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CODIMERIZATION AND CARBONYLATION OF NORMAL ALKENES AND ISOBUTYLENE

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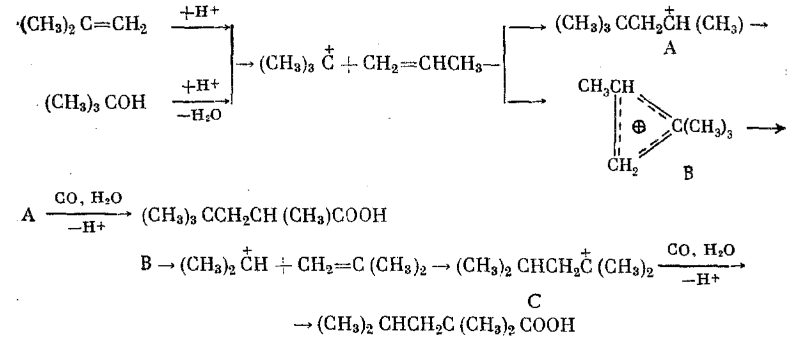
The carbonylation of alkenes and alcohols in the presence of acid catalysts is accompanied to a considerable extent by polymerization and disproportionation processes (up to 60%) [1, 2]. In order to inhibit these processes, carbonylation is carried out under a CO pressure up to 200-600 atm [1].

It has recently been shown [3] that tertiary alcohols and alkenes which have branching at the double bond are selectively carbonylated by CO in the presence of a $BF_3 \cdot H_2O$ — liquid-SO_2 catalyst (with a mole ratio of the $BF_3 \cdot H_2O$ to the alkene or alcohol equal to 2 : 1 to 4 : 1, at atmospheric pressure, and at −30°C) to form α, α-dialkylalkanoic acids. Normal alkenes are not carbonylated under these conditions.

In the present work we have shown that in the presence of the $BF_3 \cdot H_2O$ — liquid-SO_2 catalyst normal alkenes mixed with equimolar amounts of alkene with a branch at the double bond (or a tertiary alcohol) undergo selective codimerization to form carbonium ions followed by their carbonylation to form carboxylic acids with a 70-93% yield at −30°C and under 1 atm of CO.

When a 1 : 1 : 1 mixture of C_3H_6, i-C_4H_8, and CO is passed over the $BF_3 \cdot H_2O$ — liquid-SO_2 catalyst, the codimerization and carbonylation of C_3H_6 and i-C_4H_8 to form a 2 : 1 mixture of 2,4,4-trimethyl- and 2,2,4-trimethylvaleric acid take place, the former acid appearing after the intermediate formation of carbonium ion A, and the latter acid appearing after the intermediate formation of the cyclopropenyl cation B, which, upon dissociation, transfers a proton to propylene and is then converted into carbonium ion C (scheme 1).

Scheme 1



The probability of the existence of the cyclopropenyl cations has been pointed out by many workers [4], and additional support comes from the fact that in the absence of i-C_4H_8 propylene not only is not carbonylated, but is not even absorbed. It should be noted that the final gas does not contain either C_3H_6 or i-C_4H_8, indicating that they react simultaneously. The selectivity of the conversion of propylene into codimeric acids in a mixture with tert-butanol is slightly higher (87.3%) than in the mixture with isobutylene (72.5%) (Table 1).

When a 1 : 1 mixture of C_3H_6 and 2,4,4-trimethyl-1-pentene is reacted with CO, codimerization and carbonylation take place with a 70.6% yield, the C_3H_6 being 53.2% codimerized with the 2,4,4-trimethyl-1-pentene and 17.4% carbonylated to form C_{12} acids, as well as carbonylated with its splitting product, viz., isobutylene, to form C_8 acids.

