Russian Chemical Reviews

April 1988

Translated from *Uspekhi Khimii*, **57**, 529-561 (1988)

U.D.C. 542.91:542.97:547.1

Substitutional Carbonylation of Organic Compounds Catalysed by Palladium Complexes

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The results of studies on the catalytic carbonylation of organoelemental compounds, organic halides, and other substrates of the type RX, in which X is substituted by CO during the reaction, are analysed. The mechanism of the action of palladium carbonylation catalysts is examined and the principal applications of the substitutional carbonylation reactions in organic synthesis are indicated.
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I. INTRODUCTION

Among the selective methods for the preparation of oxygen-containing organic compounds, catalytic methods involving carbon monoxide play a special role. This industrially important field of homogeneous catalysis was founded as a result of the studies by Roelen[1] and Reppe[2] at the end of the 1930's and the beginning of the 1940's. Roelen showed that, in the presence of cobalt-containing catalyst, alkenes interact with CO and H_2 to form aldehydes with linear and branched structures containing one carbon atom more than the initial alkene:

$$RCH=CH_2+CO+H_2 \rightarrow RCH_2CH_2CHO+RCHMeCHO\,.$$

Reppe discovered a series of related reactions involving the carbonylation of alkenes, alkynes, and alcohols catalysed by carbonyl compounds of Group VIII metals. The products of these reactions are carboxylic acids, their derivatives, or alcohols, for example:

$$CH_2=CH_2+CO+H_2O \rightarrow EtCO_2H\,,$$

$$CH\equiv CH+CO+ROH \rightarrow CH_2=CHCO_2R\,,$$

$$MeCH=CH_2+CO+H_2O \rightarrow BuOH+CO_2\,.$$

After the publication of the above studies,[1,2] vigorous investigation of the reactions of organic compounds with carbon monoxide in the presence of transition metal complexes began. As a result, procedures such as the carbonylation of olefins, acetylenes, polyunsaturated compounds, alcohols, and nitrogen-containing compounds have been converted into large and independent branches of the catalytic chemistry of CO. The experimental data accumulated in this field as well as examples of the industrial use of the above reactions have been reflected in numerous monographs and reviews (see, for example, Refs.3–9).

The present review deals with the development of a comparatively new aspect of the chemistry of CO, which is of interest mainly for fine organic synthesis – the catalytic carbonylation of organoelemental compounds, organic halides, diazonium salts, arenes, and other substrates of the type RX (X = M, Hal, N_2BF_4, H, etc.). We have designated these reactions by the term "substitutional carbonylation", because the interaction of carbon monoxide with the substrates RX results in the substitution of the group X by the fragment CONu. Depending on the nucleophilic coreactant (Nu^-)

used, various carbonyl-containing products RCONu are formed—carboxylic acids and their derivatives, aldehydes, and ketones. Typical examples of such reactions are presented below:

$$RHal+CO+R_2'NH\rightarrow RCONR_2'+HHal,$$
$$RHgOAc+CO+R'OH\rightarrow RCO_2R'+HOAc+Hg,$$
$$RN_2BF_4+CO+R_4'Sn\rightarrow RCOR'+R_3'SnBF_4+N_2.$$

The complexes of a number of transition metals, namely palladium, nickel, cobalt, and rhodium, have been used as catalysts of the substitutional carbonylation of organic compounds. The substitutional carbonylation reactions have been studied most widely and in greatest detail under the conditions of homogeneous catalysis by palladium compounds. We have confined ourselves in the present review to other catalytic systems only when their application provides definite advantages compared with palladium complexes.

II. CARBONYLATION OF ORGANOELEMENTAL COMPOUNDS

Organic derivatives of many non-transition elements are known[3] to react with CO, forming a wide variety of oxygen-containing compounds. Unfortunately, such reactions can usually be achieved only under severe conditions (high CO pressure and temperature) and frequently proceed with a low selectivity. In many instances it is possible to overcome these difficulties by using palladium complexes as carbonylation catalysts. Catalytic carbonylation was first achieved for organic derivatives of mercury,[10] whose reactions with CO have now been most thoroughly investigated and have found applications in organic synthesis.

1. Reactions of Organomercury Compounds

It was noted in 1968[10] that, in the presence of stoichiometric amounts of $PdCl_2$, the aryl derivatives of mercury Ar_2Hg and ArHgCl interact with CO under very mild conditions: 1 atm and 20 °C. The reaction products are the acid chlorides ArCOCl when the carbonylation is carried out in an inert solvent or the esters $ArCO_2R$ when an alcohol is used as the coreactant:

$$Ph_2Hg+PdCl_2 \xrightarrow[MeCN]{CO} \underset{21\%}{PhCOCl}+HgCl_2+Pd,$$
$$4\text{-}MeC_6H_4HgCl+PdCl_2 \xrightarrow[MeOH]{CO} \underset{27\%}{4\text{-}MeC_6H_4CO_2Me}+HgCl_2+Pd.$$

As a result of the reaction, palladium(II) passes to the zero oxidation state. The application of a suitable oxidant, for example, $CuCl_2$, makes it possible to regenerate palladium(II) ($Pd + CuCl_2 \rightarrow PdCl_2 + Cu_2Cl_2$) and make the carbonylation catalytic:

$$ArHgCl \xrightarrow[CuCl_2,\ HOAc]{10\%\ PdCl_2,\ 1\ atm\ CO} ArCO_2H,$$

Ar=4-MeC_6H_4 (31%), 4-$HO_2CC_6H_4$ (56%),

In some cases, symmetrical diaryl ketones are formed in considerable amounts together with carboxylic acid derivatives (1—4 atm CO, 20 °C):[11]

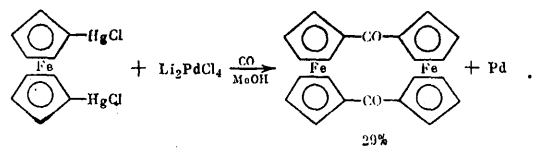
$$PhHgCl \xrightarrow[CuCl_2,\ MeCN]{10\%\ LiPdCl_4,\ CO} \underset{22-40\%}{PhCOCl}+\underset{11-29\%}{Ph_2CO}.$$

Kasahara and co-workers[12,13] achieved for the first time the carbonylation of organomercury derivatives of non-benzenoid aromatic systems—ferrocene, furan, and thiophen (50 atm CO, 70—100 °C):

$$ArHgCl+Li_2PdCl_4 \xrightarrow[MeOH]{CO} \underset{30-35\%}{ArCO_2Me}+\underset{32-40\%}{Ar_2CO}+Pd,$$

where Ar = ferrocenyl, 2-furyl, 2-(5-methoxycarbonylfuryl), and 2-thienyl.

They used the method developed for the single-stage synthesis of [1.1]ferrocenophane-1,12-dione from readily available 1,1'-di(chloromercuri)ferrocene:[12]



29%

The reaction of arylmercury acetates with CO in the presence of $Pd(OAc)_2$ (one equivalent) and added sodium acetate (two equivalents) takes place selectively at 1 atm in methanol or trifluoroacetic acid and leads to the formation of the methyl esters or anhydrides of arenecarboxylic acids respectively in high yields,[14] for example:

$$PhHgOAc+Pd(OAc)_2 \xrightarrow[NaOAc,\ MeOH]{CO} \underset{88\%}{PhCO_2Me}+Hg(OAc)_2+Pd,$$
$$PhHgOAc+Pd(OAc)_2 \xrightarrow[NaOAc,\ CF_3CO_2H]{CO} PhCO_2Ac \xrightarrow[2)\ CH_2N_2]{1)\ H^+/H_2O} \underset{86\%}{PhCO_2Me}.$$

We may note that the initial organomercury compounds can be synthesised by mercurating the corresponding arenes with mercury(II) acetate and can be used in the subsequent carbonylation without isolating them from the reaction mixture.

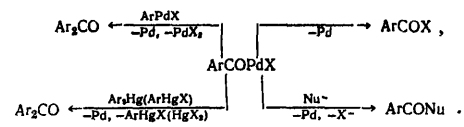
The active intermediates in the reactions of arylmercury(II) compounds in the reactions with CO described above are undoubtedly organic palladium σ-complexes, formed in the first stages of the process:[15]

$$Ar_2Hg+PdX_2\rightarrow ArPdX+ArHgX,$$
$$ArHgX+PdX_2\rightarrow ArPdX+HgX_2,$$
$$X=Hal,\ OAc.$$

In a CO atmosphere, the arylpalladium complex is readily carbonylated, affording acyl derivatives:[16,17]

$$ArPdX+CO\rightarrow ArCOPdX.$$

The possible pathways in the subsequent conversion of ArCOPdX into the final carbonyl-containing organic products are presented in the scheme below:[10,11,18]



The reductive elimination of ArCOPdX leads to ArCOX. In the presence of a nucleophilic coreactant (Nu^-) in the reaction mixture, its interaction with ArCOX or with ArCOPdX produces the carboxylic acid derivatives ArCONu. Symmetrical diaryl ketones are formed in the reaction of the acyl complex with the initial organomercury compounds or with the σ-aryl derivative of palladium. Carbonylation of organomercury compounds is frequently complicated by oxidation processes, which lead to the side products Ar_2, ArCl, etc.

The reactions of aryl derivatives of mercury with CO, catalysed by phosphine complexes of palladium, are of great interest from the synthetic point of view. These reactions are fairly selective, and, in contrast to those examined previously, are catalytic in relation to the palladium complex in the absence of specially added oxidants. Thus, on catalysis with 0.5—2 mole% $PdCl_2(PR'_3)_2$ (R' = Ph or Bu), organomercury salts of the benzene and naphthalene series

interact with CO and alcohols to form esters of arenecarboxylic acids:[19,20]

$$ArHgX \xrightarrow[70-110^\circ C,\ ROH]{\text{"Pd", 4-10 atm CO}} ArCO_2R + Hg,\quad 30-99\%$$

X=OAc, O_2CCF_3

R=Me, Et, n-C_8H_{17}, iso-Bu, CH_2=$CHCH_2$, Ph

ArHgX containing chlorine, methoxy-, methoxycarbonyl, dimethylamino-, and acetamido-groups in the aromatic ring readily enter into the reaction. Primary unsaturated alcohols, allyl alcohol, and phenol can be used as the nucleophilic coreactants. We may note that the reaction is sensitive to steric hindrance: the use of sterically hindered organomercury compounds or secondary or tertiary alcohols reduces appreciably the yield of the ester and leads to the preferential formation of ArH and $ArCO_2H$.

