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CARBONYLATION OF BRANCHED OLEFINS IN THE PRESENCE OF $BF_3 \cdot H_2O$ AND ETHYL FORMATE AT ATMOSPHERIC PRESSURE

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Esters of α, α-branched carboxylic acids may be obtained by the carbonylation of olefins with CO in the presence of acidic catalysts at 100-200 atm [1, 2]. This process may also be carried out at atmospheric pressure, using formic acid and sulfuric acid as the source of CO [3] with subsequent treatment of the reaction mixture with water or alcohol in order to decompose the acyl complex $R\overset{+}{C}O \cdot H_2SO_4$ and the separation of the forming α, α-branched carboxylic acids or their esters. Great interest lies in the one-step preparation of the esters of branched carboxylic acids by the carbonylation of olefins using ethyl formate (EF) as the source of CO and esterification agent in the presence of H_2SO_4 or H_3PO_4 [4, 5].

In the present communication, the results are given for a study of this reaction using the complex of BF_3 with water as the catalyst.

The major products of the carbonylation of 2-methyl-2-butene with EF in the presence of $BF_3 \cdot H_2O$ as the catalyst at atmospheric pressure were the ethyl esters (EE) of α, α-dimethylbutyric (α, α-DMB), α-ethylbutyric (α-EB), and of C_7, C_8, and C_9 acids (Table 1). Ethyl trimethylacetate (TMA) was also formed.

Change in the olefin (O1):catalyst (Ct):EF molar ratio affects the yields and composition of the ester products. The greatest ester yield was obtained (49.4%) for O1:Ct:EF = 1:4:8 (see Table 1, experiment 9). Doubling the catalyst concentration (runs 1 and 4) does not lead to a change in the total yield of esters (39%), though it has a significant effect on the product composition. An increase in the EF:Ct molar ratio by a factor of 2-3 (runs 1-3) with O1:Ct = 1:1 leads to an increase in the amount of C_6 acid ethyl esters and equivalent decrease in the ethyl esters of the disproportionation acids (TMA and C_7-C_9 acids). Similar behavior was found upon increasing the EF:Ct molar ratio by a factor of 2-3 for O1:Ct molar ratio = 1:2 (runs 4-6) and 1:4 (7-9).

Upon increasing the temperature from 20 to 75°C (Table 2), the total ester yield passes through a maximum at 60°C. The content of EE α, α-DMB decreases by more than a factor of 2. The content of EE α-EB drops from 37.0 to 26.5% upon increasing the temperature from 20 to 60°C and then increases to 33.7% at 70°C. The total content of the ethyl esters of the C_5, C_7, C_8, and C_9 disproportionation acids increases from 16% at 20°C to 45% at 70°C. In the case of the carbethoxylation of 2-methyl-2-pentene (Table 3) using EF in the presence of $BF_3 \cdot H_2O$, the yield of ethyl esters increases from 36 to 56% in going from 20 to 80°C and the content of the ethyl esters of the monomeric acids, α, α-dimethylvaleric (α, α-DMV) and α-methyl-α-ethylbutyric (α-M-α-EB) acids passes through a maximum 27.4% at 70°C and 62% at 30°C, respectively. The maximum total yield of the ethyl esters of α, α-DMV and α-M-α-EB is 73% at 30°C.

Examination of the ratio of the yields of the ethyl esters of α, α-DMV and α-M-α-EB with increasing temperature indicates that the ester α, α-DMV is a product of the isomerization of carbocation C which forms from carbocation B or of

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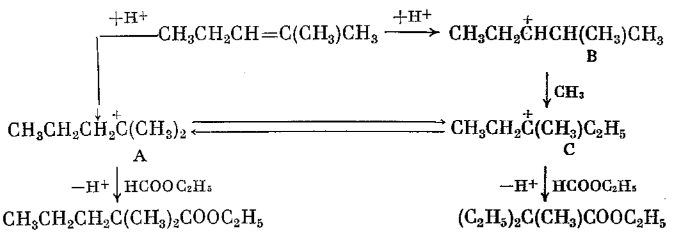
TABLE 1. Effect of the Molar Ratio of Reagents and Catalyst on the Carbethoxylation of 2-Methyl-2-butene in the Presence of $BF_3 \cdot H_2O$ at 60°C

Experiment no.	Molar ratio			Ester yield, %	Content of ethyl esters, %					
	olefin	catalyst	ethyl formate		trimethylacetic	α, α-dimethylbutyric	α-ethylbutyric	C_7	C_8	C_9
1	1	1	2	38,8	12,3	27,4	35,3	10,2	8,0	6,8
2	1	1	4	39,4	8,6	34,1	35,2	8,8	7,9	5,4
3	1	1	6	42,7	4,6	43,2	34,2	10,1	3,9	4,0
4	1	2	2	39,4	4,3	10,3	21,7	23,9	18,4	21,4
5	1	2	4	42,2	9,3	10,9	23,7	17,2	18,2	20,7
6	1	2	6	43,3	8,0	47,4	29,6	6,8	4,4	3,8
7	1	4	4	46,0	18,1	25,0	7,4	21,4	16,1	12,0
8	1	4	6	46,3	10,3	16,3	32,3	22,4	11,8	6,9
9	1	4	8	49,4	8,7	31,7	26,5	14,3	11,6	7,2

