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SYNGAS REACTIONS

II *. THE HOMOGENEOUS CATALYZED CARBONYLATION AND CYCLIZATION OF ALLYLIC SUBSTRATES

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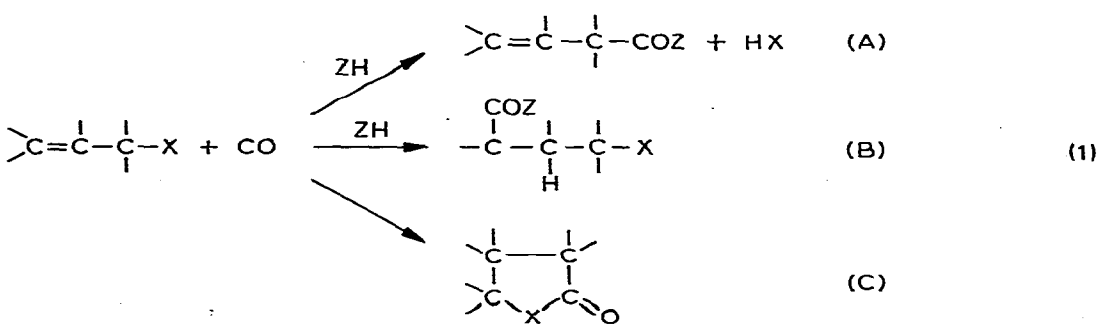
Summary

Carbon monoxide insertion and/or addition to allylic precursors may lead to the formation of both linear and cyclic carbonylation products. In examining these competing reaction paths, rhodium, platinum, palladium and nickel-based homogeneous catalysts have been developed which are particularly useful for the selective synthesis of γ-butyrolactam, *N*-alkyl-2-pyrrolidones, vinylacetate and phenylacetate esters and diesters from a variety of allylic and benzylic substrates. The extension of this catalysis to the carbonylation of certain vinylic and propargyl congeners has also been considered.

Introduction

Carbonylation is generally considered to involve the metal catalyzed reaction of CO with unsaturated compounds, or components which are able to form unsaturated compounds, and a nucleophile containing a mobile hydrogen atom to yield a carbonyl derivative [1]. In the case of allylic substrates this reaction may take at least 3 forms:



* For previous paper in this series see ref. 27.

(1) Path A involves insertion of CO into an existing carbon polar bond, to form an unsaturated aliphatic carboxylic acid derivative.

(2) Path B involves CO addition to the C—C multiple bond to produce a β- and γ-substituted carbonyl derivative.

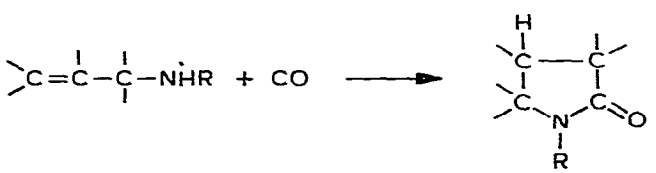
(3) Path C involves CO reaction with an allylic precursor containing a nucleophilic element and a reactive hydrogen atom in positions which favor ring closure, 5- or 6-membered ring derivatives may result.

In studying the relative importance of these three reaction paths for different allylic substrates and a variety of homogeneous catalyst systems we have developed new catalysts which generate specific, useful, products with much improved selectivity, and which also allow higher catalyst turnover numbers and reactivities than have been reported previously. Furthermore, wherever possible, we have attempted to extend this catalysis to the selective carbonylation of analogous benzylic, vinylic and propargyl derivatives.

Results and discussion

γ-Lactam syntheses

Considering first the ring closure of allylic substrates (eq. 1, path C), we have focussed primarily upon the syntheses of five-membered ring lactams and their homologues. In the past soluble cobalt catalysts have been employed to effect these syntheses [2,3]. Generally, however, this catalysis suffers from the intrinsic disadvantages of requiring stringent reaction conditions, e.g. 280°C (which favors competing allylic isomerization and polymerization [3], plus the formation of 6-membered ring alkyl pyridines [2]), and consequently they exhibit poor selectivity to the desired γ-lactam. The advantages of using certain homogeneous rhodium catalysts for the synthesis of γ-butyrolactam from allylamine (eq. 2) are illustrated in Table 1. These advantages include:



(2)

(a) They allow lactam synthesis under significantly milder conditions of temperature and pressure than hitherto has been possible.

TABLE 1

γ-BUTYROLACTAM FROM ALLYLAMINE

Rhodium catalyst	Rh (mmole)	Allylamine (mmole)	Temp (°C)	Press. (atm)	Run time (h)	γ-Butyrolactam yield (mole %) [b]
$Rh(CO)(PPh_3)_2Cl$	1.25 [a]	125	150	136	2	67
$Rh(PPh_3)_3Cl$	1.25	125	150	136	2	68
$Rh_2Cl_2(C_2H_4)_4$	0.63	125	150	220	12	30
$Rh(C_5H_7O_2)_3$	0.63	125	120	136	12	28
$RhCl_3$	1.25	125	150	190	2	35

[a] [Rh] = 15 m*M* (solvent toluene). [b] γ-Butyrolactam yield basis allylamine charged.