The conversion of the organomercury compounds ArHgX and Ar_2Hg into symmetrical diaryl ketones has been achieved under very mild conditions (1 atm CO, 20 °C) by using a system comprising metal complex and nucleophilic (I^- ion) catalysts and by carrying out the carbonylation in inert solvents [hexamethylphosphoramide (HMP), tetrahydrofuran (THF), and acetone]:[21,22]

$$ArHgX \xrightarrow[Bu_4NI]{1\%\ PhPd(PPh_3)_2I,\ CO} Ar_2CO + HgX_2 + Hg,\quad 78-99\%$$

X=Cl, Br, OAc

$$Ar_2Hg \xrightarrow[Bu_4NI\ or\ NaI]{0.5\%\ [Rh(CO)_2Cl]_2,\ CO} Ar_2CO + Hg,\quad 77-90\%$$

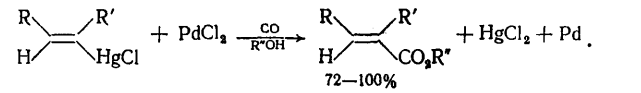
These reactions can serve as convenient methods of synthesis of substituted benzophenones $(YC_6H_4)_2CO$ (Y = H, 4-Me_2N, 4-H_2N, 4-MeO, 4-Me, 4-Cl, or 2-HO). The method is also applicable to the synthesis of heterocyclic ketones, which has been demonstrated for the conversion of 2-thienylmercury bromide into $(2\text{-}C_4H_3S)_2CO$.

The mechanism of the carbonylation of aryl derivatives of mercury in the presence of phosphine complexes of palladium differs from that presented above. The catalytically active species in the given case is the zerovalent palladium derivative PdL_2 (L = phosphine ligand) obtained by the reduction of the initial palladium complexes by organomercury compounds. As an example, the scheme for the catalytic cycle involving the formation of diaryl ketones by the carbonylation of organomercury compounds in the presence of $PhPd(PPh_3)_2X$ is presented below:[22]

$$PhPdL_2X + RHgX \rightarrow PhR + HgX_2 + PdL_2,$$
$$RHgX + PdL_2 \rightarrow RPd(HgX)L_2 \rightarrow RPdL_2X + Hg;$$
or
$$RHgPdL_2X$$
$$RPdL_2X + CO \rightarrow RCOPdL_2X$$
$$RCOPdL_2X + RHgX \rightarrow RCOPdRL_2 + HgX_2,$$
$$RCOPdRL_2 \rightarrow RCOR + PdL_2.$$

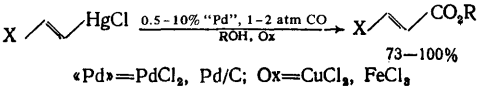
As a result of the oxidative addition of the organomercury salt to PdL_2 (the insertion of the zerovalent palladium complex in the Hg–C or Hg–X bond[23]) and the elimination of metallic mercury, the aryl derivative of palladium $RPdL_2X$ is obtained. The carbonylation of $RPdL_2X$ and the subsequent transmetallation reaction give rise to the diorganic complex $RCOPdRL_2$. The reductive elimination reaction of the latter leads to a ketone and the initial catalytically active PdL_2 species. We may note that the above scheme shows only one of the possible pathways leading to the formation of ketones in the carbonylation of organomercury salts. Clearly, the reaction involving the exchange between RHgX and $RPdL_2X$ can precede the insertion of CO in the C–Pd bond and metallic mercury may be eliminated in the last stages of the process. The addition of the iodide ion plays an important role. The I^- ion apparently accelerates[22] the exchange reaction of $RCOPdL_2X$ with RHgX (nucleophilic catalysis[24]) and facilitates the insertion of the zerovalent palladium complex in the Hg–C or Hg–X bond.

The use of vinyl derivatives of mercury as the initial substrates in the carbonylation reactions opens up pathways to the synthesis of αβ-unsaturated carbonyl compounds. Thus vinylmercury chlorides react with CO and $PdCl_2$ (one equivalent) in the presence of water or alcohols, forming αβ-unsaturated carboxylic acids or their esters in high yields (1 atm CO, -78–20 °C):[18]



R, R′=Alk, Ar, vinyl; R″=H, Me, Et

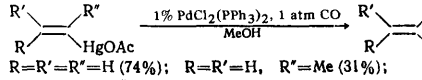
The carbonylation takes place with complete retention of the configuration of the vinyl fragment. By adding oxidants for zerovalent palladium [copper dichloride[18] or iron(III) chloride[25]], it was possible to make the reaction catalytic:



«Pd»=$PdCl_2$, Pd/C; Ox=$CuCl_2$, $FeCl_3$

X=Cl, Ph, Bu; R=H, Me, Et, Pr

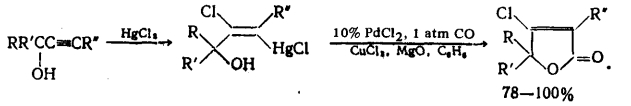
The need to add oxidants disappears when the process catalysts are phosphinepalladium complexes:[19,20]



R=R′=R″=H (74%); R=R′=H, R″=Me (31%);
R=R′=Ph, R″=H (36%)

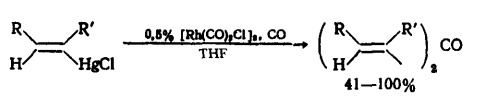
The cause of this phenomenon, which arises from the reaction mechanism, were considered in our previous communication in relation to the carbonylation of aryl derivatives of mercury.

If the organomercury compound contains the hydroxy-group, then under certain steric conditions the latter can behave as the nucleophile in the carbonylation process. Such a reaction results in intramolecular cyclisation, which leads to the formation of a lactone. This precise idea has in fact been the basis of an elegant method of synthesis of β-chloro-$\Delta^{\alpha\beta}$-butenolides, which involves two stages: the mercuration of propargyl alcohols and the subsequent carbonylation of the resulting organomercury derivatives:[26,27]



The yield of the lactone increases when the reaction with CO is carried out in the presence of magnesium, which binds the HCl evolved.

Symmetrical divinyl ketones have been synthesised by carbonylating vinylmercury chlorides at 1 atm at 25 °C in THF in the presence of a rhodium catalyst:[28]

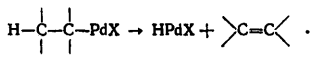


R=H, Ar, Alk; R′=H, Alk

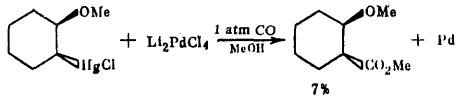
The possibility of using palladium complexes as catalysts in this reaction has not been investigated.

The interaction of alkylmercury compounds with CO has been studied comparatively little. The difficulty of carrying out the reaction is associated with the instability of the intermediate alkyl

complexes of palladium and other transition metals, which tend to undergo a rapid β-elimination reaction:

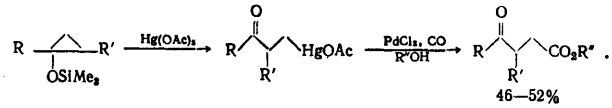


As a result of this side process, the yield of the carbonylation products is usually low:[29]



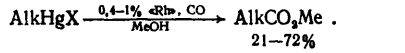
7%

The undesirable elimination reaction can be avoided by using initial substrates containing an electron-accepting substituent in the β-position relative to the mercury atom. Thus β-acetoxymercurikетones interact with $PdCl_2$ (one equivalent) and alcohols in a CO atmosphere, forming γ-ketoacid esters in satisfactory yields:[30]



46—52%

The carbonylation of alkylmercury(II) derivatives in methanol at an elevated CO pressure (2—63 atm), catalysed by $(Ph_3P)_3RhCl$, leads to methyl esters of alkanecarboxylic acids, the yield of the latter reaching 72%:[19,20]

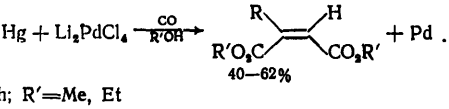


21—72%

X = OAc, Br
Alk = Et, n-C_6H_{13}, n-$C_{12}H_{25}$, $MeCO_2(CH_2)_2$, $BuCH(OMe)CH_2$, 2-methoxycyclohexyl

The examples presented make it necessary to revise the initial sceptical attitude towards the synthetic possibilities of the reactions of alkyl derivatives of mercury with CO and show that it is essential to investigate them more widely. The synthetic use of the stereoselectivity of this reaction, which proceeds with the preferential retention of the configuration at the carbon atom linked to the metal, is promising.[29]

Dialkynylmercurys interacts with CO in an alcoholic medium at 20 atm and 25 °C with formation of a substituted maleate as the main product:[31]



40—62%

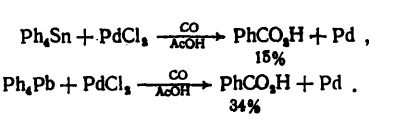
R=Et, Ph; R′=Me, Et

The authors believe that $RC{\equiv}CCO_2R'$ is formed in the first stage of the process and subsequently undergoes hydroalkoxycarbonylation.

2. The Reactions of Other Organoelemental Compounds

The carbonylation of other organoelemental compounds has been studied to a much lesser extent.