The codimerization and carbonylation of α-olefins with a > C_3 composition and i-C_4H_8 (or tert-butanol) proceed in such a manner that $\overset{+}{C}(CH_3)_3$ at first forms from i-C_4H_8 or tert-butanol and is added according to

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TABLE 1. Codimerization and Carbonylation of 1:1 Mixtures of Normal or Cyclic Alkenes and Branched Alkenes or tert-Butanol in the Presence of a Catalytic System*

n-Alkene	Branched olefin or tertiary alcohol	Yield of acids, %	Total content of codimeric acids, %	Relative concentrations of acids, % (the codimeric acids are listed first)
Propylene	i-C_4H_8	100	72.5[a]	2:1 mixture of 2,4,4-trimethyl- and 2,2,4-trimethylvaleric, 72.5; trimethylacetic, 5.4; α,α-dimethylbutyric, 1.0; C_7, 6.0; C_9, 7.8; C_{13}, 7.2.
"	tert-Butanol	100	87.3[b]	2:1 mixture of 2,4,4-trimethyl- and 2,2,4-trimethyl-valeric, 87.3; trimethylacetic, 4.2; α,α-dimethylbutyric, 0.8; C_7, 1.8; C_9, 2.8; C_{13}, 3.1.
"	2,4,4-Trimethyl-1-pentene	96.7	70.6[c]	C_{12}, 53.2; codimeric C_8 acids from propylene and isobutylene, 17.4; trimethylacetic, 4.1; α,α-dimethylbutyric, 4.3; C_7, 5.6; C_9, 5.4.
1.4:1.4:1 mixture of 1-butene, trans-2-butene, and cis-2-butene	i-C_4H_8	98.0	33.4	2-Ethyl-4,4-dimethylvaleric, 12.7; 2,3,4,4-tetramethylvaleric, 15.0; 2-ethyl-2,3,3-trimethylbutyric, 5.7; trimethylbutyric, 19.9; α,α-dimethylbutyric, 9.3; C_7, 8.2; 2,2,4,4-tetramethylvaleric, 15.3; C_{13}, 14.4.
Same	tert-Butanol	87.5	84.9	2-Ethyl-4,4-dimethylvaleric, 19.2; 2,3,4,4-tetramethylvaleric, 56.1; 2-ethyl-2,3,3-trimethylbutyric, 9.6; trimethylacetic, 4.9; α,α-dimethylbutyric, 1.2; C_7, 3.0; C_{13}, 6.0.
1:2.3 mixture of 1-pentene and 2-pentene	i-C_4H_8	85.5	40.8	2-Neopentylvaleric, 9.2; 2,2,3-trimethylhexan-4-oic, 12.4; 3-ethyl-2,4,4-trimethylvaleric, 15.3; 1:1 mixture of 2-n-propyl-2,3,3-trimethyl- and 2,2-diethy-3,3-dimethylbutyric, 3.9; trimethylacetic, 15.9; α,α-dimethylbutyric, 14.6; C_7, 6.4; 2,2,4,4-tetramethylvaleric, 17.8; 2-isopropyl-3,3-dimethylbutyric, 4.5.
Same	tert-Butanol	89.8	91.3	2-Neopentylvaleric, 7.2; 2,2,3-trimethylhexan-4-oic, 37.2; 3-ethyl-2,4,4-trimethylvaleric, 1:1 mixture of 2-n-propyl-2,3,-3-trimethyl- and 2,2-diethyl-3,3-dimethylbutyric, 9.7; trimethylacetic, 2.0; α,α-dimethylbutyric, 2.2; C_7, 2.3; 2,2,4,4-tetramethylvaleric, 2.2.
1-Hexene	i-C_4H_8	100.0	81.2	4:1 mixture of 2-neopentylcaproic and 2,2,3-trimethylheptan-4-oic, 81.2; trimethylacetic, 8.9, α,α-dimethylbutyric, 2.3; C_7, 3.9; C_9, 3.7.