(b) Furthermore the rhodium catalysts, particularly the phosphine-stabilized rhodium catalysts such as $Rh(CO)(PPh_3)Cl$, allow formation of lactams in improved yields, and higher catalyst turnover numbers [4].

(c) Certain of these rhodium catalysts remain active after carbonylation of the allylic substrate is complete, and therefore they may be recycled with additional quantities of allylic material to produce more desired lactam.

This rhodium catalyst recycle capability is illustrated in Fig. 1. Here we use allylamine as the substrate, toluene solutions of chlorocarbonylbis(triphenylphosphine)rhodium(I) as catalyst, and recovery of the γ-butyrolactam after each catalyst cycle by fractional distillation in vacuo.

Similar homogeneous rhodium catalysts may also be employed for the synthesis of γ-butyrolactam from allylic halides in the presence of CO plus ammonia (eq. 3), and the synthesis of *N*-alkyl-substituted-2-pyrrolidones from allylic halides in the presence of CO plus primary alkylamines (eq. 4).

$$CH_2{=}CH{-}CH_2Cl + CO + NH_3 \xrightarrow{Rh-I^-} \text{(N-H lactam)} + HX \qquad (3)$$

$$\begin{matrix} CH_2{=}CH{-}CH_2I + CO + RNH_2 \xrightarrow{Rh} \\ CH_2{=}CH{-}CH_2Cl + CO + RNH_2 \xrightarrow{Rh-I^-} \end{matrix} \text{(N-R lactam)} + HX \qquad (4)$$

While solubilized cobalt catalysts are generally ineffective for these reactions we find that a number of simple rhodium salts and complexes (e.g. $Rh(acac)_3$ and $RhCl(PPh_3)_3$ in CH_3CN) produce the *N*-alkyl-2-pyrrolidones in high selectivity. In the case of allyl halide substrates, this is particularly true where iodide ion is the promoter [5]. The synthesis of *N*-methyl-1-pyrrolidone from allyl chloride and methylamine catalyzed by $Rh(acac)_3/KI$ in acetonitrile is illustrated in Fig. 2. Comparable yields of γ-butyrolactam are obtained when the same rhodium-iodide catalyst system is used to carbonylate allyl chloride in the presence of excess ammonia [4]. Again it is noteworthy that these catalysts remain active upon recycling with fresh feed (Fig. 2).

Vinylacetate ester syntheses

We have previously demonstrated the versatility of homogeneous palladium-Group IVB metal halide bimetallic catalysts for the selective carbonylation of a variety of alkenes and alkynes to linear fatty acid derivatives [6—8]. Related catalysis has now proven useful in the carbonylation of allylic substrates to linear unsaturated acid derivatives [9,10] (see eq. 1 path A). Starting with allylic alcohols, two classes of reaction have been examined (eq. 5 and 6). Allyl vinylacetate synthesis in >80 mole % yields is illustrated in Table 2 for three representative palladium bimetallic catalysts solubilized in aprotic solvents like benzene. The catalyst needed consists of three components:

$$2\ \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}C(R'')-CH_2OH + CO \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}C(R'')-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2-C(R'')=C<\begin{matrix} R \\ R' \end{matrix} + H_2O \qquad (5)$$

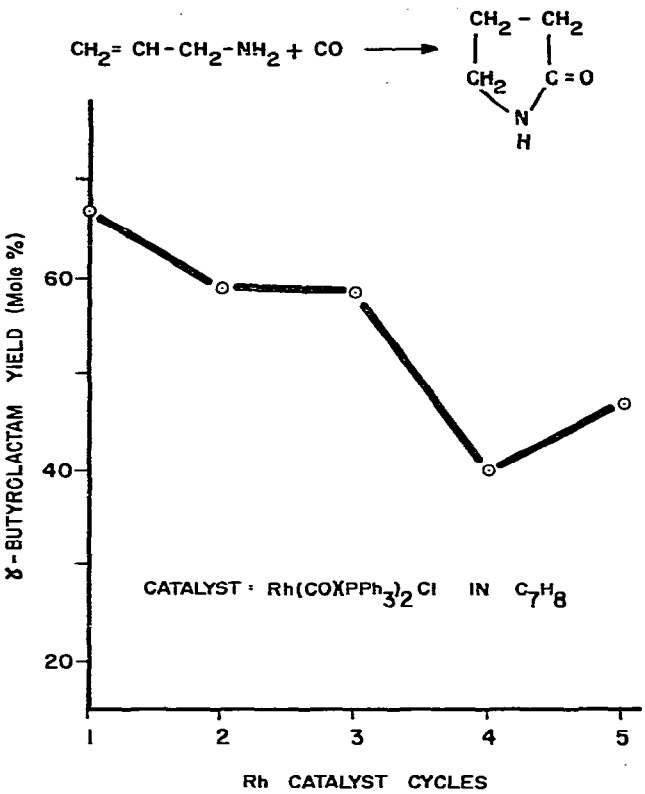


Fig. 1. γ-Butyrolactam synthesis from allylamine, multicycle rhodium catalysis. Experimental conditions as given in Table 1.