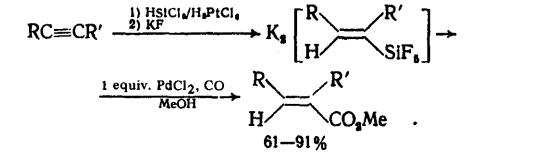
Tetraphenyl-tin and tetraphenyl-lead react with CO and palladium chloride at 1 atm and 20 °C in acetic acid with formation of benzoic acid, but the yields are low in both reactions:



15%

34%

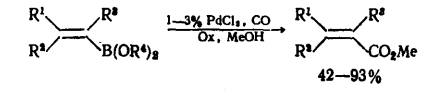
The carbonylation of the readily available vinyl derivatives of silicon—(*E*)-alkenylpentafluorosilicates— was achieved.[32] The reaction takes place stereospecifically and leads to high yields of the esters of (*E*)-αβ-unsaturated carboxylic acids (1 atm CO, 25 °C):



61—91%

It is noteworthy that, in contrast to alkenylpentafluorosilicates, the corresponding alkenyltrialkylsilanes are relatively unreactive: they are carbonylated at a low rate. Phenyl- and benzylpentafluorosilicates do not interact with CO under the conditions investigated.

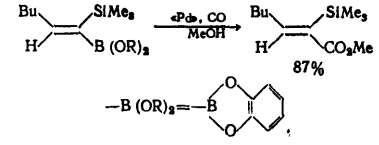
A convenient method of stereocontrolled synthesis of αβ-unsaturated acid esters, based on the reaction of alkenylboronates with CO and methanol in the presence of palladium chloride (1 atm, 0 to 50 °C), has been proposed.[33] The use of *p*-benzoquinone as the oxidant for zerovalent palladium makes this reaction catalytic:



42—93%

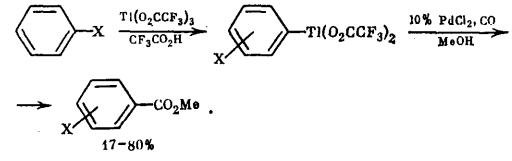
R^1, R^2, R^3=H, Alk, Ar; Ox = *p*-benzoquinone

It is of interest that, when the initial substrate contains a silicon—carbon bond together with the boron—carbon bond, the former is not involved in the reaction:



87%

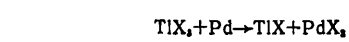
The carbonylation of the monoaryl compounds of thallium $ArTl(O_2CCF_3)_2$ in methanol leads to the methyl esters of arenecarboxylic acid (1 atm CO, 20 °C):[34,35]



17—80%

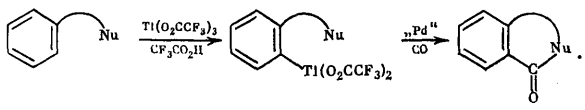
X = t-Bu, H, MeO, F, AcNH, H_2NCONH, PhCO

The reaction is catalytic with respect to palladium in the absence of specially added oxidants, because the thallium(III) salt, formed in the exchange interaction of organothallium derivatives with $PdCl_2$, regenerates the catalyst:

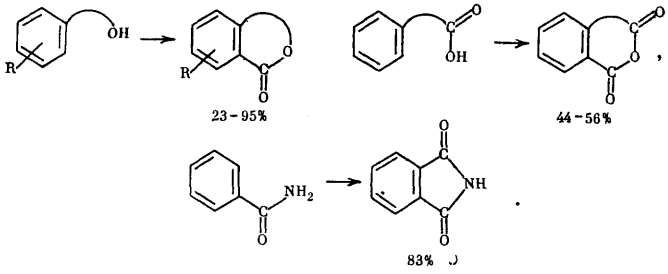


The initial arylthallium compounds can be obtained by the direct electrophilic substitution of thallium in arenes. This reaction is distinguished by high regioselectivity. Thus the fluorine atom and the t-Bu groups in methanol direct the attack by the thallium-substituting reagent almost exclusively to the *para*-position, while AcNH, PhCO, and other groups which are coordinated to the thallium(III) salt direct the attack to the *ortho*-position in the benzene ring. Among *ortho*-directing substituents, those which are capable of acting as nucleophiles in the carbonylation stage, for example CH_2OH, $(CH_2)_2OH$, CO_2H, $CONH_2$, etc. occupy a special

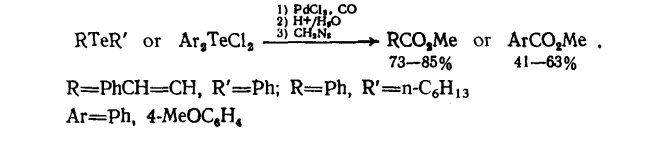
place. In this case the thallium substitution process and subsequent carbonylation result in intramolecular cyclisation:



The method has been used to synthesise a series of cyclic products—substituted γ- and δ-lactones, phthalic and homophthalic anhydrides, and phthalimide:[34,35]



The reaction of alkylbenzenes with CO (4—7 atm) in the presence of thallium trifluoroacetate and catalytic amounts of a palladium(II) salt leads to alkylbenzoic acids.[36] For example, a mixture of isomeric methylbenzoic acids has been obtained from toluene (*para*:*meta*:*ortho* = 91:5:4) in 81% yield relative to $Tl(O_2CCF_3)_3$ [Tl(III):Pd(II) ≃ 73:1]. The monoaryl derivatives of thallium(III), formed *in situ*, are in all probability intermediates in these reactions. The carbonylation of organic compounds of tellurium(II) and tellurium(IV) in the presence of stoichiometric amounts of $PdCl_2$ (1—20 atm CO, 20—30 °C) has been achieved in a recently published study:[37]



R=PhCH=CH, R′=Ph; R=Ph, R′=n-C_6H_{13}

Ar=Ph, 4-$MeOC_6H_4$

The reaction of the asymmetric telluride PhCH = CHTePh with CO leads mainly to an αβ-unsaturated acid ester, i.e. PhCH = $CHCO_2Me$. In the case of n-C_6H_{13}TePh, a benzoic acid derivative is formed, namely $PhCO_2Me$.

Thus the carbonylation of organoelemental compounds in the presence of palladium complexes makes it possible to obtain a wide variety of carbonyl-containing products. In many instances, these are chemoselective and stereoselective processes in which catalytic amounts of palladium compounds are used.

III. CARBONYLATION OF ORGANIC HALIDES

Not only organoelemental compounds but purely organic reagents can serve as sources of organic groups in substitutional carbonylation reactions catalysed by palladium complexes. Among such compounds, organic halides have found the widest application. The possibility of achieving reactions of this kind is based on the formation of σ-organopalladium compounds $RPdL_2X$ (L = ligand) as a result of the oxidative addition of the halide RX to a zerovalent palladium complex:[38—40]

$$PdL_n + RX \rightarrow \textit{trans}\text{-}RPdL_2X + (n-2)L .$$

In view of the importance of the oxidative addition reaction for the understanding of the data described in this Section, we shall deal briefly with its main features.[40] Firstly, aryl and vinyl halides as well as benzyl, allyl, and certain other halides can be used in the reaction (in the case of alkyl halides containing a β-hydrogen atom, the organopalladium compounds formed are unstable and tend to undergo rapid β-elimination of palladium hydride). Secondly, the reactivity of the organic halides towards zerovalent palladium usually falls in the sequence RI > RBr > RCl. Thirdly, in the case of aryl halides, the rate of oxidative addition diminishes on passing from substrates containing electron-accepting groups to halogeno-derivatives containing electron-donating substituents. Fourthly, the reaction with vinyl halides proceeds with complete retention of the configuration of the vinyl group. Benzyl and allyl halides interact with zerovalent palladium complexes with the preferential inversion of the configuration of the carbon atom linked to the halogen. Finally, zerovalent palladium is used in the atomic state in the oxidative addition reactions. This can be achieved most simply by using zerovalent palladium complexes. As a result of oxidative addition, the coordination number of palladium increases by 2. Hence it follows that the initial zerovalent palladium complexes must be coordination-unsaturated or can readily dissociate under the reaction conditions.

The first communications concerning the carbonylation of organic halides under the conditions of catalysis by palladium compounds appeared in 1963—1964.[41—43] However, up to the middle 1970's, the number of studies were small and the initial substrates used were mainly allyl halides. The carbonylation occurred under severe conditions at high CO pressures and temperatures. Only after the discovery of the reaction involving the oxidative addition of organohalides to zerovalent palladium complexes[38] and the elucidation of the role which phosphine and certain other electron-donating ligands play in the stabilisation of intermediate organopalladium compounds, was it possible to reduce significantly the temperature and pressure at which carbonylation takes place and to extend the reaction to a wide range of organic halides.[44—48] Since then systematic research into the catalytic carbonylation of organic compounds began and this led to the development of new convenient methods of synthesis of a wide variety of carbonyl-containing products.

1. The Synthesis of Carboxylic Acids and Their Derivatives

The reaction of organic halides RX with CO catalysed by palladium complexes has found the widest application in the synthesis of carboxylic acids and their derivatives—esters and amides:

$$RX + HNu + CO \xrightarrow{\text{«Pd»}} RCONu + HX .$$

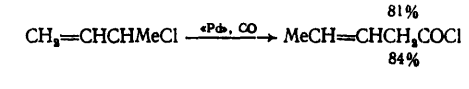
Nu=OH, OR′, NR'_2

Carbonylation without the addition of a nucleophilic coreactant has been least investigated and takes place under much more severe conditions with formation of carboxylic acid halide:

$$RX + CO \xrightarrow{\text{«Pd»}} RCOX .$$

For example, allyl chlorides and bromides interact with CO in the presence of a palladium catalyst at a pressure of 77—500 atm and a temperature of 80—150 °C in benzene or in the absence of a salt, forming the halides of αβ-unsaturated carboxylic acids.[42,43,49—51] The yield of the target product is fairly high under certain conditions and can become quantitative.[43] The palladium catalyst is usually added to the reaction mixture in the form of a π-allyl complex[43,50,51] or a palladium(II) salt.[42,49] The use of palladium black leads to the formation of a less active catalytic system.[43]

Despite the fact that the carbonylation can be accompanied by the allylic rearrangement, it is regioselective: only one product is obtained, in which the carbonyl group is linked to the least substituted carbon atom of the allyl fragment:[43,50]



In both reactions described above, the oxidative addition of the initial substrate to zerovalent palladium results in the formation of the same intermediate – bis(1-methyl-π-allylpalladium chloride).

