the fluorinated σ -dienyl, π -allylidene, and π -pentadienylidene complexes. The results of studying the reaction of (I) with the anions $[\eta^5-C_5H_5W(CO)_3]^{-1}$ and $[\eta^5-C_5H_5MO(CO)_3]^{-1}$ are given in the present communication.

The reaction of $[n^5-C_5H_5W(CO)_3]^-$ with (I) in THF at $-20^{\circ}C$ gives the σ -complex (II), which represents orange crystals that are readily soluble in the common organic solvents, and in the solid state are stable in the air and for several hours in solution.

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