3. A concerted mechanism has been proposed and theoretically substantiated for the formation of vinylcyclopropane derivatives from substituted cyclopropenes and olefins in the coordination sphere of copper without the participation of vinylcarbenes or their complexes.

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Pd(II) PHOSPHINE COMPLEX-CATALYZED CARBONYLATION OF 1-NONENE IN METHANOL

AND ACETONE-METHANOL SOLUTIONS

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The reaction of olefins with CO and alcohols (hydrocarboalkoxylation), catalyzed by palladium phosphine complexes, constitutes a convenient one-step method for the synthesis of carboxylic acid esters [1, 2]. The principal disadvantage of this method lies in the fact that the reaction generates a mixture of hard-to-separate products, the ratio of which depends in a complex manner on a series of factors: the reaction medium, the structure and concentration of the phosphine ligands, the CO pressure, etc. For this reason, the eluci-

dation of the rules governing the effects of these factors on the yield and selectivity of hydrocarboalkoxylation is of special importance and would contribute to the goal of selecting optimum process conditions.

In the reaction of 1-nonene with CO and water, the catalytic system acetone- $Pd(Cl)_2-(PPh_3)_2-nPPh_3$ (n = 2-4) allows one to obtain the linear product in relatively high yield and selectivity at comparatively low CO pressure and temperature [3]. The research approach documented in [3] for the study of Pd complex-promoted homogeneous catalysis has been applied in this study in the search for the optimum relationship between yield and selectivity in the reaction of 1-nonene with CO and methanol and the above-mentioned catalytic system in pure methanol or a mixture of methanol and acetone. We have also investigated the possibility of replacing the starting bis(triphenylphosphine)palladium dichloride complex with a catalyst having the composition $PdCl_2-PPh_3$.

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TABLE 1. Effect of CO Pressure (p_{CO} , atm) and Concentration of Triphenylphosphine on the Yield and Selectivity (S) of the (Pd(II)-Catalyzed Hydrocarboalkoxylation of 1-Nonene in Methanol (experiments 1-7) or Acetone-Methanol (experiments 8-26) at 90°C

Expt. ^a	v_{a}/v_{M}^{b}	$p_{\rm CO}$	P/Pd ^C	Yi e ld of esters, % ^d				- 9
				(I)	(11)	(111)	total	Se
$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ 21 \\ 22 \\ 23 \\ 24 \\ 25 \\ 26 \\ \textbf{a}_{\intercal} \end{array} $	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 5 \\ 9 \\ 14 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ $	$\begin{array}{c} 7\\ 13\\ 24\\ 7\\ 13\\ 24\\ 13\\ 13\\ 13\\ 13\\ 13\\ 13\\ 13\\ 13\\ 13\\ 13$	$\begin{array}{c} 0 \\ 0 \\ 2 \\ 2 \\ 4 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 2 \\ 4 \\ 6 \\ 8 \\ 15 \\ 0 \\ 2 \\ 2 \\ 2 \\ 2 \\ 4 \\ 1 \\ 2 \\ 4 \\ 1 \\ 2 \\ 4 \\ \end{array}$	$\begin{array}{c} 17\\23\\38\\29\\40\\45\\42\\41\\57\\33\\21\\22\\61\\41\\57\\57\\60\\16\\14\\50\\55\\57\\60\\61\\39\\59\\66\\73\\\end{array}$	$\begin{array}{c} 8\\ 12\\ 18\\ 10\\ 14\\ 15\\ 11\\ 20\\ 27\\ 29\\ 20\\ 20\\ 20\\ 20\\ 20\\ 20\\ 20\\ 34\\ 13\\ 18\\ 21\\ 8\\ 20\\ 19\\ 15\\ \end{array}$	4 7 5 6 - - - 5 6 - - - - - - - - - - - - -	$\begin{array}{c} 29\\ 40\\ 63\\ 44\\ 59\\ 66\\ 53\\ 69\\ 92\\ 62\\ 41\\ 42\\ 86\\ 82\\ 46\\ 19\\ 17\\ 75\\ 98\\ 70\\ 78\\ 89\\ 47\\ 79\\ 85\\ 88\\ 47\\ 79\\ 85\\ 88\\ 88\\ 88\\ 88\\ 88\\ 88\\ 88\\ 88\\ 88$	$\begin{array}{c} 59\\ 58\\ 59\\ 66\\ 68\\ 79\\ 60\\ 62\\ 53\\ 51\\ 52\\ 72\\ 72\\ 72\\ 72\\ 85\\ 84\\ 82\\ 67\\ 76\\ 82\\ 77\\ 74\\ 83\\ 75\\ 78\\ 83\\ 75\\ 78\\ 83\\ 75\\ 83\\ 78\\ 83\\ 78\\ 83\\ 75\\ 78\\ 83\\ 75\\ 78\\ 83\\ 78\\ 83\\ 75\\ 78\\ 83\\ 75\\ 78\\ 83\\ 78\\ 78\\ 83\\ 78\\ 78\\ 83\\ 78\\ 78\\ 83\\ 78\\ 78\\ 78\\ 78\\ 78\\ 78\\ 78\\ 78\\ 78\\ 78$
In experiments 1-22 the starting catalyst was $PdCl_2(PPh_3)_2$ and the male ratio of [nonenal[Pd] = 11/. In experimenta								
23-26 the starting complex was PdCl ₂ and the mole ratio [non-								
ene]/[Pd] = 87.								
^b Acetone:methanol volume ratio.								
^C Mole ratio of [PPh ₃]/[PdCl ₂ (PPh ₃) ₂] in experiments 1-22, and								
$[PPh_3]/[PdCl_2]$ in experiments 23-26.								
"Calculated based on 1-nonene.								
"Percent ratio of isomer (I) to the total yield of all esters.								