1-Hexene	tert-Butanol	84.7	90.4	4 : 1 mixture of 2-neopentylcaproic and 2, 2, 3-trimethylheptan-4-oic, 90.4; total C_5, C_6, C_7, and C_9, 9.6.
"	i-C_4H_8	95.5	95.0[d]	4 : 1 mixture of 2-neopentylcaproic and 2, 2, 3-trimethylheptan-4-oic, 95.0; total C_5, C_6, and C_7, 5.0.
"	2-Methyl-1-pentene	100.0	91.4	16.4 : 60 : 15.0 mixture of 7, 7-dimethyldecan-5-oic, 5, 6, 6-trimethylnonan-4-oic, and 2-n-butyl-2, 3, 3-trimethylcaproic, 91.4; C_7, 8.6.
1-Heptene	i-C_4H_8	95.2	93.0	4 : 1 mixture of 2-neopentylenanthic and 2, 2, 3-trimethyloctan-4-oic, 93.0; C_8, 7.0.
1-Heptene	tert-Butanol	89.2	81.7	4 : 1 mixture of 2-neopentylenanthic and 2, 2, 3-trimethyloctan-4-oic, 81.7; total C_5, C_6, C_7, and C_9, 18.3.
1-Octene	i-C_4H_8	100.0	79.0	4 : 1 mixture of 2-neopentyloctanoic and 2, 2, 3-trimethylnonan-4-oic, 79.0; total C_5, C_6, C_7, C_9, and C_{13}, 21.0
"	tert-Butanol	81.3	79.2	4 : 1 mixture of 2-neopentyloctanoic and 2, 2, 3-trimethylnonan-4-oic 79.2; total C_5, C_6, C_7, C_9, and C_{13}, 20.8.
1-Nonene	i-C_4H_8	92.0	95.5	4 : 1 mixture of 2-neopentylnonanoic and 2,2,3-trimethyldecan-4-oic, 95.5; total C_5, C_6, and C_7, 4.5
1-Decene	i-C_4H_8	97.1	97.0	4 : 1 mixture of 2-neopentyldecanoic and 2, 2, 3-trimethylundecan-4-oic, 97.0; C_5 C_6, and C_7, 3.0.
1-Dodecene	i-C_4H_8	96.1	93.8	4 : 1 mixture of 2-neopentyldodecanoic and 2, 2, 3-trimethyltridecan-4-oic, 93.8; total C_5, C_6, and C_7, 6.2
1-Pentadecene	i-C_4H_8	95.0	92.0	3 : 1 mixture of 2-n-heptyl-2-tert-butylnonanoic and 3-tert-butylnonanoic and 3-tert-butyl-2-n-hexyldecanoic, 92.0; total C_5, C_6, and C_7, 8.0
1-Hexadecene	i-C_4H_8	92.5	96.0	4 : 1 mixture of 2-neopentylhexadecanoic and 2, 2, 3-trimethylheptadecan-4-oic, 96.0; total C_5, C_6, and C_7, 4.0

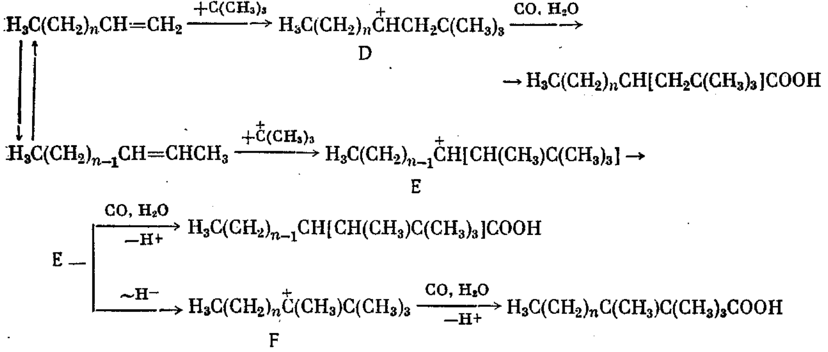
* $BF_3 \cdot H_2O$ — liquid-SO_2 system, mole ratio of $BF_3 \cdot H_2O$ to the mixture of olefins or the mixture of the olefin and tert-butanol equal to 2 : 1, —30 to —40°C, 1 atm of CO, reaction time equal to 2 h.

[a] A 1 : 1 : 1 mixture of C_3H_6, i-C_4H_8, and CO was used, the reaction time was 4 h, the rate of formation of the carboxylic acids was 0.1 mole/mole catalyst · h, the final gas contained only carbon monoxide, and 0.5 mole of $BF_3 \cdot H_2O$ was taken in the reaction. b) A 1 : 1 mixture of C_3H_6 and CO was used, the reaction time was 4 h, the rate of formation of the carboxylic acids was 0.05 mole/mole catalyst · h, the final gas contained only CO, and 0.5 mole of $BF_3 \cdot H_2O$ was taken in the reaction. c) The catalyst : 2, 4, 4-trimethyl-1-pentene mole ratio was 2 : 1, and the rate of formation of the acids was 0.2 mole/mole catalyst · h. d) A 2 : 1 mixture of 1-hexene and i-C_4H_8 was used, and the yield of acids is given as calculated for an equimolar mixture of these olefins.