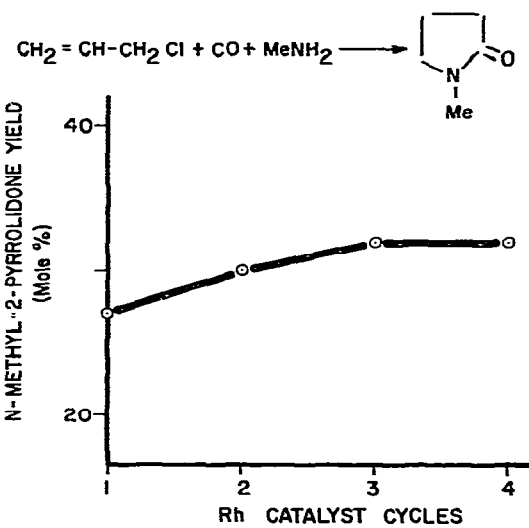


Fig. 2. *N*-Methyl-2-pyrrolidone synthesis from allyl chloride, multicycle rhodium catalysis. Catalyst: $Rh(acac)_3$ (1.25 mmole) plus KI (4.2 g) in acetonitrile (75 ml). Run conditions: initial [CH_2=CH-CH_2Cl] / [Rh] = 100; 8 h; 120°C; 135 atm.

TABLE 2

ALLYL VINYLACETATE FROM ALLYL ALCOHOL [a]

$$CH_2{=}CH{-}CH_2OH + CO \rightarrow CH_2{=}CH{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}OCH_2{-}CH{=}CH_2 + H_2O$$

Palladium catalyst	Pd (mmole)	Allyl alcohol (mmole)	Solvent	Allyl alcohol conv. (%)	Allyl vinylacetate yield (mole %) [b]
$Pd[P(C_6H_5)_3]_2Cl_2$ —10 $SnCl_2$	0.5 [a]	100	C_6H_6	>98	88
$Pd[P(p\text{-}CH_3 \cdot C_6H_4)_3]_2Cl_2$—10 $SnCl_2$	0.5	100	C_6H_6	59	78
$Pd[P(C_6H_5)_3]_2Cl_2$—10 $GeCl_2$	0.5	100	C_6H_6	80	84

[a] Experimental conditions: [Pd], 6.2 m*M*; 200 atm; 80°C. [b] Allyl vinylacetate yield basis allyl alcohol converted.

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}\underset{\underset{R''}{|}}{C}{-}CH_2OH + CO + R'''OH \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}\underset{\underset{R''}{|}}{C}{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}OR''' + H_2O \qquad (6)$$

(1) A palladium(II) halide salt selected from the group such as $PdCl_2$ and $PdBr_2$.

(2) Complexed with one or more group VB donor ligands such as PPh_3 and $P(p\text{-}CH_3 \cdot Ph)_3$.

(3) In combination with a Group IVB metal halide co-catalyst, e.g. $SnCl_2$, $GeCl_2$.

The bis(triphenylphosphine)palladium(II)—tin(II) chloride catalyst generally functions well in aprotic solvents like benzene, but higher turnover numbers are achieved using the allylic alcohol both as reactant and solvent [9]. At higher temperatures (200°C) and pressures the same synthesis has been effected with tris[tris(*p*-fluorophenyl)phosphine]platinum [11].

The addition of a second nucleophile, e.g. methanol, leads to the formation of methyl vinylacetate (eq. 6), but now the competing reaction is isomerization to the thermally more stable propionaldehyde [12]. A variety of other (partially hindered) allylic alcohol derivatives may also be carbonylated to allyl vinylacetate ester derivatives using the same $(Ph_3P)_2PdCl_2$—$SnCl_2$ combination (see Table 3). Pertinent examples include the synthesis of 2-methylallyl-3-methyl-3-butenoate from 2-methylallyl alcohol (where the rate of carbonylation is markedly slower than for allyl alcohol), crotyl 3-pentenoate from crotyl alcohol, and cinnamyl 4-phenyl-3-butenoate from cinnamyl alcohol.

In the case of allylic halide substrates, the carbonylation to linear unsaturated acid products (via CO insertion, eq. 1, path A) by homogeneous nickel, palladium and other Group VIII metal catalysts is well documented [13—15]. Our interest has been in seeking catalysts which give both improved turnover numbers and greater selectivity to specific products, although a second objective has been the extension of this catalysis to the carbonylation of the corresponding vinyl, propargyl and benzyl halides.

TABLE 3

SYNTHESES OF SUBSTITUTED ALLYLIC VINYLACETATE ESTERS [a]

Allyl alcohol	Alcohol conv. (%)	Allyl vinylacetate ester	
		Identity	Yield (mole %)
$CH_2=C(CH_3)-CH_2OH$	55	$CH_2=C(CH_3)-CH_2-O-C(=O)-CH_2-C(CH_3)=CH_2$	>98
$CH_3-CH=CH-CH_2OH$	>98	$CH_3-CH=CH-CH_2-O-C(=O)-CH_2-CH=CH-CH_3$	90
$CH_3-(CH_2)_2CH=CH-CH_2OH$	95	$CH_3-(CH_2)_2-CH=CH-CH_2-O-C(=O)-CH_2-CH=CH-(CH_2)_2-CH_3$	80
$C_6H_5CH=CH-CH_2OH$	60	$C_6H_5CH=CH-CH_2-O-C(=O)-CH_2-CH=CHC_6H_5$	50

[a] Experimental conditions: $(Ph_3P)_2PdCl_2$—10 $SnCl_2$ catalyst; benzene solvent; initial [allyl alcohol]/[Pd] = 200; 80°C; 135 atm CO. [b] Allyl vinylacetate yield basis allyl alcohol converted.