In certain cases the carbonylation is complicated by the migration of the double bond in the acid halide from the βγ-position to the conjugated αβ-position:[49]

$$CH_2{=}CHCH_2Cl \xrightarrow{«Pd», CO} CH_2{=}CHCH_2COCl + MeCH{=}CHCOCl\ .$$

Allyl chlorides are less active than the corresponding bromides. Thus the rates of carbonylation of $CH_2=CHCH_2Cl$ and $CH_2=CHCH_2Br$ are in the ratio $1:\sim 0.08$ under identical conditions.[50] The structure of the allyl group also influences the reactivity of the halogeno-derivatives. The relative rates of the reaction increase in the sequence[50]

$$CH_2{=}CHCH_2Cl > MeCH{=}CHCH_2Cl \cong CH_2{=}CHCHMeCl > > \text{3-chlorocyclo-octene} \cong CH_2{=}CMeCH_2Cl > CH_2{=} {=}CHCHCl_2 \cong ClCH_2CH{=}CHCH_2Cl,$$

in the ratios 1:0.5: 0.04: 0.01.

The carbonylation of a mixture of allyl chloride and a conjugated diene leads to the formation of a derivative of the dienecarboxylic acid together with the chloride of a βγ-unsaturated acid,[50] for example:

$$CH_2{=}CHCH_2Cl + CH_2{=}CHCH{=}CH_2 \xrightarrow{«Pd», CO} \rightarrow \underset{36\%}{CH_2{=}CHCH_2COCl} + \underset{28\%}{CH_2{=}CH(CH_2)_2CH{=}CHCH_2COCl}.$$

Aryl, vinyl, benzyl, and alkyl chlorides, which are less reactive in the oxidative addition reaction, do not interact with CO under the conditions which are usually employed in the reactions of allyl chlorides.[43] The conversion of halogenoarenes into aroyl halides in the presence of palladium catalysts can be achieved at high temperature and CO pressures.[52,53] Thus arenecarboxylic acid fluorides have been obtained by carbonylating halogenoarenes at 300 – 350 °C and 600 – 900 atm in the presence of alkali metal fluorides:[53]

$$ArX + MF \xrightarrow[0.5-78\%]{«Pd», CO} ArCOF + MX,$$

"Pd" = $PdCl_2$ or Pd/C; M = alkali metals; X = F, Cl, Br, I

Summarising, one may say that the synthesis of the acid halides RCOX by the reaction of RX with CO is of limited importance and is applicable mainly to the synthesis of the halides of βγ-unsaturated acids from allyl halides. The catalytic cycle in the formation of RCOX apparently includes stages involving the oxidative addition of RX to zerovalent palladium, the insertion of CO in the C – Pd bond in the complex RPdX, and the reductive elimination of RCOPdX (we considered previously all the reactions of the palladium complexes incorporated in the cycle described). Under the conditions used in the synthesis of acid halides, palladium-containing intermediates readily decompose with the liberation of the relatively inactive palladium black. The reason for their instability is the absence from the reaction mixture of ligands capable of stabilising these palladium compounds. The deactivation of the homogeneous palladium catalyst necessitates the carrying out of the carbonylation of organic halides under very severe conditions. The carbonylation of allyl substrates is an exception, probably because of the high reactivity of allyl halides in the oxidative addition to zerovalent palladium and the stability of the π-allyl complexes of palladium obtained as a result of the oxidative addition.

The palladium catalyst can be stabilised in solution by adding phosphine ligands (other electron-donating ligands are used for this purpose more rarely). However, the acid halides RCOX cannot be obtained from RX and CO when the reacion is catalysed by phosphine complexes of palladium, because the oxidative addition of RX and the subsequent carbonylation of the resulting $RPd(PR'_3)_2X$ leads to the stable acyl derivative $RCOPd(PR'_3)_2X$,[17] which is incapable of reductive elimination. It was found that such acyl complexes readily react with certain nucleophiles. Thus the reaction with the alcohols R″OH yields the esters RCO_2R''.[48,54] This makes it possible to realise the catalytic cycle and to achieve the conversion of the halogeno-derivatives RX into the esters RCO_2R'' under the conditions of homogeneous catalysis by phosphine complexes of palladium:

$$RX + PdL_n \rightarrow RPdL_2X + (n-2)L,$$
$$RPdL_2X + CO \rightarrow RCOPdL_2X,$$
$$RCOPdL_2X + R''OH \rightarrow RCO_2R'' + HPdL_2X,$$
$$HPdL_2X + (n-2)L \rightarrow HX + PdL_n,$$
$$HX + B: \rightarrow BHX.$$
$$L = Pr'_3 \text{ and/or CO and B: } = \text{base}$$

The scheme presented reflects the generally accepted treatment of the mechanism of the alkoxycarbonylation of organic halides.[17,55] However, it is noteworthy that the available literature data do not rule out an alternative version of the mechanism of this reaction postulating the involvement in the catalytic cycle of the alkoxycarbonyl and not acyl complexes of palladium:[44]

$$RX + L_nPdCO \rightarrow RPd(CO)LX + (n-1)L,$$
$$RPd(CO)LX + R''OH + B: + L \rightarrow RPd(CO_2R'')L_2 + BHX,$$
$$RPd(CO_2R'')L_2 + CO + (n-2)L \rightarrow RCO_2R'' + L_nPdCO\ .$$

During the alkoxycarbonylation of RX, the strong acid HX accumulates and can cause the protolysis of the intermediate σ-organopalladium compounds[54] and may thereby exert an inhibiting effect on the course of the reaction. Organic or inorganic bases, among which tertiary amines,[44,47] potassium carbonate[56] and sodium acetates,[47] have found the most extensive application, are usually employed to remove the HX. One cannot rule out the possibility that the role of the base is also manifested in the reactivation of the nucleophile:[48]

$$R''OH + B: \rightleftarrows R''O^- + BH^+.$$

Aromatic halides are most often used as the initial substrates in the alkoxycarbonylation reaction, for example:[44]

$$ArX + BuOH \xrightarrow[100°C,\ Bu_3N]{1.5\%\ «Pd»,\ 1\ atm\ CO} \underset{46-96\%}{ArCO_2Bu}$$

X=Br, I; Ar=4-YC_6H_4 (Y=H, MeO, MeO_2C, NC), 2,6-$Me_2C_6H_3$, 1-naphthyl

The triphenylphosphine complexes of palladium $PdX_2(PPh_3)_2$ and $PhPd(PPh_3)_3X$ are effective catalysts of the process. In the case of aryl iodides, which are more reactive in oxidative addition than bromides, the reaction proceeds smoothly in the presence of palladium acetate (apparently Bu_3N plays the role of the weak stabilising ligand in this instance).

The reactivity of the halides depends on the structure of the allyl group and decreases in the sequence 4-NCC_6H_4Br > PhBr > 4-$MeOC_6H_4Br$ in the ratio 275:1:0.23 (the method of competing reactions). Judging from the half-life in the carbonylation reaction, iodobenzene is only slightly more reactive than bromobenzene. This probably shows that the oxidative addition is not the rate-limiting stage of the process.[44]† It is of interest that the steric hindrance generated by the *ortho*-substituents in 1-iodo-2,6-dimethylbenzene does not prevent the reaction: 2,6-$Me_2C_6H_3CO_2Bu$ was obtained in 63% yield.[44]

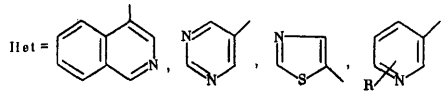
†According to Fauvarque et al.,[39] the reactivity of aryl bromides in the oxidative addition to zerovalent palladium is significantly lower than that of the corresponding iodides.

The methoxycarbonylation of aryl halides can be achieved successfully only at an elevated pressure: methyl benzoate is synthesised by the reaction of iodobenzene with methanol and CO at 3–14 atm.[47,56] Under milder conditions, (18 °C, 1 atm CO) the carbonylation takes place with a low yield.[48]

It has recently been possible to extend the reaction to heterocyclic halogenoderivatives.[57] The ethyl esters of isoquinoline-4-carboxylic, pyrimidine-5-carboxylic, and thiazole-5-carboxylic acids as well as those of substituted pyridine-carboxylic acids have been obtained in high yields:

$$HetX + EtOH \xrightarrow[100^\circ C,\ Et_3N]{PdCl_2(PPh_3)_2,\ 7\ atm\ CO} HetCO_2Et$$

X = Br, Cl; 35–100%

Het = 

The tin and sodium alkoxides Et_3SnOMe and NaOMe can be used conveniently as the coreactant in the alkoxycarbonylation reactions of aryl iodides instead of alcohols:[58–60]

$$ArI + \underset{\text{or NaOMe}}{Et_3SnOMe} \xrightarrow[20^\circ C]{2\%\ PhPd(PPh_3)_2I,\ 1\ atm\ CO} ArCO_2Me\ .$$

75–99%

Ar = 4-XC_6H_4 (X = H, MeO_2C, NC, NO_2), 1-naphthyl

The use of such powerful nucleophiles made it possible to convert ArI into $ArCO_2Me$ not only under very mild conditions but also at a high rate. Thus the carbonylation of 1-iodonaphthalene in the presence if NaOMe terminates after 4 h and leads to 1 $MeO_2CC_{10}H_7$ in 90% yield,[60] while that analogous reaction of 1-bromonaphthalene with $BuOH/Bu_3N$ does not go to completion even after 80 h: 46% of 1-$MeO_2CC_{10}H_7$; degree of conversion of 1-$C_{10}H_7Br$ 81%.[44]

The alkoxy-derivatives of aluminium,[61] boron,[62] titanium, and zirconium[63] are less reactive in the reactions with aryl halides and CO. The carbonylation in the $ArBr-E(OR)_n$ system can be achieved only at an elevated temperature in the presence of a zerovalent palladium complex (E = Ti) or a mixed catalyst containing zerovalent palladium and rhodium(I) complexes (E = Al, B, or Zr):

$$ArBr + E(OR)_n \xrightarrow[75-150\ ^\circ C]{cat.,\ 1\ atm\ CO} ArCO_2R$$

40–98%

E = Al, B(n = 3); Ti, Zr (n = 4); cat. = 6% $Pd(PPh_3)_4$ or 6–8% $Pd(PPh_3)_4$ + 9–11% $[(hexa\text{-}1,5\text{-}diene)RHCl]_2$

Ar = XC_6H_4 (X = H, 4-MeO, 4-CH_2=CH, 3-Me), 1-naphthyl

R = Et, Pr, iso-Pr, Bu, t-Bu

Vinyl iodides and bromides interact with CO and ROH to form the esters of αβ-unsaturated carboxylic acids (1–87 atm, 60–125 °C):[44]

$$RR'C{=}CR''Y + BuOH \xrightarrow[Bu_3N]{1.5\%\ «Pd»,\ CO} RR'C{=}CR''CO_2Bu\ .$$

58–95%

X = Br, I; «Pd» = $PdX_2(PPh_3)_2$

A mixture of geometrical isomers is usually obtained in which the product with retention of the configuration predominates. A decrease of temperature to 60–80 °C and the addition of an excess of triphenylphosphine make it possible to increase the stereoselectivity of the process, but the rate of carbonylation then falls markedly. Together with *cis-trans* isomerisation, the formation of side products is observed in some cases as a result of the migration of the double bond in the ester from the αβ- to the βγ-position.