Markovnikov's rule to the first carbon atom of the α-olefin to form the codimeric carbonium ions D, which are converted with CO and water into 2-neopentylalkan-1-oic acids. In the case of β-olefins formed by the isomerization of α-olefins, the addition of $C(CH_3)_3$ takes place at the second C atom to form carbonium ions D, which are converted with CO and water into 2, 2, 3-trimethylalkan-4-oic acids. Carbonium ions D, which have tertiary H atoms on the C atoms adjacent to the carbonium ion centers, are inclined to a small extent to undergo displacement of the hydride ions to form tertiary carbonium ions E, which are converted with CO and water into 2, 2, 3-trimethylalkan-3-oic acids (Scheme 2).

Scheme 2

Codimerization and carbonylation of α-olefins and isobutylene or tert-butanol.



$$H_3C(CH_2)_nCH{=}CH_2 \xrightarrow{+\overset{+}{C}(CH_3)_3} \underset{D}{H_3C(CH_2)_n\overset{+}{C}HCH_2C(CH_3)_3} \xrightarrow{CO,\ H_2O} \rightarrow H_3C(CH_2)_nCH[CH_2C(CH_3)_3]COOH$$

$$\Big\downarrow\!\uparrow$$

$$H_3C(CH_2)_{n-1}CH{=}CHCH_3 \xrightarrow{+\overset{+}{C}(CH_3)_3} \underset{E}{H_3C(CH_2)_{n-1}\overset{+}{C}H[CH(CH_3)C(CH_3)_3]} \rightarrow$$

$$E \xrightarrow[-H^+]{CO,\ H_2O} H_3C(CH_2)_{n-1}CH[CH(CH_3)C(CH_3)_3]COOH$$

$$E \xrightarrow{\sim H^-} \underset{F}{H_3C(CH_2)_n\overset{+}{C}(CH_3)C(CH_3)_3} \xrightarrow[-H^+]{CO,\ H_2O} H_3C(CH_2)_nC(CH_3)C(CH_3)_3COOH$$

where n = 1-13.

For example, C_9 acids were obtained from a mixture of 1-butene and 2-butene with i-C_4H_8 (or tert-butanol). These include 2-ethyl-4, 4-dimethylvaleric acid, 2, 3, 4, 4-tetramethylvaleric acid, and 2-ethyl-2, 3, 3-trimethylbutyric acid, which arise from carbonium ions of types D, E, and F, respectively, the highest selectivity for the conversion into the codimeric acids (84.9%) being achieved in the mixture with tert-butanol.

Five codimeric C_{10} acids were obtained from a mixture of 1-pentene and 2-pentene with i-C_4H_8 (or tert-butanol), viz., 2-neopentylvaleric acid, 2, 2, 3-trimethylhexan-4-oic acid, and 3-ethyl-2, 4, 4-trimethylvaleric acid, which appear as a result of the carbonylation of the carbonium ions formed by the addition of $\overset{+}{C}(CH_3)_3$, respectively, to the first C atom of 1-pentene or the second and third C atoms of 2-pentene, as well as a 1 : 1 mixture of 2-n-propyl-2, 3, 3-trimethylbutyric acid and 2, 2-diethyl-3, 3-dimethylbutyric acid, which form from carbonium ions of type E. In the mixture with tert-butanol the pentenes were converted into the codimeric acids with a higher selectivity (91.3%).

1-Hexene in a mixture with i-C_4H_8 was quantitatively converted into carboxylic acids, 81.2% of which were codimeric, the latter containing 80% 2-neopentylcaproic acid and 20% 2, 2, 3-trimethylheptan-4-oic acid, which formed from carbonium ions of types D and E. The low relative concentration of the latter acid should be attributed to the low extent of isomerization of 1-hexene to form 2-hexene prior to the step following the addition of the tert-butyl carbonium ion to the normal alkane. The fact that the mixture of codimeric acids did not contain a third isomer, which might have formed as a result of the reaction of the carbonium ion appearing following the addition of $\overset{+}{C}(CH_3)_3$ to the third C atom of 2-hexene with CO and water is apparently attributable to steric hindrances and the great advantage in the addition of $\overset{+}{C}(CH_3)_3$ to the second C atom of 2-hexene. An increase in the mole ratio of 1-hexene to i-C_4H_8 from 1 : 1 to 2 : 1 resulted in an increase in the selectivity of the conversion to the codimeric acids from 81.2 to 95.0% with a high total yield of carboxylic acids. 1-Hexene mixed with 2-methyl-1-pentene was also converted into codimeric acids with a high selectivity. 1-Heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 7-pentadecene, and 1-hexadecene in mixtures with i-C_4H_8 were converted into codimeric acids with high yields.