In Table 4 we illustrate the synthesis of vinylacetate esters via allyl chloride carbonylation (eq. 7) using the same palladium and related platinum bimetallic catalysts [9]. It may be noted that:

(1) Yields and selectivity to vinylacetate ester are generally superior to those reported previously [15,16].

(2) Both palladium and platinum bimetallic complexes are excellent catalysts for this reaction.

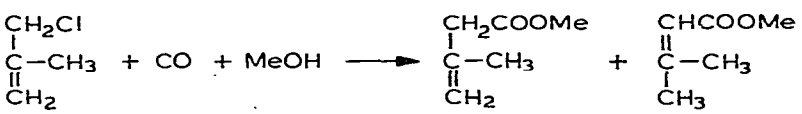
(3) There is no evidence for methyl chlorobutyrates, apparently CO addition to the double bond is not a competing reaction (eq. 1, path B).

(4) There is negligible methyl crotonate formation, apparently isomerization of the double bonds is extremely slow.

(5) Diesters are normally formed only as minor by-products. However, the presence of excess PPh_3 does favor dicarbonylation and the preparation of dimethyl pentandioates (see last entry), mainly dimethyl α-methylsuccinate and dimethyl glutyrate.

(7)

In contrast to the allylic alcohols (Table 3), substituted allylic halides readily yield more than one monocarbonylated product and alternate reactions may predominate. Methyl 3-methyl-3-butenoate and methyl 3-methyl-2-butenoate are prepared, for example, from 2-methylallyl chloride (eq. 8) in 11 and 5 mole % yields respectively [9].



(8)

Benzyl halide carbonylation

Turning now to the extension of this catalysis to benzyl halogenides, the benzyl halide derivative, α,α′-dichloro-*p*-xylene, is of particular interest since its

TABLE 4

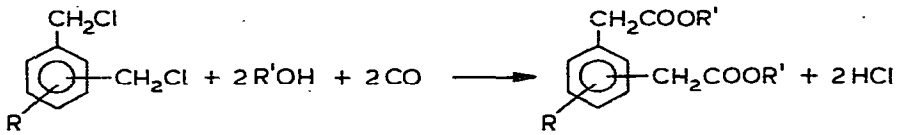
METHYL VINYLACETATE FROM ALLYL CHLORIDE

$CH_2{=}CH{-}CH_2{-}Cl + CO + MeOH \rightarrow CH_2{=}CH{-}CH_2{-}COOMe + HCl$

Catalyst	Solvent	Allyl chloride [a] conv. (%)	Major products	
			Identity	Yield (mole%)
$Pd(PPh_3)_2Cl_2$—10 $SnCl_2$	MIBK	80	Methyl vinylacetate [b]	91
	Benzene	99	Methyl vinylacetate	75
$Pd(AsPh_3)_2Cl_2$—10 $SnCl_3$	Benzene	>95	Methyl vinylacetate	51
$PtCl_4$—10 $SnCl_2$	Benzene	>95	Methyl vinylacetate	70
$Pd(PPh_3)_2Cl_2$—10 $SnCl_2$—5 PPh_3	Benzene	>95	Dimethyl pentandioates [c]	68
			Methyl vinylacetate	34

[a] Initial $[CH_2{=}CHCH_2Cl]/[Pd] = 100$; [Pd] = 5.3 m*M*; 200 atm CO; 80°C. [b] No evidence for methyl chlorobutyrates or methyl crotonate. [c] A mixture of dimethyl glutyrate and dimethyl α-methylsuccinate.

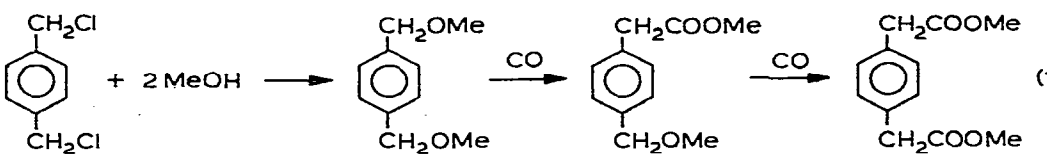
dicarbonylated derivatives, the *p*-phenylenediacetate esters, are homologues of the terephthalate esters. The cobalt-catalyzed carbonylation of α,α'-dichloro-*p*-xylene to dimethyl-*p*-phenylenediacetate in 32% yield has been described previously [14]. Palladium homogeneous catalysts have been employed here to demonstrate the synthesis (eq. 9) of *p*-phenylenediacetate esters, *o*-phenylenediacetate esters and dimethyl 2,3,5,6-tetramethylphenylene-1,4-diacetate (from 3,6-bis(chloromethyl)durene) [17].