The carbonylation of vinyl bromides in the presence of sodium, aluminium, boron, titanium, and zirconium alkoxides has been described only for individual examples.[59–63] The limited amount of experimental data precludes definite conclusions about the synthetic possibilities of these reactions.

The alkoxycarbonylation of allyl halides has been studied inadequately. The reaction is carried out in the presence of palladium catalysts not containing phosphine ligands under severe conditions (97–500 atm, 80–160 °C), which led to low yields of βγ-unsaturated carboxylic acid esters (29–52%).[41–43]

The methyl and butyl esters of phenylacetic acid were obtained in satisfactory yields by the carbonylation of $PhCH_2Cl$[47] or $PhCH_2Br$[56] catalysed by $PdCl_2(PPh_3)_2$. The reactions of benzyl halides can be complicated by the formation of side products as a result of the substitution of the halogen by the alkoxy-group, while in the case of substrates of the type ArCH(Alk)Hal, containing a hydrogen atom in the β-position in the alkyl chain, unsaturated compounds can be produced. Thus the carbonylation of α-bromoethylbenzene in the presence of methanol leads to methyl 2-phenylpropionate (49%), α-methoxyethylbenzene (24%), and styrene (12%).[64]

The interaction of propargyl chloride with CO in methanol is accompanied by the hydromethoxycarbonylation of the triple bond and affords methyl itaconate $CH_2=C(CO_2Me)CH_2CO_2Me$ in 66% yield.[65]

Yet another type of halide used as the initial substrates in the synthesis of esters comprises α-halogenoketones. Thus the synthesis of $PhCOCH_2CO_2Me$ (64%) by the reaction of $PhCOCH_2Br$ with CO in methanol has been described.[47]

The alkoxycarbonylation of halogeno-derivatives of saturated hydrocarbons (primary bromoalkanes) and also of phenylethyl bromide whose reactivity is similar to theirs has been achieved only recently[62,63] (1 atm CO, 90–150 °C):

$$RBr + E(OBu)_n \xrightarrow{cat.,\ CO} RCO_2Bu\ .$$

42–88%

E = B (n = 3), Ti (n = 4); R = n-C_8H_{17}, n-$C_{12}H_{25}$, $PhCH_2CH_2$

cat. = 6% $Pd(PPh_3)_4$ (E = Ti) or 6% $Pd(PPh_3)_4$ + 9% $[(hexa\text{-}1,5\text{-}diene)RhCl]_2$ (E = B)

The diester $BuO_2C(CH_2)_6CO_2Bu$ (76%) is formed in the analogous reaction of $Br(CH_2)_6Br$ with $B(OBu)_3$.[62]

At high CO pressures, double carbonylation of organic halides can take place, which is of great interest as a method of synthesis of derivatives of α-ketoacids (150 atm CO, 15–120 °C):[66]

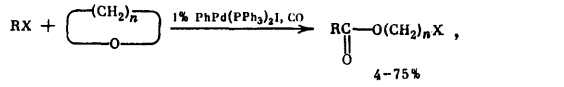
$$RX + R'OH \xrightarrow[Et_3N]{1\%\ «Pd»,\ CO} \underset{0-62\%}{RCOCO_2R'} + \underset{3-95\%}{RCO_2R'}\ .$$

RX = PhI, PhBr, 4-MeC_6H_4I, 4-$MeOC_6H_4I$, 2-iodothiophen, 5-bromothiazole, (*E*)-PhCH=CHBr

Under these conditions, the interaction of the halides RX with CO in alcohols leads to a mixture of the esters RCO_2R' and $RCOCO_2R'$, the mole fraction of the latter ranging from 0 to 91% depending on the nature of the initial reactants, the catalysts, and other factors. In order to increase the yield of α-ketoacid esters, it is essential to use as catalysts the complexes $PdCl_2L_2$, where L is the phosphine ligand with a conical angle of 145–170 °C (for example, Ph_3P, iso-Pr_3P, etc. and the process must be carried out at high pressures and low temperatures. It is recommended that the alcohols R'OH with R' = Bu, t-$BuCH_2$, iso-Pr, or cyclo-C_6H_{11} be used; when R' = Me, t-Bu, Ph, or $PhCH_2$, the only reaction product is RCO_2R'.

The ester $RCH(CO_2Et)CH_2CCl_3$ (29–60%) has been obtained together with CCl_4, RCH=CH, and CO in ethanol together with the products of the addition of carbon tetrachloride to the double bond of the initial alkene $RCHClCH_2CCl_3$ (16–33%).[67] It is not possible to extend this method to other organic halides.

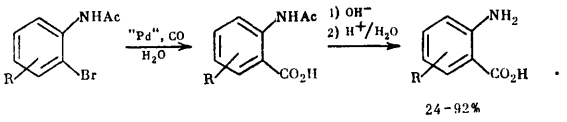
It has been proposed[68] that cyclic ethers, namely epoxides, oxetan, THF, and tetrahydropyran, be used as nucleophilic coreactants in the alkoxycarbonylation reaction (20 atm CO, 120–130 °C):



RX = PhI, PhBr, 4-AcC_6H_4Br, PhCH=CHBr, PhCH=$CHCH_2Cl$, $PhCH_2Cl$, $PhCOCH_2Cl$; $n = 2-5$

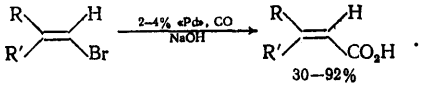
On passing from epoxides to less strained oxygen-containing heterocycles, the rate of carbonylation and the yield of products (esters of halogenohydrins) decrease sharply: oxiran > oxetan > THF > tetrahydropyran. The reactivity of tetrahydropyran does not differ from that of the acyclic dibutyl ether and the compound is almost inactive in this reaction.

The carbonylation of organic halides under the conditions of homogenous catalysis by palladium complexes is used widely in the synthesis of a wide variety of carboxylic acids. Thus the reaction of aryl halides (substituted bromobenzenes and 1- and 2-bromonaphthalenes) with CO(2–3 atm) and H_2O at 110–130 °C in the presence of the base Bu_3N and catalytic amounts of $PdX_2(PPh_3)_2$ (X = Cl or Br) or $Pd(PPh_3)_4$ leads to $ArCO_2H$ in a yield up to 94%.[69] The authors used the method to obtain anthranilic acids:



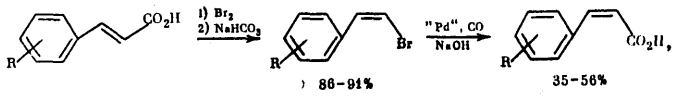
24–92%

The carboxylation of RX has been achieved[70-75] in a two-phase system: an aqueous solution of sodium hydroxide–organic solvent (C_6H_6, *p*-$Me_2C_6H_4$, CH_2Cl_2, or $EtCMe_2OH$). Tetrabutylammonium iodide,[70] tetrahexylammonium bisulphate,[72,74] benzyltriethylammonium chloride,[73,75] etc. were used as the phase transfer catalysts. We may note that the presence of a quatenary ammonium salt is not obligatory, at least in reactions with participation of benzyl halides.[72] Depending on the structurre of the halogeno-derivative RX, the following reactivity series were observed: $PhCH_2X$ > PhX and RI > RBr > RCl.[71] The carboxylation in a two-phase system usually takes place under very mild conditions. This is especially important in the reactions of halides of the vinyl type, because it makes it possible to convert them into αβ-unsaturated acids with the retention of both (*E*)- and (*Z*)-configurations of the vinyl group (1 atm CO, 20–50 °C):[73,75]



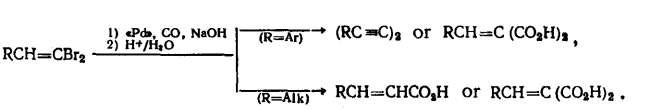
«Pd»=$Pd(PPh_3)_4$, $Pd(Ph_2PCH_2CH_2PPh_2)$;
R, R′=H, Ar, Alk

A convenient method of synthesis of *cis*-cinnamic acids from the corresponding *trans*-isomers is based on this reaction (1 atm CO, 20 °C):[73]

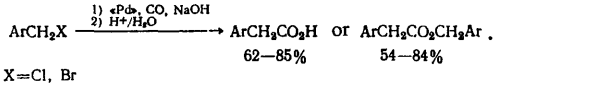


86–91% 35–56%

Depending on the nature of the initial dibromide the organic solvent employed, the interaction of 1,1dibromoalk-1-enes with CO leads to different products–diynes, αβ-unsaturated monoacids, or methylenemalonic acids (1 atm CO, 40–75 °C):[74]