The composition of the codimeric acids and their structure were established by GLC, PMR, and mass spectrometry, and in some cases ^{13}C NMR was employed. The PMR and mass spectra pointed out the formation of two codimeric acids from the α-olefins and i-C_4H_8 in a 4 : 1 ratio, which were the products of the carbonylation of the codimeric carbonium ions that appeared as a result of the addition of $\overset{+}{C}(CH_3)_3$ to the first C atom of the α-olefin and the second C atom of the β-olefin formed upon isomerization of the α-olefin.

The cyclic olefins, viz., cyclopentene and cyclohexene, in mixture with i-C_4H_8 or tert-butanol were 80-90% carbonylated exclusively to form the following codimeric acids: 1-tert-butylcyclopentan-1-oic acid and 1-tert-butylcyclohexan-1-oic acid, respectively. The selectivity of the process increased as the mole ratio of $BF_3 \cdot H_2O$ to the sum of the olefins or the olefin and the alcohol was lowered from 2:1 to 1:2.

Thus, in a mixture of an iso alkene and a normal or cyclic alkene in an atmosphere of CO in the presence of the $BF_3 \cdot H_2O$ — liquid-SO_2 system, a tertiary carbonium ion forms from the iso alkene and can subsequently be converted along three paths. First, it can add CO and water to form a carboxylic acid. Second, the carbonium ion can add one or two molecules of the iso alkene, CO, and water to form dimeric and trimeric carboxylic acids. Third, the carbonium ion can be added to the normal or cyclic alkene to form a codimeric carbonium ion, which is then converted into carboxylic acid. Under these conditions normal alkenes do not form carbonium, and the codimeric acid, therefore, forms predominantly from an equimolar mixture of an iso alkene and a normal alkene.

EXPERIMENTAL

The experiments were carried out in a 250-ml conical flask, which was placed in a beaker with a heat-insulating covering and cooled by an acetone — dry-ice mixture. The flask was charge with 95 ml (2.2 moles) of liquid SO_2 and the complex $BF_3 \cdot H_2O$ (d = 1.778) in an amount equivalent to 0.125 to 0.5 mole. The system was tested for hermetic sealing, a stirrer was introduced, the system was blown through with CO, and a mixture of liquid $i\text{-}C_4H_8$ and a normal alkene in a 1:1 mole ratio was added from a cooled dropping funnel. The complex $BF_3 \cdot H_2O$ was obtained by saturating water with BF_3 while the vessel was cooled with ice water.

The carboxylic acids were isolated from the reaction mixtures after dilution with water in the usual manner. The composition of the acids obtained up to C_{13} was determined by GLC [5] on an LMKh-8 MD chromatograph with a 2.5 m × 2 mm stainless steel column with 10% polyethylene glycol adipate and 3% H_3PO_4 on Chromosorb G. A flame-ionization detector was used, the flow rate of the carrier gas, He, was 50 ml/min at 186°C, and the acids above C_{13} were determined in the form of their methyl esters at 150-190°C.

The original olefins C_3H_6, $i\text{-}C_4H_8$, 1-hexene, 2-methyl-1-pentene, cyclopentene, cyclohexene, and hexadecene had a purity greater than 98%. The 7-pentadecene [bp 121.5-122.8°C (7 mm); n_D^{20} 1.4408; d_4^{20} 0.7764] was synthesized from $n\text{-}C_7H_{15}MgCl$ and CO according to [6]. The tert-butanol had a purity greater than 99.0%. The mixture of butenes contained 36.7% $\alpha\text{-}C_4H_8$, 36.7% trans-$\beta\text{-}C_4H_8$, and 26.6% cis-$\beta\text{-}C_4H_8$. The mixture of pentenes was 30% 1-pentene, 43.8% trans-2-pentene, and 26.2% cis-2-pentene.

The fine rectification of the methyl esters of the C_8 acids (110 g) obtained by the codimerization of C_3H_6 and $i\text{-}C_4H_8$ or tert-butanol in a column with an efficiency of 90 theoretical plates yielded a fraction (84.0 g) with bp 171.2-171.6°C (760 mm), n_D^{20} 1.4225, and d_4^{20} 0.8960, which was a 2:1 mixture of methyl 2,4,4-trimethylvalerate and methyl 2,2,4-trimethylvalerate according to the data from the PMR and ^{13}C NMR spectra (Brüker WP-60 spectrometer at a frequency of 15.08 MHz) and the mass spectrum.