The reaction was carried out at 90°C and a CO pressure in the range 7-24 atm over a 6-h period; the yields of esters and selectivity (S, the percent ratio of the linear isomer to the total yield of all esters) were determined by GLC. At the conclusion of the reactions the systems were observed to be homogeneous, as expected; the only exceptions were the experiments carried out without the addition of free triphenylphosphine, where Pd black or a metallic mirror formed on the walls of the reaction vessel.

The main products of the carbonylation of 1-nonene under these conditions are methyl decanoate (I) and methyl α -methylpelargonate (II) [reaction (1)]; small amounts of methyl α -ethylcaprylate (III) are also formed (yields <1% are not entered in Table 1). The formation of (III) apparently results from the isomerization of 1-nonene to 2-nonene under the reaction conditions, and subsequent carbonylation of the latter [reactions (2) and (3)]. It should be mentioned, however, that 2-nonene may also be a source of (II) [reaction (3)].

$$C_{7}H_{15}CH = CH_{2} + CO + CH_{3}OH \xrightarrow{Pd/PPh_{3}} C_{3}H_{10}COOCH_{3} + C_{7}H_{15}CHCOOCH_{3}$$
(1)

$$C_{7}H_{15}CH = CH_{2} \xrightarrow{Pd/PPh_{3}} C_{6}H_{13}CH = CHCH_{3}$$
(2)

 CH_3

When the reaction is carried out in methanol in the absence of free triphenylphosphine (Table 1, experiments 1-3), low yields of esters are obtained, apparently because of decomposition of the catalyst as evidenced by deposition of Pd black). Under these conditions an increase in CO pressure from 7 to 24 atm is accompanied by an increase in the total yield of esters from 41 to 66%; this is probably related to an increase in the rate of the reaction as a result of the higher CO concentration in the solution.

The addition of a twofold excess of triphenylphosphine stabilizes the Pd complex and increases the yield of esters at the CO pressures under investigation (experiments 4-6); the selectivity of the reaction is also enhanced from 59% (P/Pd = 0) to 68% (P/Pd = 2). This latter fact may be rationalized in terms of an increase in the concentration of catalytically active intermediates, which inhibits the formation of products (II) and (III) [1]. An increase in the amount of excess PPh₃, up to a P/Pd ratio of 4, at a CO pressure of 13 atm, leads to a further increase in the selectivity of the reaction in favor of the linear isomer (79%, experiment 7). This may be explained in terms of a retardation of the rates of reactions (2) and (3); in the presence of a fourfold excess of PPh₃ isomer (III) is not observed and the amount of (II) also decreases somewhat (compare experiments 6 and 7).

It should be noted that in methanol as the reaction medium the process selectivity is almost independent of the CO pressure in the range 7-24 atm (compare experiments 1-3 or 4-6). This indicates that the effect of CO is primarily a kinetic effect and that the composition of the catalytically active intermediate does not change as p_{CO} is varied, i.e., coordinated triphenylphosphine is not displaced by CO [4].

The hydrocarboalkoxylation of olefins can thus be accomplished in methanol at relatively low CO pressures, although the yields of products are not very high (29-66%). It is known, however, that the hydrocarboalkoxylation of olefins can be improved if the alcohols are diluted with different types of solvents; the following experiments address the alcohol/solvent relationship [5, 6]. For the reaction of 1-nonene with CO and methanol in acetone as solvent we have investigated the dependence of the yield and selectivity of the reaction on the volume ratio of acetone to alcohol. In the absence of added PPh₃ (see Table 1, experiments 3, 8-12) the yield of esters reaches a maximum at $V_{acetone}/V_{methanol} = 2$. Further increases in the acetone/methanol volume ratio are accompanied by a decrease in the total yield of products back to the level observed for the reaction in pure methanol (see experiments 2 and 10-12); the isomer (III), however, is practially not produced under these conditions. The latter fact may be attributed either to a suspension of the isomerization of 1-nonene or to a decrease in the rate of carbonylation of 2-nonene in the presence of small amounts of methanol.