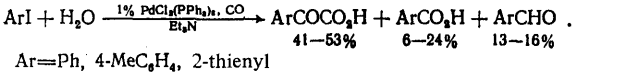


The carbonylation of benzyl halides in an aqueous sodium hydroxide solution–organic solvent system (1–5 atm CO, 20 to 95 °C) is used to synthesise arylacetic acids[70-72] and their benzyl esters.[72] The reaction pathway is determined mainly by the nature of the palladium catalyst and by the presence or absence of a quaternary ammonium salt (phase transfer catalyst):



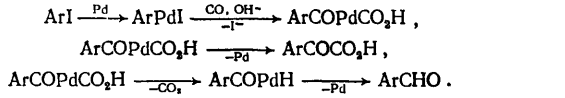
X=Cl, Br

It is noteworthy that the product of the double carbonylation of the initial halides, namely $ArCOCO_2H$, as well as a small amount of the aldehyde ArCHO are obtained together with $ArCO_2H$ from aryl iodides and H_2O at a high CO pressure (150 atm CO, 40–80 °C):[76]

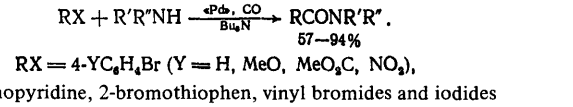


Ar=Ph, 4-MeC_6H_4, 2-thienyl

The mechanism of the formaion of the α-ketoacid and the aldehyde proposed by the authors is presented in the Scheme below (the ligands not involved in the reaction have been omitted from the Scheme):



The interaction of the halides RX with CO and the amines R′R″NH (1 atm, 100 °C), catalysed by 1.5 mole% of $PdX_2(PPh_3)_2$, leads to the carboxylic acid amides RCONR′R″.[45] Halogeno-derivatives of the aryl and vinyl types can be used as the initial substrates in the reaction. The amine base (Bu_3N) is as a rule added to neutralise, together with the amine reactant (R′R″NH), the acid HX evolved in the carbonylation reaction:



RX = 4-YC_6H_4Br (Y = H, MeO, MeO_2C, NO_2),
3-bromopyridine, 2-bromothiophen, vinyl bromides and iodides
R′R″NH=$PhNH_2$, $PhCH_2NH_2$, $(CH_2)_4NH$

The conversion of organic halides into amides is achieved at a higher rate than that of the analogous alkoxycarbonylation reaction. For example, the amide $PhCONHCH_2Ph$ is formed 17 times faster in the reaction of PhBr with CO and $PhCH_2NH_2$ than the ester $PhCO_2Bu$ in the carbonylation of PhBr in the presence of BuOH.[45] It may be that this difference between the rates is the reason why the conversion of vinyl iodides and bromides into amides proceeds with complete retention of the configuration of the alkenyl group[45] in contrast to the alkoxycarbonylation of these compounds.[44]

It has been shown[60] that Me_3SnEt_3 reacts with ArI (Ar = Ph or 4-$NO_2C_6H_4$) and CO under very mild conditions (20 °C, 1 atm) with formation of $ArCONEt_2$ (82–90%). When the organo-tin nucleophile is replaced by the corresponding amine (Et_2NH), both the selectivity and the rate of the amide formation reaction decrease sharply.

Initially two fundamentally different mechanisms were proposed for the conversion of organic halides into amides in the presence of palladium catalysts[45] the acyl ($RCOPdL_2X$) or carbamoyl [$RPd(CONR'R'')L$] complexes of palladium were initially considered as intermediates (cf. with the alkoxycarbonylation mechanism described above). The experimental data obtained in later studies[59,60,77] showed that the reaction apparently takes place via the second pathway, i.e. the catalytic cycle in which the carbamoyl complexes participate is realised:

$$RX + PdL_n \rightarrow RPdL_2X + (n-2)L,$$
$$RPdL_2X + CO \rightleftarrows [RPd(CO)L_2]^+X^-,$$
$$[RPd(CO)L_2]^+X^- + R'R''NH + B: \rightarrow RPd(CONR'R'')L_2 + BHX,$$
$$RPd(CONR'R'')L_2 + (n-2)L \rightarrow RCONR'R'' + PdL_n,$$
$$L = PR_3 \text{ and/or } CO$$

Under certain conditions the reactions of organic halides with CO in the presence of primary or secondary amines lead to double carbonylation products – α-ketoacid amides (10 – 40 atm CO, 20 – 100 °C):[78,79]

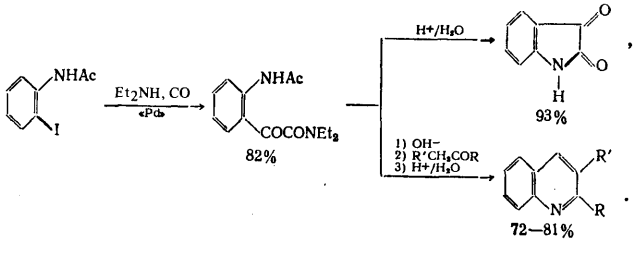
$$RX + R'R''NH \xrightarrow[0.5-1\%\ «Pd»,\ CO]{} \underset{0-98\%}{RCOCONR'R''} + \underset{2-92\%}{RCONR'R''}.$$

X=Br, I; R=4-YC_6H_4 (Y=H, Me, MeO, Cl), 2-thienyl, 3-pyridyl, PhCH = CH

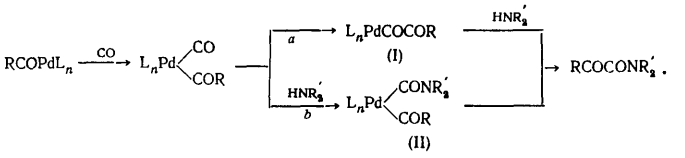
R'=R''=Me, Et, Pr, iso-Pr; R'R''= $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

The overall yield of the mixture of acid amides is 3 – 100%. The molar ratio RCOCONR'R''/RCONR'R'' varies within wide limits (0/100 – 98/2) and depends on a number of parameters. The formation of the α-ketoamide is promoted by the increase in the CO pressure, the decrease in the reaction temperature, the use of non-polar solvents.[78,80] The nature of the catalyst – a phosphinepalladium complex – plays a major role.[78] In the case of complexes with monodentate ligands – PdX_2L_2 and $PhPdL_2X$ – the relative content of RCOCONR'R'' in the mixture of products increases with increasing basicity of the phosphine L: $Me_2PhP > EtPh_2P > Ph_3P$. When the complexes PdU_2L, where L is a bidentate ligand of the type $Ph_2P(CH_2)_nPPh_2$, are used as the catalysts, the reaction selectivity calculated relative to RCOCONR'R'' diminishes as a function of *n* in the sequence 4 > 3 > 5 > 2. α-Ketoacid amides are obtained in high yields when RX is carbonylated in the presence of Et_2NH, Pr_2NH, or piperidine.[78-80] The reactions with weaker bases, namely Me_2NH and morpholine, and also with the sterically hindered iso-Pr_2NH afford mainly the monocarbonylation products.[78-80]

The method of synthesis of isatin and quinoline derivatives, proposed by Ozawa et al.,[81] is based on the double carbonylation of *o*-iodoacetanilide:



The acylpalladium complexes $RCOPdL_n$ (L = X, PR'_3 and/or CO), formed as a result of the oxidative addition of RX to zero-valent palladium and the subsequent interaction of $RPdL_n$ with CO, are undoubtedly active intermediates in the double carbonylation reactions considered. The conversion of $RCOPdL_n$ into α-ketoamides of carboxylic acids can be achieved in principle via two different mechanisms:[79,80] via the stage involving the formation of the acylformyl derivative of palladium (I) or of the acylcarbamoyl complex (II):



On the basis of a careful study of the reactions of the palladium complexes $RPdL_2X$, $RCOPdL_2X$, and $RCOCOPdL_2X$ (L = phosphine ligands), modelling the possible pathways in the catalytic process, it has been recently possible[77,82-84] to demonstrate that the double carbonylation of organic halides proceeds with participation of compounds (II) (pathway *b*).

It is of interest that not only primary and secondary but also tertiary amines can be used as the nucleophilic coreactants in the conversion of the halogeno-derivatives RX into amides (20 atm CO, 120 °C):[85]

$$RX + R'_2R''N \xrightarrow[0.6\%\ PhPd(PPh_3)_2I,\ CO]{} \underset{11-75\%}{RCONR'R''} + R'X.$$

RX=PhI, PhCH=CHBr, EtI

R'=R''=Et, Pr, Bu; R'=Et, R''=Ph

On passing from triethylamine to tripropyl- and tributyl-amines, which contain more bulky substituents, the yield of RCONR'R'' falls significantly. The fact that the carbonylation of EtI in the presence of $PhNEt_2$ proceeds with the selective dissociation of the N – Et bond and affords the *N*-ethyl-*N*-phenylamide of propionic acid in a high yield (75%) is noteworthy.

Non-activated iodoarenes and iodoarenes containing weak electron-accepting substituents interact with CO and organo-tin mercaptides to form thiolocarboxylic acid esters (1 atm CO, 20 °C):[58,59]

$$ArI + Et_3SnSR \xrightarrow[5-10\%\ PhPd(PPh_3)_2I,\ CO]{} \underset{62-96\%}{ArCOSR}.$$

Ar=Ph, 4-ClC_6H_4, 1-naphthyl, 2-thienyl; R = Ph, Et

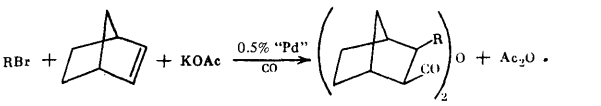
When the initial halide contains strong electron-accepting groups, ArCOSR cannot be obtained; the main reacion product is in this case the sulphide ArSR.

Aryl iodides have been converted into α-ketonitriles[86] (8 – 20 atm CO, 100 °C:

$$ArI + KCN \xrightarrow[1-3\%\ PhPd(PPh_3)_2I,\ CO]{} \underset{45-92\%}{ArCOCN} + \underset{1-22\%}{ArCN},$$

Ar=4-XC_6H_4 (X=H, Me, MeO), 2-thienyl.