2,3,4,4-Tetramethylvaleric acid, mp 102.6°C (from hexane), was isolated by crystallization from the mixtures of carboxylic acids obtained by codimerization of the mixture of butenes with $i\text{-}C_4H_8$ or tert-butanol. The methyl ester had bp 120°C (17 mm), n_D^{20} 1.4338, and d_4^{20} 0.9064. Rectification of the methyl esters of the acids (118 g) obtained from the mixture of butenes and $i\text{-}C_4H_8$ or tert-butanol yielded 68.1 g of a 1:1 mixture of methyl 2-ethyl-4,4-dimethylvalerate and methyl 2,3,4,4-tetramethylvalerate with bp 187.7-188.5°C (760 mm) and n_D^{20} 1.4305, which, when saponified, provided a 1:1 mixture of acids with bp 165-167°C (15.5 mm), n_D^{20} 1.4418, and d_4^{20} 0.9306, as well as a fraction (6.0 g) of methyl 2-ethyl-2,3,3-trimethylbutyrate with bp 193-194.1°C (760 mm), n_D^{20} 1.4370, and d_4^{20} 0.9126 and an acid with mp 115°C (from hexane).

The mixture of the methyl esters of the carboxylic acids obtained by the codimerization and carbonylation of the mixture of pentenes with $i\text{-}C_4H_8$ or tert-butanol could not be separated by rectification; therefore, the identification and composition of the mixture were determined from the GLC data and the mass spectra. The fraction with bp 62.5-63.0°C (5 mm), n_D^{20} 1.4348, and d_4^{20} 0.8967 contained the methyl esters of the following acids: 10.1% 2-neopentylvaleric, 37.1% 2,2,3-trimethylhexan-4-oic, 49% 3-ethyl-2,4,4-trimethylvaleric, and 3.8% of a 1:1 mixture of 2-n-propyl-2,3,3-trimethylbutyric and 2,2-diethyl-3,3-dimethylbutyric acid.

The mixtures of carboxylic acids obtained by the codimerization and carbonylation of 1-hexene with $i\text{-}C_4H_8$ or tert butanol were converted into mixtures of their methyl esters (bp 102-103°C (11 mm), n_D^{20} 1.4340, d_4^{20} 0.8776], which 80% methyl 2-neopentylcaproate and 20% methyl 2,2,3-trimethylheptan-4-oate according to the data from the PMR and mass spectra, as well as the ^{13}C NMR spectra.

The carboxylic acids obtained as a result of the codimerization and carbonylation of 1-hexene and 2-methyl-1-heptene contained 16.4% 7,7-dimethyldecan-5-oic acid, 60.0% 5,6,6-trimethylnonan-4-oic acid, and 15.5% 2-n-butyl-2,3,3-trimethylcaproic acid [the methyl esters of the mixture of these acids had bp 115-119°C (8.5 mm), n_D^{20} 1.4390, and d_4^{20} 0.8821).