(9)

The next Table (5) illustrates the synthesis of dimethyl *p*-phenylenediacetate from α,α'-dichloro-*p*-xylene using a series of homogenous palladium and nickel catalysts. While a number of ligand-stabilized palladium halide and nickel halide complexes, such as $(Ph_3P)_2PdCl_2$ and $(Ph_3P)_2NiCl_2$, are effective for this synthesis, simple palladium salts, like $PdCl_2$, as well as palladium complexes in combination with the Group IVB metal halides $SnCl_2$ and $GeCl_2$, proved ineffective in this instance.

Analyses of typical product solutions show α,α'-dimethoxy-*p*-xylene is consistently the major by-product. Furthermore, methyl *p*-(methoxymethyl)phenylacetate has been detected (Table 5), while separate experiments demonstrate the successful carbonylation of this monoester to the desired diester. We conclude then that a competing step in these synthesis is the nucleophilic replacement of halogen in α,α'-dichloro-*p*-xylene by the alcohol coreactant to give the corresponding chloroether or diether [18] (eq. 10), this could be followed by successive carbonylation to either the mono or diester derivatives.



(10)

Vinyl and propargyl halide carbonylation

In view of this success in using homogeneous palladium bimetallic catalysts to achieve the selective carbonylation of allylic halides and alcohols (eq. 1, path A), an attempt was made to extend the technique to the carbonylation of analogous vinylic and propargyl halides as a route to other unsaturated linear acid esters, e.g. the synthesis of acrylate esters (eq. 11).

$$CH_2 = CH—X + CO + ROH \rightarrow CH_2 = CH—COOR + HX \quad (11)$$

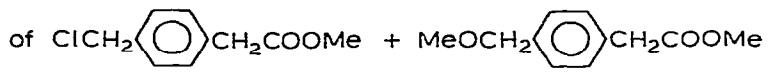
Several research groups have examined the reaction of vinyl chloride with CO [19,20,22]; generally, however, the predominant reaction is CO addition to the vinylic double bond (eq. 1, path B), rather than halide displacement. Consequently, the predominant products are α-chloropropionate [19] and dichloropropionate esters [20]. More recently, Heck and coworkers have demonstrated that triphenylphosphine-palladium complexes, in the presence of a proton

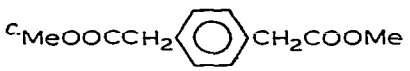
TABLE 5

$\alpha'\alpha'$-DICHLORO-p-XYLENE CARBONYLATION [a]

Catalyst	Dichloroxylene conv. (%)	Phenyl acetates [a] yield (mole %)	p-Phenylenediacetate [c] yield (mole %)
$Pd[P(C_6H_5)_3]_2Cl_2$	>95	33	52
$Pd[As(C_6H_5)_3]_2Cl_2$	>95	40	27
$Pd[C_6H_5CN]_2Cl_2$	>95	47	40
$Ni[P(C_6H_5)_3]_2Cl_2$	>95	37	31
$PdCl_2$		<1	<1
$Pt[As(C_6H_5)_3]_2Cl_2$		<1	<1
$Pd[P(C_6H_5)_3]_2Cl_2$—$SnCl_2$		<1	<1

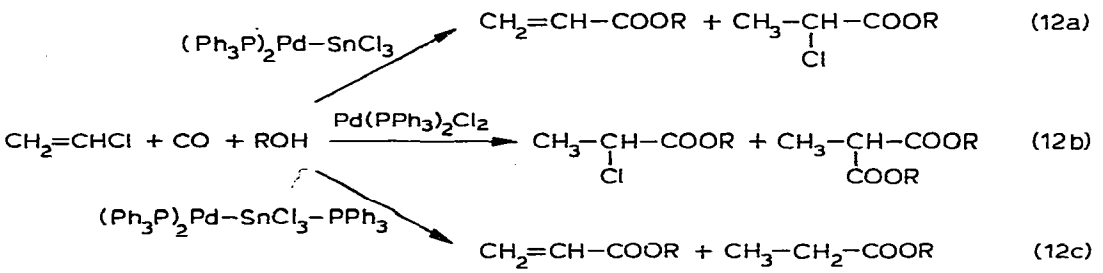
[a] Experimental conditions: Initial $[C_6H_4(CH_2Cl)_2]/[Pd] = 50$; [Pd] = 4 m*M* (methanol solvent); NaOAc, 60 mmole, 24 atm CO; 80°C.

[b] Mixture of 

[c] 

scavenger (excess tertiary amine), will direct the carbonylation of vinylic iodides and bromides to the formation of the corresponding acrylate esters [21]. Closson and Ihrman have employed palladium-on-carbon catalysts [22].

Using the ligand-stabilized palladium—Group IVB metal halide catalyst combinations our initial experiments showed vinyl bromide could be selectively carbonylated to methyl acrylate at moderate conversions (Table 6). Vinyl chloride, on the other hand, may produce any of four major products (eq. 12) according to whether the predominant reactions are CO insertion, CO addition or hydrogenation of the C—C double bond.