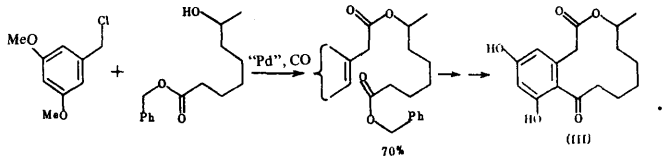
The carbonylation in the RBr – KOAc – norbornene (or norbornadiene) system, catalysed by tetrakis(triphenylphosphine)palladium, is accompanied by the insertion of both the alkene and CO in the C – Pd bond in the intermediate $RPd(PPh_3)_2Br$ (1 atm CO, 80 °C):[87]



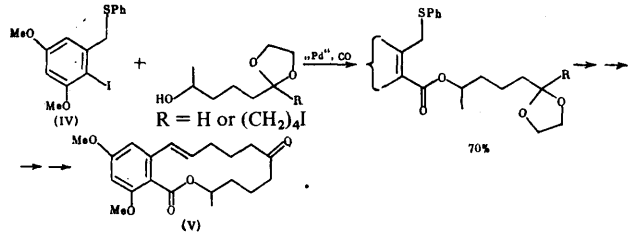
R = Ph, $PhCH_2$, MeO_2CCH_2, PhCH=CH, n-$C_6H_{13}CH$ = CH

A mixed anhydride is apparently formed initially, but it is unstable and readily disproportionates. The reactions considered above have found application in fine organic synthesis.

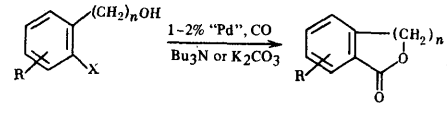
A method of synthesis of the macrolide(III) (curvularin), which is encountered in nature, has been developed. The key stage is the alkoxycarbonylation of 3,5-dimethoxybenzyl chloride:[88]



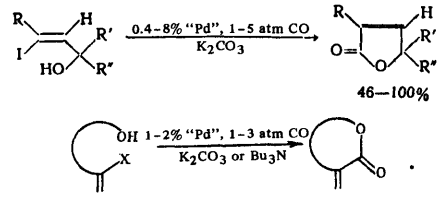
The dimethyl ether of zearalenone (V), a macrolide with a structure similar to that of curvularin, has been synthesised from the aryl iodide (IV) using a catalytic reaction:[89,90]



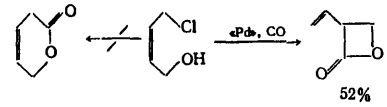
Hitherto, we have discussed the interaction of organic halides with CO and a wide variety of nucleophilic coreactants without dealing with the carbonylation of substrates containing a nucleophilic substituent (OH, NH_2, etc.) in the same molecule. On the other hand, the reactions of such halogenoderivatives with CO are of special interest from the synthetic point of view, because, unless this is prohibited by geometrical considerations, the latter can occur as intramolecular reactions leading to various heterocyclic compounds. For example, in the presence of an OH grup in the side chain of halogenobenzene, cyclisation takes place readily with formation of benzolactones (1–4 atm CO, 50–130 °C).[56,91] Special mention should be made of the possibility of obtaining in this way derivatives of the phthalide (n = 1) and 3,4-dihydroisocoumarin (n = 2) series, many of which are encountered in natural objects and exhibit biological activity:[35]



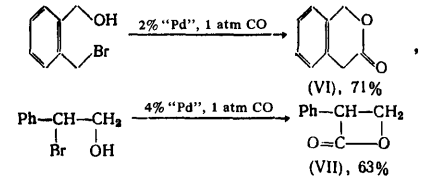
The reactions of vinyl halides, containing a hydroxy-group, have been used successfully for the synthesis of compounds of important classes such as $\Delta^{\alpha\beta}$-butenolides[56] and α-methylene-substituted γ-, δ-, and ε-lactones:[92,93]



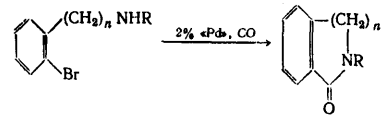
It has been found[56] that a chloro-derivative of the allylic type—*cis*-4-chlorobut-2-en-1-ol—interacts with CO under very mild conditions (1 atm, 20 °C) in the presence of 4 mole% of $Pd(CO)(PPh_3)_3$ as the catalyst. The reaction leads to a four-membered ring lactone:



o-Bromomethylbenzyl alcohol and 2-bromo-2-phenylethanol react to form 3-isochromanone (VI) and the β-lactone of tropic acid (VII) respectively in satisfactory yields:[56]

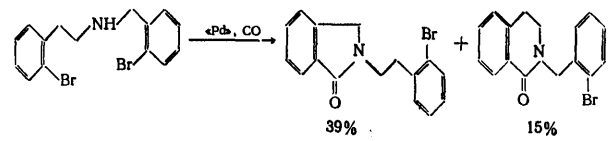


The conversion of *o*-(aminoalkyl)bromobenzenes into γ-, δ-, and ε-benzolactams hs been achieved[94,95] (1 atm CO, 100 °C):

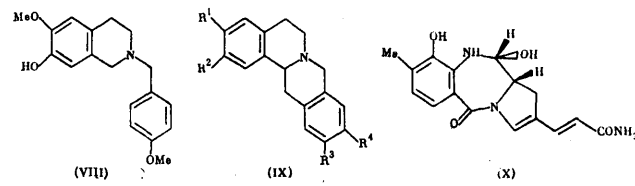


n=1–3; R=H, $PhCH_2$, Ac

When the intramolecular cyclisation can proceed via different pathways affording both six- and five-membered lactams, the latter is formed preferentially:[94]

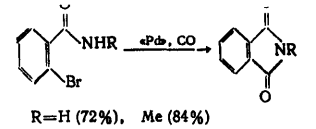


The simplest alkaloids (VIII) and (IX), whose composition includes the tetrahydroisoquinoline system, have been synthesised using this elegant and convenient method for the construction of nitrogen-containing rings:[96,97]



Recently there has been a growth of interest in benzo-1,4-diazepines and their oxo-derivatives, among which substances active as tranquillisers, soporifics, and antibiotics have been discovered. A method has been developed for the synthesis of a series of physiologically active 1,4-benzodiazepines based on the cyclisation reaction catalysed by palladium complexes. One of the antibiotics synthesised in this way is anthramycin (X).[99]

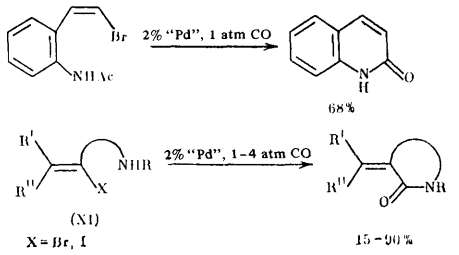
o-Bromobenzamides interact with CO at 1 atm and 100 °C in the presence of the $Pd(OAc)_2-PPh_3$ catalytic system with formation of phthalimides:[95]



R=H (72%), Me (84%)

Vinyl halides are also used as the initial substrates in the synthesis of nitrogen-containing heterocyclic compounds. Thus the conversion of (*Z*)-*o*-acetamido-β-bromostyrene into 2-quinolone can be

readily achieved.[95] The carbonylation of the vinyl derivatives (XI) leads to a wide variety of the substituted α-methylene-β-lactams, α-methylene-γ-lactams, and α-methylene-δ-lactams:[93,103,104]



The possible applications of this method in the synthesis of β-lactam antibiotics are being sought.[105]

2. The Synthesis of Aldehydes

The halogen in organic halides can be readily replaced by the formyl group using the carbonylation reaction.

In the presence of the synthesis gas ($CO:H_2$ = 1:1) and a palladium catalyst, iodo- and bromo-arenes of the benzene and heterocyclic series as well as vinyl derivatives are converted into the corresponding aldehydes in satisfactory yields.[46,106] The reaction takes place at approximately 100 atm and 80–150 °C in the presence of a base (a tertiary amine or pyridine):

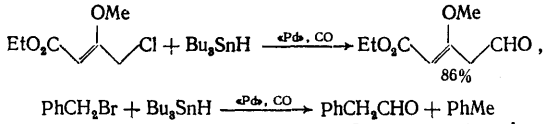
$$RX + CO + H_2 \xrightarrow[65-99\%]{1-3\%\ «Pd»} RCHO\ .$$

«Pd»=PdX_2, $PdX_2(PPh_3)_2$; X=Br, I; R=Ar, vinyl.

In the case of vinyl halides, side products may be formed as a result of *cis–trans* isomerisation and the migration of the double bond. Substituents in halogenoarenes such as the cyano- and acetoxy-groups are not involved in the reaction. However, when an attempt was made to obtain *p*-nitrobenzaldehyde by formylating *p*-bromonitrobenzene, only polymeric products were isolated. In certain cases the reduction of the carbon–halogen bond is observed. Thus, the reaction of *o*-dibromobenzene leads to benzaldehyde (66%). However, in the reaction involving *p*-dibromobenzene, the normal product *p*-$(HCO)_2$.C_6H_4 with two aldehyde groups was obtained (74%).

The mechanism of the formylation of RX is in many respects analogous to the mechanisms of the reactions examined before: the active intermediate is the acyl complex of palladium $RCOPdL_2X$, the interaction of which with H_2 leads to the aldehyde RCHO.[46]

The use of tributyl-tin hydride as the reductant made it possible to convert organic halides into aldehydes under much milder conditions (1–3 atm CO, 50 °C).[107] Apart from aryl and vinyl iodides, allyl chlorides and benzyl bromide can serve as the initial substrate:



«Pd»=$Pd(PPh_3)_4$

Formylation by the method of Baillargeon and Stille[107] is more chemoselective than the analogous reaction using synthesis gas: the methoxycarbonyl, keto-, and even nitro-groups are not involved in the reaction. In the reaction of *p*-bromoiodobenzene it is possible to achieve the selective substitution of iodine by the formyl group; the yield of *p*-bromobenzaldehyde reaches 88%. The formation of aldehyde is sometimes complicated by a side reaction involving the reduction of the initial halogeno-derivative RX to RH. For halogenoarenes containing strong electron-accepting substituents, this reaction may become the main one. For example, the formylation of *p*-$NO_2C_6H_4I$ leads to *p*-nitrobenzaldehyde (38%) and nitrobenzene (62%). Nevertheless, the yield of the aldehyde is usually high and in many cases reaches 90–100%.