The carboxylic acids formed from heptene and i-C_4H_8 (or tert-butanol) were 80% 2-neopentylenanthic acid and 20% 2,3,3-trimethyloctan-4-oic acid [the methyl esters of the mixture of these acids had bp 108-111°C (11 mm), n_D^{20} 1.4310, and d_4^{20} 0.8810]. In a similar manner a 4:1 mixture of 2-neopentyloctanoic acid and 2,2,3-trimethylnonan-4-oic acid was obtained from 1-octene and i-C_4H_8 or tert-butanol, and the methyl esters had bp 132-137°C (9 mm), n_D^{20} 1.4408, and d_4^{20} 0.8808. 1-Nonene and i-C_4H_8 yielded a 4:1 mixture of 2-neopentylnonanoic acid and 2,2,3-trimethyldecan-4-oic acid, and the methyl esters had bp 150-155°C (10 mm), n_D^{20} 1.4500, and d_4^{20} 0.8776. 1-Decene and i-C_4H_8 yielded a 4:1 mixture of 2-neopentyldecanoic acid and 2,2,3-trimethylundecan-4-oic acid, and the methyl esters had bp 159-160°C (12 mm), n_D^{20} 1.4428, and d_4^{20} 0.8744 1-Dodecene and i-C_4H_8 yielded a 4:1 mixture of 2-neopentyldodecanoic acid and 2,2,3-trimethyltridecan-4-oic acid, and the methyl esters had bp 180-185°C (10 mm), n_D^{20} 1.4491, and d_4^{20} 0.8721. 7-Pentadecene and i-C_4H_8 yielded a 3:1 mixture of 2-n-heptyl-2-tert-butylnonanoic acid and 3-tert-butyl-2-n-hexyldecanoic acid, and the methyl esters had bp 180-190°C (12 mm), n_D^{20} 1.4480, and d_4^{20} 0.8135. 1-Hexadecene and i-C_4H_8 yielded a 4:1 mixture of 2-neopentylhexadecanoic acid and 2,2,3-trimethylheptadecan-4-oic acid, and the methyl esters had bp 195-200°C (10 mm), n_D^{20} 1.4520, and d_4^{20} 0.8066. A 0.125 mole portion of cyclopentene and a 0.125-mole portion of i-C_4H_8 in the presence of 0.125 mole of $BF_3 \cdot H_2O$ in 95 ml of liquid SO_2 allowed to react for 2 h at −40°C produced 1-tert-butylcyclopentan-1-oic acid in a 72.1% yield with mp 175.7°C (from hexane). The acid chloride had bp 114-116°C (11 mm) and mp 50°C, and the methyl ester had bp 177-178°C (14 mm), d_D^{20} 1.4605, and d_4^{20} 0.9714. Under similar conditions cyclohexene and i-C_4H_8 provided an 87.2% yield of 1-tert-butyl-cyclohexan-1-oic acid, bp 131.5°C (from hexane). The acid chloride had bp 134-136°C (20 mm), and the methyl ester had bp 110-112°C (13 mm), n_D^{20} 1.4658, and d_4^{20} 0.9687. The reaction of a 1:1 mixture of cyclopentene and tert-butanol with CO under 1 atm at a temperature of −30°C in the presence of $BF_3 \cdot H_2O$ with a 1:1 mole ratio of the latter to the sum of the olefin and the alcohol produced 1-tert-butylcyclopentan-1-oic acid in an 82.6% yield, and 1-tert-butylcyclohexan-1-oic acid was obtained from a 1:1 mixture of cyclohexene and tert-butanol in a 90.0% yield. The reaction of the methyl ester of 1-tert-butylcyclopentan-1-oic acid with $LiAlH_4$ in a medium of boiling n-octane (~120°C) yielded 1-tert-butylcyclopentylcarbinol, bp 187-188°C (13 mm), mp 149°C (from hexane). In an analogous manner, the reduction of the methyl ester of 1-tert-butyl-cyclohexan-1-oic acid by $LiAlH_4$ in a medium of n-octane yielded 1-tert-butylcyclohexylcarbinol, bp 120-121°C (12 mm), mp 67.5°C (from hexane). ^{13}C NMR spectrum of 1-tert-butylcyclohexan-1-oate (δ, ppm): 53.729 (s, C^1), 50.633 (q, OCH_3), 36.698 [s, $\underline{C}(CH_3)_3$], 29.202 (t, C^2), 26.470 (q, CH_3), 25.893 (t, C^4), 24.436 (t, C^3). The addition of the shift reagent $Eu(dpm)_3$ in $CDCl_3$ to the sample shifted the resonance signals to weaker fields (respectively): 54.184, 51.210, 36.062, 29.505, 27.714, 26.682, 26.045, 24.648. According to these spectra, the greatest shift was observed in the case of the C^1, OCH_3, $\underline{C}(CH_3)_3$, and $C(\underline{C}H_3)_3$ atoms. This supports the location of the tert-butyl group in the gem position relative to the carbomethoxyl group on the cyclohexane ring. The tert-butyl groups in 1-tert-butylcyclohexan-1-oic acid and 1-tert-butylcyclopentan-1-oic acid are, in all likelihood, located in equatorial positions [7].

CONCLUSIONS

An equimolar mixture of a normal (or cyclic) alkene and an alkene with a branch at the double bond (or a tertiary alcohol) in the presence of the $BF_3 \cdot H_2O$ — liquid-SO_2 catalytic system under 1 atm of CO at a temperature of −30 to −40°C undergoes selective codimerization followed by carbonylation and the formation of codimeric carboxylic acids with 70 to 93% yields.

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