Generally selectivity to each of these product ester fractions is very sensitive to the palladium catalyst structure. For example:

(1) Benzene solutions of bis(triphenylphosphine)palladium-tin(II) chloride yield an approximately 2 : 1 mix of acrylate ester and α-chloropropionate ester (eq. 12a).

(2) Palladium-phosphine complex alone, in the absence of tin(II) chloride co-catalyst produces methyl α-chloropropionate (46% yield, 74% selectivity) and dimethyl α-methylmalonate (18% selectivity, eq. 12b).

TABLE 6

METHYL ACRYLATE FROM VINYL HALIDES [a]

Vinyl halide	Palladium catalyst	Ester products		
		Identity	Sel. (%)	Yield (mole %)
CH_2=CHBr	$Pd(PPh_3)_2Cl_2$—10 $SnCl_2 \cdot 2H_2O$	CH_2=CH—COOMe	>95	25
CH_2=CHCl	$Pd(PPh_3)_2Cl_2$—10 $SnCl_2$—5 PPh_3	CH_2=CH—COOMe	90	84
CH_3CH=CHCl	$Pd(PPh_3)_2Cl_2$—10 $SnCl_2$—5 PPh_3	C_3H_7COOMe		44
		$C_2H_5CHCOOMe$ (Cl)		15

[a] Experimental conditions: initial $[CH_2$=CHX$]/[Pd]$ = 50; [Pd] = 11 m*M* (benzene solvent); 135 atm; 95°C.

(3) The $(Ph_3P)_2PdCl_2$—$SnCl_2$ combination in the presence of excess phosphine yields methyl acrylate as the major product and methyl propionate as a coproduct (Table 6, eq. 12c).

More detailed experiments confirmed [9] that methyl acrylate selectivity in reaction 12c is improved through the addition of excess phosphine, substituting anhydrous tin(II) chloride as the co-catalyst in place of the dihydrate, and maintaining a large excess of alcohol coreactant to ensure homogeneity during the carbonylation sequence (Table 6).

The extension of this work to propargyl halide was less successful; experiments carried out at ambient and more forcing conditions (e.g. 20°C, 2000 psi) with the $(Ph_3P)_2PdCl_2$—$SnCl_2$—PPh_3 catalyst combinations in benzene both resulted in significant propargyl chloride conversion (54—100%), but dimethyl itaconate was the major product fraction (eq. 13). As with $Fe(CO)_5$ catalysis [23], both the acetylenic and chloromethylene functions react with CO.

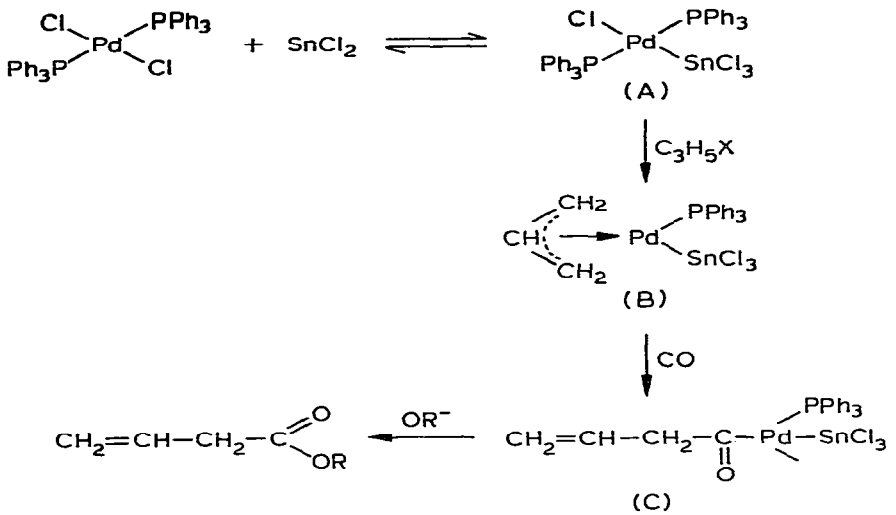
$$CH{\equiv}C{-}CH_2Cl + 2CO + 2MeOH \longrightarrow CH_2{=}\underset{\displaystyle COOMe}{\underset{|}{C}}{-}CH_2COOMe + HCl \qquad (13)$$

Mechanism

While no definitive conclusions can be drawn regarding the mechanisms of syntheses 2 to 13, in the case of allylic substrate carbonylation to vinylacetate esters via palladium bimetallic catalysis, this likely proceeds as depicted in Scheme 1. Simple mixing of the bis(triphenylphosphine)palladium(II) chloride and tin(II) chloride catalyst components in solution leads to rapid formation of the known complex A [6,24], where the high *trans* effect of the $SnCl_3$ ligand should labilize coordinated chloride with regard to displacement by donor solvent or carbon monoxide. Pressuring these solutions with CO, we have not been able to spectroscopically detect ν(CO), indicating the equilibrium of eq. 14 lies far to the left [24]. However, the presence of allylic halide/alcohol allows formation of isolatable π-allyl-Pd complexes, such as B, of known structure [25]. Subsequent π—σ rearrangement and CO insertion into the Pd—Alkenyl interme-