One fact deserves attention, and that is that dilution of the alcohol with acetone up to a volume ratio of acetone/methanol = 2 results in a significant increase in the yield of esters at all CO pressures studied, regardless of the amount of free PPh₃ in the system. Thus, in pure methanol in the presence of a two-fold excess of PPh₃, the total yields of esters at $P_{CO} = 7$, 13, and 24 atm are 44% (experiment 2), 59% (experiment 4), and 66% (experiment 7), respectively; in the presence of a mixed acetone-methanol solvent system (V_{acetone}/V_{methanol} = 2), at the same pressures the yields are increased to 70% (experiment 20), 86% (experiment 13), and 89% (experiment 22), respectively.

The selectivity of the reaction is only noticeably improved (by 8-16%) at $p_{CO} = 7$ atm; at other pressures the difference in selectivity between the reaction in methanol and in an acetone/methanol (2/1 ratio) mixture is not large (3-6%), and in several cases the selectivity is actually greater for the reaction in pure methanol (compare experiments 6 and 9, 5 and 14).

Inasmuch as the highest yield and selectivity for the hydrocarboalkoxylation of 1-nonene are observed in an acetone-methanol mixture with a volume composition of 2:1, further studies of the effects of PPh₃ and CO pressure were carried out in this reaction medium (experiments 13-26).

Just as in the reaction of 1-nonene with CO and water [3], the following results were obtained: As the P/Pd ratio is increased ($p_{CO} = 13$ atm, experiments 9, 13-17), the total yield of products decreases, while the selectivity increases to a distinct level, and then remains constant. In the case of small amounts of added PPh₃ the decreased yields are probably associated with an inhibition of the process of isomerization to give the branched isomer, since the yield of isomer (I) does not change (experiments 9, 13, and 14); as the P/Pd ratio is increased further (starting at P/Pd = 6), the amount of product (I) begins to decrease, and the ester (III) is not observed (experiments 15-17). The presence of excess PPh₃ affects the reaction process in a similar manner at other CO pressures (compare experi-

ments 18 and 20, 19 and 22); this effect has also been observed in the carbonylation of propene in the system methyl ethyl ketone-methanol- $PdCl_2(PPh_3)_2$ (95 atm, 110°C) [6].

Just as in the hydrocarboxylation of 1-nonene [3], an increase in the CO pressure leads to an increase in the conversion of olefin as the yields of isomers (II) and (III) increase (the amount of (I) remains relatively constant at 55-60%), i.e., the selectivity of the reaction decreases (compare experiments 18, 9, and 19, or 13, 20-22). The difference between these two reactions lies in the fact that in the carbonylation of nonene in the presence of CH_3OH an increase in the CO pressure favors the formation of (III), which is not formed in aqueous acetone. These results can be accounted for by an increased rate of reaction for (2) and (3) at high CO pressures; this explanation can also account for the increased yield of (II).

Based on the results described herein, the following optimum conditions are recommended for the reaction of olefins with CO and methanol catalyzed by the complex $PdCl_2(PPh_3)_2$ in acetone: low CO pressure (7-13 atm) and a small excess (2- to 4-fold) of PPh₃, at an acetone/ methanol ratio of 2:1. In addition, the data from experiments 23-27 suggest that the catalytic complex can also be obtained by using the simpler catalyst system (PdCl₂ + PPh₃). Under these conditions the same P/Pd ratio (including the triphenylphosphine which enters into complex formation) results in a slightly higher selectivity and an insignificant amount of (III) compared to the reaction using preformed $PdCl_2(PPh_3)_2$ (compare experiments 9 and 25, 13 and 26).

EXPERIMENTAL

The carbonylation of 1-nonene was carried out in a thermostated steel autoclave fitted with a magnetic stirrer. $PdCl_2(PPh_3)_2$ (5.35 \cdot 10⁻⁵ mole), 1-nonene (6.3 \cdot 10⁻³ mole), and triphenylphosphine were added to an acetone-methanol mixture (total volume = 6 ml). The glass reactor containing the reaction mixture was placed in the autoclave, and the mixture was purged twice with CO up to p_{CO} = 7 atm; the mixture was then pressurized to the required CO pressure, stirred, and heated. After 1.5 h the reactor temperature reached 90°C. The reaction mixture was maintained at this temperature for 4 h. The reaction products were analyzed by GLC on a Tsvet 110 chromatograph using glass columns (2 m long, diameter 3 mm) packed with AW chromatone (0.2-0.25-mm mesh) containing 3% H₃PO₄ impregnated with 10% polyethyleneglycol [7].