TABLE 2. Temperature Effect on the Carbonylation of 2-Methyl-2-butene by Ethyl Formate (EF) in the Presence of $BF_3 \cdot H_2O$ (Ct) for Molar Ratio O1:Ct:EF = 1:4:8

T., °C	Ester yield, % of starting alcohol	Content of ethyl esters, %					
		trimethylacetic	α,α-dimethylbutyric	α-ethylbutyric	C_7	C_8	C_9
20	32,2	3,2	46,9	37,0	7,9	2,0	3,0
30	38,3	6,3	42,4	36,3	6,1	4,1	4,8
40	39,4	6,4	41,4	30,6	12,0	3,9	5,7
50	42,2	9,9	33,2	28,1	15,2	9,0	4,6
60	49,4	8,7	31,7	26,5	14,3	11,6	7,2
75	44,4	8,2	21,7	33,7	12,3	13,7	10,4

the isomerization of carbocation A. Carbonium ions A and C are presumably in dynamic equilibrium. Carbonium ion A is clearly less stable under the reaction conditions than carbonium ion C. The formation of carbonium ions A and B may occur by two parallel pathways:



The possibility of adding a proton to the less-substituted carbon atom under acidic carbonylation conditions was shown in our earlier work [6]. The secondary carbonium ion B as the less stable ion isomerizes into ion C through the migration of a methyl group along the chain with displacement of a hydride ion. In addition to the ethyl esters of C_7 acids, the ethyl esters of trimethylacetic and C_6 acids are also formed. The fraction of ethyl trimethylacetate in the reaction products passes through a minimum of 11.4% at 30°C. The fraction of the C_6 esters varies from 8 to 17%. The ester mixture contains 15% C_8 esters at 80°C (see Table 3).

The carbonylation of the di- and triisobutylenes in the presence of $BF_3 \cdot H_2O$ (Table 4) and EF involves the disproportionation of the isobutylene monomeric fragment, which is later converted into ethyl trimethylacetate. The disproportionation of di- and triisobutylenes is enhanced with increasing temperature. Thus, at 20-40°C, diisobutylene undergoes carbethoxylation to yield ethyl esters in 67-68% yield, which consist of 90% C_9 acid esters and only 10% ethyl trimethylacetate. The ethyl ester yield drops from 71.5 to 32.7% with a further increase in temperature from 50 to 90°C, while the fraction of C_9 acid esters in the mixture drops from 85.7 to 37%. The fraction of the ethyl esters of the disproportionation acids (ethyl trimethylacetate, and the C_7 and C_{13} acid esters) increases from 5 to 63%.

In the presence of $BF_3 \cdot H_2O$ as catalyst, triisobutylene reacts with EF analogously to diisobutylene (see Table 4), although the maximum yield of ethyl esters from triisobutylene occurs at 80-90°C and not at 50°C. Disporportionation of triisobutylene to di- and isobutylene is observed (Table 5). Even at low temperature (20-40°C), triisobutylene is converted under the conditions studied to ethyl esters in 50-59% yield, which consists of 82-89% C_9 acid esters and 11-18% ethyl trimethylacetate. With increasing reaction temperature from 50 to 90°C, the ester yield in the carbethoxylation of triisobutylene using EF increases from 59 to 71-72%. The esters consist mainly of the ethyl esters of the disproportionation

TABLE 3. The Temperature Effect on the Carbonylation of 2-Methyl-2-pentene by Ethyl Formate (EF) in the Presence of $BF_3 \cdot H_2O$ (Ct) with Molar Ratio Ol:Ct:EF = 1:4:8

T., °C	Ester yield, % of original olefin	Ester composition, %				
		trimethylacetic	C_6	α, α-dimethylvaleric	α-methyl- and α-ethylbutyric	C_8
20	36,0	33,8	8,6	11,4	46,2	–
30	50,5	11,4	15,5	11,2	61,9	–
40	53,2	18,9	12,0	9,4	59,7	–
50	54,1	24,3	17,2	11,6	46,9	–
60	55,0	26,0	16,1	14.2	43,7	–
70	56,8	32,0	8,2	27,4	32,4	–
80	55,9	38,3	11,7	16,2	18,7	15,1

TABLE 4. Temperature Effect on the Carbonylation of Diisobutylene by Ethyl Formate (EF) in the Presence of $BF_3 \cdot H_2O$ with Molar Ratio Ol:Ct:EF = 1:4:8

T., °C	Ester yield, % of original olefin	Ester composition, %			
		trimethylacetic	C_7	C_9	C_{13}
20	67,0	8,3	–	91,7	–
30	63,8	8,2	–	91,8	–
40	68,5	11,5	–	88.5	–
50	71,5	5,2	–	94,8	–
60	68,4	4,9	9,4	85,7	–
70	66,9	9,8	13,8	76,4	–
80	59,9	13,1	17,1	58,0	11,8
90	32,7	21,6	19,7	37,0	21,7