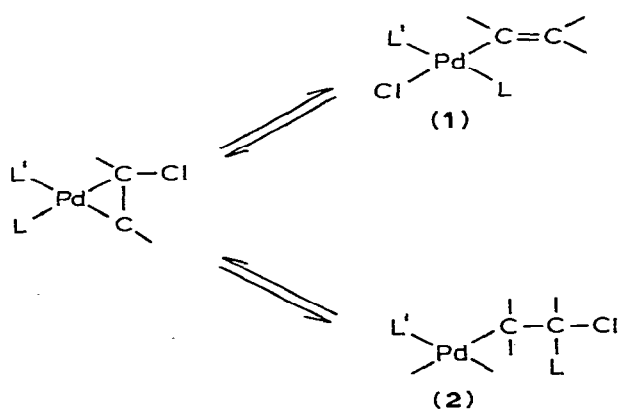
$$(Ph_3P)_2Pd(SnCl_3)^+ + CO \rightleftharpoons (Ph_3P)_2Pd(SnCl_3)(CO)^+ \qquad (14)$$

SCHEME 1. Vinylacetate ester synthesis.



diate produces the corresponding Pd—acenyl species C; both steps are well established in palladium chemistry [13], with the formation of C being favored by increases in CO pressure and the presence of strongly coordinating ligands, e.g. PPh_3 and polar solvents. The $(PPh_3)_2PdCl_2$—$SnCl_2$ catalyst does not readily add a second CO molecule to the double bond of the newly formed vinylacetate ester (Tables 2 and 3), instead we find reactions 1B and 9 are favored only where, either the $SnCl_3$; is displaced from the Pd coordination sphere by excess triphenylphosphine (Table 4), or the Group IVB metal halide components is absent (Table 5).

Some modification of Scheme 1 would be necessary in the case of vinyl halide conversion to acrylate esters (eq. 12a and c). Where the vinyl halide is initially π-bonded to Pd so as to favor rearrangement to a Pd—alkenyl species 1, subsequent CO insertion would lead to acrylate esters, but initial palladation followed by carbonylation of 2 could produce halopropionate esters [13]. In the case then of Pd bimetallic catalysts, where L and L′ are good nucleophiles the predominent path would be via 1, as in the syntheses of Table 6. Alternatively, carbonylation could be preceeded by halide displacement and Pd catalyzed vinyl ether formation [26], while acrylate ester formation might involve attack of carboalkoxy species upon the Pd—alkenyl [21].



Additional data, to be published shortly, should aid in distinguishing between these mechanistic alternatives.

Experimental

γ-Butyrolactam from allylamine

To a degassed sample of allylamine (125 mmole) and toluene (75 ml) contained in a glass-lined reactor equipped for pressurizing, heating, cooling and means of agitation is added, under a nitrogen environment, 1.25 mmole of the rhodium salt, chlorocarbonylbis(triphenylphosphine)rhodium. The reactor is sealed, flushed with CO and pressured under carbon monoxide (100 atm) while heating the agitated mixture to 120° C. Pressure is adjusted to 136 atm with CO and the mixture held at temperature for 2 to 12 hours. At the end of this time, carbonylation is terminated by rapid cooling and venting of the reactor. The crude product is filtered, distilled under reduced pressure (1—10 mm Hg) to remove toluene solvent and fractionally distilled to recover the γ-butyrolactam.

The crude liquid product is analyzed by GLC. Typical conversion and yield data are as follows:

Allylamine conversion	>95 mole %
γ-Butyrolactam yield	67 mole %
Liquid recovery	99%

Samples of γ-butyrolactam were also recovered by preparative GLC, and identified by a combination of NMR, IR, mass spec. and elemental analyses.

Found: C, 56.6; H, 8.4. C_4H_7NO Calcd.: C, 56.5; H, 8.3%. IR C=O, 1685 cm^{-1}. N—H, 3240 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.25 (s, 1H), 3.42 (t, 2H), 2.25 (t, 2H), 2.13 ppm (m, 2H).

The remaining by-products consist primarily of alkyl-substituted pyridines and unidentified polymeric material.

Allyl vinylacetate from allyl alcohol

To a deoxygenated, substantially water-free, mixture of benzene (75 ml) and allyl alcohol (100 mmole, 6.80 ml) contained in an appropriately sized, glass-lined pressure reactor, is charged under a nitrogen purge with stirring, 0.96 g of tin(II) chloride (5.0 mmole) and 0.35 g of $PdCl_2[P(C_6H_5)_3]_2$ complex (0.5 mmole). Stirring is continued for 2—5 minutes to give a clear, yellow solution with little residual solids. The charged reactor is flushed with nitrogen, sealed, pressurized with CO to 3000 psig, and heated to 80° C. The reactor is held at 80° C with rocking for 6 hours and cooled.

65 g of pale yellow liquid is recovered and analysis by gas chromatography shows conversion of allyl alcohol >98%. Distillation under reduced pressure (1 cm) produced a fraction which was worked-up to give 5.55 g of allyl vinylacetate product (yield 88 mole %).