CONCLUSIONS

1. The hydrocarboalkoxylation of 1-nonene may be achieved in satisfactory yield and selectivity in methanol or acetone-methanone mixtures at low CO pressures and in the presence of a small excess of triphenylphosphine relative to the catalytic complex $PdCl_2(PPh_3)_2$.

2. Both the yield and selectivity of the reaction in methanol are noticeably improved as the amount of triphenylphosphine added is increased; an increase in the CO pressure increases the total yield of products, but the selectivity remains almost constant.

3. In an acetone-methanol mixture the highest yield and selectivity in favor of the linear reaction product (methyl decanoate) are obtained when the composition is 2:1; as the amount of excess acetone reaches 9:1, the reaction parameters are similar to those on pure methanol.

4. In an acetone-methanol mixture the process selectivity is enhanced by both increased amounts of triphenylphosphine and lower CO pressures.

5. When the complex $PdCl_2(PPh_3)_2$ is replaced by the simpler catalyst system $(PdCl_2 + PPh_3)$ the selectivity of the reaction is improved and the amount of the third isomeric product (methyl α -ethylcaprylate) is minimal.

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STEREODIRECTIVITY IN THE RADICAL TELOMERIZATION OF PROPYLENE WITH CC14, INITIATED BY METAL CARBONYL SYSTEMS

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The similar stereodirectivity in telomerization when peroxide initiation is exchanged for initiators of a different type is an argument in favor of a stepwise free-radical mechanism for the reactions initiated by these initiators. The stereodirectivity of the telomerization of propylene with CCl₄ can be estimated from the relative amounts of the individual racemic diastereoisomeric forms of the telomers, which contain two or more asymmetric carbon atoms. Capillary chromatography and chromato-mass spectrometry have been used [1] to show that one of the components of the telomer fraction CCl₃ [CH₂CH(CH₃)]₃Cl (T₃), which was assigned the structure of the iso-form T₃ [2], is a mixture of structural isomers of T₃ formed by the inverse addition of individual propylene units. It was also shown that the other two components of T₃, each of which was separated on the capillary column into two peaks, consisted of the four racemic diastereoisomeric forms of the telomer T₃. We have previously determined the stereodirectivity of the telomerization of propylene with CCl₄ initiated by Cr(CO)₆ [3], Mo(CO)₆, W(CO)₆ [4], and Mn₂(CO)₁₀ [5]. More precise knowledge of the structures of the components of the T₃ telomer fraction requires further study of the stereodirectivity of this reaction when initiated by metal carbonyls.

The object of the present investigation was to determine the relative amounts of the racemic diastereoisomeric forms of the telomers $CCl_3CH_2CH_2CH_2CH_2CH_3(T_2)$ and CCl_3CH_2 . $\overset{*}{CH}(CH_3)CH_2CH_2CH_3(CH_3)CH_2CH_3(T_3)$, formed in the telomerization of propylene with CCl_4 when initiated by tert-butyl hydroperoxide (TBP), $Cr(CO)_6$, $Fe(CO)_5 + DMF$, and $W(CO)_6 + PPh_3$. The studies were carried out using ¹³C NMR and capillary GLC.

In order to determine the relative amounts of the diastereoisomeric forms of T_2 and T_3 in the reaction mixture by their ¹³C NMR spectra, it was first necessary to examine the spectra of the pure T_1 , T_2 , and T_3 . The ¹³C chemical shifts of these compounds (Table 1) were in good agreement with those calculated by the structural increment method for polyhaloalkanes [6] in all cases except for the CS of the methine carbon atom in T_2 . This was due to the fact that the structural increment method was designed for linear polyhaloalkanes, and can give anomalous CS for branched polyhaloalkanes. It will be seen from Table 1 that the spectrum of T_2 , which can exist in two racemic diastereoisomeric forms, contains two sets of signals, whereas the spectrum of T_3 , which can exist as four diastereoisomeric forms, contains four sets of signals.

The relative amounts of the diastereoisomeric forms of T_2 in the reaction mixture were found from the ratios of the integral intensities of the first and second sets of signals for T_2 in the ¹³C NMR spectrum. Most of the signals for T_2 overlapped with the ¹³C signals for T_3 (Table 1), but since the amounts of T_2 in the reaction mixture with the reactant ratios used were much greater than those of T_3 (see Experimental), the superimposition of the ¹³C signals for T_3 can only result in slight distortions in the intensities of the ¹³C signals for T_2 . The results of the calculations of the ratios of the two diastereoisomeric forms of T_2 in the reaction mixture are shown in Table 2.

As a result of the overlapping of most of the ¹³C signals in T_2 and T_3 , it was not possible to determine the ratios of the diastereoisomeric forms of T_3 for all the ¹³C signals

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