TABLE 5. Temperature Effect on the Carbonylation of Triisobutylene by Ethyl Formate (EF) in the Presence of $BF_3 \cdot H_2O$ (Ct) with Molar Ratio Ol:Ct:EF = 1:4:8

T., °C	Ester yield, % of original alcohol	Ester composition, %			
		trimethylacetic	C_6+C_7	C_9	C_{13}
20	50,2	18,0	–	82.0	–
30	56,2	11,0	–	89,0	–
40	56,2	11,0	–	89,0	–
50	59,2	4,9	–	87,2	7,9
60	65,1	5,3	4,8	71,2	11,5
70	70,0	13,3	6,5	57,5	13,3
80	72,2	35,4	22,6	12,4	16,7
90	71,6	35,8	21,5	11,8	17,1

acids: ethyl trimethylacetate and C_9 and C_6 acid esters. The ethyl esters of C_{13} acids are formed in small amounts (7-17%). We should note that the fraction of C_9 acid esters in the ester mixture drops from 87 to 12% upon increasing the reaction temperature from 50 to 90°C. The increase in the fraction of C_{13} acid esters from 8 to 17% in the ester mixture upon an increase in temperature from 50 to 90°C is related to the increasing rate of carbethoxylation of triisobutylene with a concurrent increase in the extent of disproportionation of the starting olefin.

Thus, our results indicate that the ethyl esters of α, α-branched carboxylic acids may be prepared in high yields (50-70%) in the one-stage carbethoxylation of branched olefins using ethyl formate at 1 atm in the presence of $BF_3 \cdot H_2O$. The molar ratio of the substrate to the catalyst and ethyl formate and the reaction temperature have a significant effect on the olefin carbethoxylation process.

EXPERIMENTAL

We used samples of 2-methyl-2-butene (bp 38-38.5°C, n_D^{20} 1.3870), 2-methyl-2-pentene (bp 68-70°C, n_D^{20} 1.3998), diisobutylene (a 1:1 mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with bp 102-104°C, n_D^{20} 1.4133), triisobutylene (a 1:1 mixture of 1,1-dineopentylethylene and 2,2,4,6,6-pentamethyl-3-heptene with bp 177-178°C and n_D^{20} 1.4303), and ethyl formate (EF) (bp 54.2°C, n_D^{20} 1.3598). The $BF_3 \cdot H_2O$ catalyst (d = 1.77) was prepared by the saturation of distilled water cooled by ice at 0°C with gaseous BF_3.

A flask was loaded with 24.3 ml (0.5 mole) $BF_3 \cdot H_2O$ and a dropping funnel was loaded with 0.125 mole olefin and 1 mole EF. The flask was connected to a Tishchenko bottle filled with n-heptane and placed in a water bath heated to the reaction temperature. The mixture of olefin and EF was added to the catalyst dropwise over ∿1.5 h with stirring. After completing the addition of the mixture of olefin and EF to the catalyst, the reaction mixture was stirred for an additional hour. The reaction products were washed with a small amount of 10% aqueous KOH and then with several portions of saturated aqueous NaCl and of water. The ethyl esters of the carboxylic acids were analyzed by gas–liquid chromatography [7].

CONCLUSIONS

The carbonylation of branched olefins using ethyl formate occurs in one stage at atmospheric pressure in the presence of $BF_3 \cdot H_2O$ as catalyst with the production of the ethyl esters of α, α-branched carboxylic acids in yields up to 50-70%.

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POLYMERIZATION OF 1,2-DIMETHYLENECYCLOBUTANE

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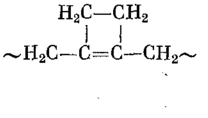
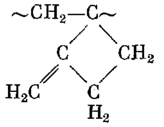
Polymers containing strained four-membered carbocycles in their chains are of considerable interest, but there is little information in the literature on their synthesis, owing to the difficulties in obtaining the corresponding monomers. The most promising monomer for the preparation of such polymers is 1,2-dimethylenecyclobutane (1,2-DMCB), which is obtained by the thermal dimerization of allene. Polymerization of 1,2-DMCB can result in the formation of two types of chain units



1,4-unit



1,2-unit

Polymerization of 1,2-DMCB by free-radical initiators has been reported briefly [1, 2]. According to the IR spectra and data on the rate of oxidation by peracids, the resulting poly-DMCB contained 66-80% of 1,4-units and 20-34% of 1,2-units [1, 2].

This communication reports a study of the microstructure and some of the properties of the 1,2-DMCB polymer obtained by radical polymerization. The polymerization was carried out with technical allene dimerization product following several distillations, consisting mainly of a mixture of 1,2- and 1,3-DMCB in a ratio of 7:3, separation of which (bp's 74 and 69°C, respectively) was found to be very difficult, owing to the ready thermal polymerization of 1,2-DMCB under the conditions of the fractionation. In view of the very low reactivity of the 1,3-isomer in comparison with the conjugated 1,2-DMCB, the pure 1,2-isomer was not isolated for this investigation.

Polymerization of DMCB was carried out either in benzene solution, or as an aqueous emulsion. Polymerization

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