Methyl vinylacetate from allyl chloride

To a glass-lined reactor provided with stirring, heating, cooling and pressurizing means is added 66 parts by weight of benzene and 12 parts by weight

of methanol. The solution is deoxygenated with nitrogen, and 1.12 parts by weight of tin(II) chloride dihydrate (5.0 mmole), 0.35 parts by weight of bis-(triphenylphosphine)palladium(II) chloride (0.5 mmole), and 3.82 parts by weight of allyl chloride (50 mmole) are added with stirring. Stirring is continued for 5—10 minutes at which time the solution is reddish in color. The autoclave is sealed, purged with nitrogen and carbon monoxide, and heated to 80° C under 3000 psig of carbon monoxide. After 6 hours at temperature, the reactor is allowed to cool, vented to reduce pressure, and 79 parts by weight of clear liquid recovered and analyzed by GLC.

Based on the allyl chloride charged, the yield of methyl vinylacetate is estimated at 75 mole %. The remainder of the carbonylated product is dimethyl α-methyl-succinate (yield 6.0%) and dimethyl glutyrate (yield 2.8%).

Methyl acrylate from vinyl chloride

To a stirred, deoxygenated mixture of benzene (66 g) and methanol (12 g) contained in the appropriate glass-lined reactor is charged, under a nitrogen purge, 1.88 g of anhydrous tin(II) chloride (10 mmole), 0.70 g of bis(triphenylphosphine)palladium(II) chloride (1.0 mmole) and 1.31 g of triphenylphosphine (5.0 mmole). The charged reactor is flushed with carbon monoxide, sealed, pressured to 100 psi with CO and heated to 95° C for ca. 15 min. Vinyl chloride (3.1 g) is then injected into the reactor from a side ampoule and the pressure adjusted to 2000 psi with additional CO. After 1—6 hours at temperature, the reactor is cooled, vented and 75 g of clear liquid recovered for analysis.

Dimethyl p-phenylenediacetate from α,α'-dichloro-p-xylene

To the appropriately sized, glass-lined reactor is charged a degassed sample of methanol (100 ml), 3.50 g (20 mmole) of α,α'-dichloro-*p*-xylene, 8.16 g (60 mmoles) of sodium acetate and 0.28 g (0.4 mmole) of bis(triphenylphosphine)-palladium(II) chloride. The mixture is agitated to solubilize most of the solids, the reactor flushed with carbon monoxide, pressurized up to about 200 psig with CO and heated to 80° C for 48 hours. After cooling, a clear yellow product solution is recovered and analyzed by GLC. Dimethyl-*p*-phenylenediacetate is isolated as a pure product giving a yield of 52%. The remainder is by-products such as the monoacetate.

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References

1 J. Falbe, Carbon Monoxide in Organic Synthesis, Springer-Verlag, New York, 1970, p. 78.
2 J. Falbe and F. Korte, Chem. Ber., 98 (1965) 1928.
3 A. Matsuda, Bull. Chem. Soc. Jap., 41 (1968) 1876.
4 J.F. Knifton, U.S. Patent 4, 111, 952 (1978).
5 J.F. Knifton, U.S. Patent 4, 110, 340 (1978).
6 J.F. Knifton, J. Org. Chem., 41 (1976) 2885.

7 J.F. Knifton, J. Mol. Catal., 2 (1977) 293.
8 J.F. Knifton, J. Amer. Oil Chem. Soc., 55 (1978) 496.
9 J.F. Knifton, U.S. Patent 3, 991, 101 (1976).
10 J.F. Knifton, U.S. Patent 4, 025, 547 (1977).
11 G.W. Parshall, Z. Naturfoschg. 18b (1963) 772.
12 H.C. Clark and H. Kurosawa, Inorg. Chem., 12 (1973) 357 and references therein.
13 J. Tsuji, Acc. Chem. Res., 2 (1969) 144.
14 R.F. Heck and D.S. Breslow, J. Amer. Chem. Soc., 85 (1963) 2779.
15 W.T. Dent, R. Long and Gr.H. Whitfield, J. Chem. Soc., (1964) 1588.
16 J. Tsuji, J. Kiji and M. Morikawa, Tetrahedron Lett., 26 (1963) 1811.
17 J.F. Knifton and R.M. Suggitt, U.S. Patent 4, 016, 194 (1977).
18 J.F. Stille and P.K. Wong, J. Org. Chem., 40 (1975) 532.
19 N.V. Kutepow, K. Bittler and D. Neubauer, German Patent 1, 227, 023 (1966).
20 J. Tsuji, M. Morikawa and J. Kiji, J. Amer. Chem. Soc., 86 (1964) 4851.
21 A. Schoenberg, I. Bartoletti and R.F. Heck, J. Org. Chem., 39 (1974) 3318.
22 R.D. Closson and K.G. Ihrman, U.S. Patent 3, 457, 299 (1969).
23 F. Wada and T. Matsuda, Bull. Chem. Soc. Jap., 46 (1973) 510.
24 T.F. Murray and J.R. Norton, J. Amer. Chem. Soc., 101 (1979) 4107.
25 R. Mason, G.B. Robertson, P.O. Whimp and D.A. White, Chem. Commun., (1968) 1655.
26 E.W. Stern, M.L. Spector and H.P. Leftin, J. Catal., 6 (1966) 152.
27 J.F. Knifton, J. Catal., 60 (1979) 27.