Pri-Bar and Buchman[108] were able to replace tin hydride, which is sensitive to atmospheric oxygen, by the mild reductant poly(methylhydrosiloxane):

$$RX + [-SiMeH-O-]_n \xrightarrow[80-125°C]{\text{"Pd", 3 atm CO}} \underset{14-96\%}{RCHO}\ .$$

"Pd" = $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$/polystyrene

RX = iodo- and bromo-arenes and benzyl bromide

$PdCl_2(PPh_3)_2$ deposited on cross-linked polystyrene is an effective catalyst. The immobilisaion of the palladium complex on a polymeric carrier made it possible, on the one hand, to retain the activity characteristic of the homogeneous catalyst and, on the other hand, to simplify significantly the problem of the separation of the palladium compounds from the reaction products.

The possibility of using HCOONa as the reductant in the formylation reaction (3 atm CO, 125 °C) has been demonstrated for iodo- and bromo-benzenes.[108] The yield of benzaldehyde was 80% and 58% respectively.

3. The Synthesis of Asymmetric Ketones

Carbonylation in the RX (organic halide)–R'M (organometallic compound) system, catalysed by palladium complexes, constitutes a convenient method of synthesis of asymmetric ketones:

$$RX + R'M \xrightarrow{«Pd»,\ CO} RCOR' + MX\ .$$

The reaction mechanism is in broad outline analogous to the mechanisms of the reactions considered in this Section. The first stage of the catalytic cycle is the oxidative addition of RX to the zerovalent palladium complex. The carbonylation of the $RPdL_2X$ formed and the subsequent interaction of the acyl derivative $RCOPdL_2X$ with R'M lead to the ketone RCOR' and the initial catalytically active zerovalent palladium species.

Tin derivatives have found the widest application as organometallic reagents in this reaction. They are resistant to the action of atmospheric oxygen and moisture, are readily available, and, what is most important, are inert not only in relation to the keto-group of the products COR' but virtually in relation to any important functional group. This permits the synthesis of ketones containing different substituents.

The carbonylation of the iodoarenes 4-XC_6H_4I in the presence of aryl-, vinyl-, phenylethynyl-, and alkyl-stannanes leads to the corresponding ketones in high yields (1–30 atm CO, 20–120 °C):[109,110]

$$4\text{-}XC_6H_4I + RSnR'_3 \xrightarrow[HMP]{«Pd»,\ CO} 4\text{-}XC_6H_4COR + ISnR'_3\ ,$$

X=H, Cl, MeO_2C, CN, NO_2; R=4-YC_6H_4 (Y=MeO, Me, H, Cl, NO_2), C_6F_5, 2-thienyl, H_2C=CH, PhC≡C, Me, Bu

"Pd" = $PhPd(PPh_3)_2I$, $(\pi\text{-}C_3H_5PdCl)_2$

The reaction takes place under very mild conditions (1 atm CO, 20 °C) when it is catalysed by bis(π-allylpalladium chloride) (1 mole%).[110] In the reactions involving the most active tin compounds $RSnMe_3$ (R=CH_2=CH, 2-thienyl, or PhC≡C), the cross-coupling side product 4-XC_6H_4R is formed together with the carbonylation product. This undesirable process can be suppressed by carrying out the reaction in a less polar solvent–acetone.[111]

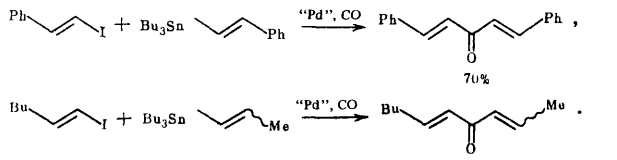
The halides of the heterocyclic series react analogously. Thus 2-C_4H_3SCOPh (95%) and 2-C_5H_4NCOPh (91%) have been obtained by carbonylating 2-iodothiophen and 2-iodopyridine in the presence of trimethylphenyltin.[111]

The reactions of β-bromostyrene with tetramethyltin,[109] of 1-iodohex-1-ene with tributylphenyltin, and of 1-iodopent-1-ene with $PrC{\equiv}CSnBu_3$ [112] at 4–30 atm CO and 45–120 °C lead to the corresponding αβ-unsaturated ketones in 46–62% yields. A method of synthesis of asymmetric divinyl ketones from vinyl iodides and alkenyltin derivatives (4 atm CO, 45–50 °C) has been developed:[112]

$$R^1R^2C{=}CR^3I + R^4R^5C{=}CHSnAlk_3 \xrightarrow{2\%\ «Pd»,\ CO} \rightarrow Alk_3SnI + R^1R^2C{=}CR^3CCH{=}CR^4R^5\ ,\quad (O)\quad 45\text{–}93\%$$

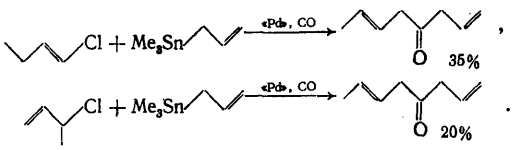
«Pd» = $PdCl_2L_2$, $PhCH_2PdL_2Cl$; L = PPh_3

We may note that the *trans*-configuration of the alkenyl group in the initial halide and the organostannane is retained in the reaction product. In the case of *cis*-organostannanes the carbonylation also takes place with the preferential retention of the geometry of the double bond, but the subsequent isomerisation of the ketone under the reaction conditions can lead to the *trans*-product, for example:

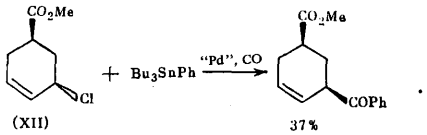


cis/*trans* = 6 24 h: *cis*/*trans* = 2.5
48 h: only *trans*-isomer, 62%

Allyl halides interact with aryl-, vinyl-, and allyl-trialkylstannanes at 4–52 atm CO with formation of βγ-unsaturated ketones.[113-115] Organotrimethylstannanes are usually employed in order to reduce the steric hindrance generated by the alkyl substituents in the organotin compound. The reactions of allyl bromides proceed less selectively than those of allyl chlorides. Although the carbonylation can be accompanied by the allylic rearrangement, it is regioselective: only one product is obtained in which the carbonyl grup is linked to the least substituted carbon atom of the allyl fragment:[114]



As shown for compound (XII), the stereochemical result of the reaction corresponds to inversion of the configuration at the carbon atom linked to the halogen:[115]



(XII) 37%

cis/*trans* = 26:74 *cis*/*trans* = 70:30

Vinylstannanes interact with allyl halides in a CO atmosphere with retention of both the *cis*- and the *trans*-geometry of the vinyl group.[115]

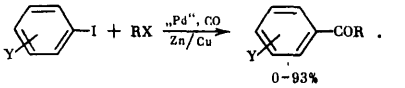
Benzyl chloride reacts with tetramethyltin and CO to form phenylacetone (86%).[109] *p*-Nitrobenzyl phenyl ketone has been obtained analogously in 85% yield from *p*-nitrobenzyl bromide and trimethylphenyltin.[110] The reaction of PhCHRBr (R = Me or Et) with R'_4Sn (R' = Me or Ph) and CO is complicated by side processes involving isomerisation and β-elimination,[116] for example:

$$PhCHMeBr + Me_4Sn \xrightarrow[120°C]{PdCl_2(AsPh_3)_2,\ 20\ atm\ CO} \rightarrow \underset{70\%}{PhCHMeCOMe} + \underset{4\%}{PhCH_2CH_2COMe} + \underset{14\%}{PhCH{=}CH_2}\ .$$

Carbonylation in an α-halogenocarboxylic acid ester–organotin compound system constitutes a method of synthesis of β-ketoacid derivatives. Thus the reaction of ethyl α-bromoacetate with CO and tetraphenyltin leads to ethyl benzoylacetate (67%).[109] MeCH.(COMe)CO_2Et has been obtained from ethyl α-bromopropionate and tetramethyltin (62%).

The conversion of halogeno-derivatives of saturated hydrocarbons into ketones has been described for only one example: methyl iodide interacts with trimethylphenylstannane in a CO atmosphere to form acetophenone (94%).[110]

The organozinc compounds RZnX, obtained *in situ* from primary or secondary iodoalkanes or benzyl chlorides using the zinc–copper couple, react with aryl iodides at 1 atm CO in the presence of 1 to 2 mole% of $Pd(PPh_3)_4$.[117] The yield of the target product $YC_6H_4.COR$ is 56–93% for aryl iodides containing electron-donating substituents (Y = 4-MeO or 2- and 4-Me) and unsubstituted iodobenzene (Y = H), but in the presence of electron-accepting groups in the benzene ring of the halogenoarene (Y = 4-Br or 2-MeO_2C) it falls to 0–38%. It is also noteworthy that primary alkyl iodides are more reactive than secondary alkyl iodides:



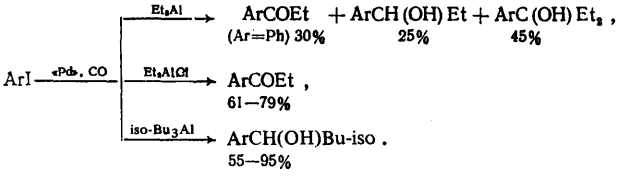
X = I; R = Me, n-Pr, iso-Pr, iso-Bu, n-C_8H_{17}, cyclo-C_6H_{11}
X = Br; R = $PhCH_2$, 4-$ClC_6H_4CH_2$

Carbonylation in the RX–iso-Bu_2AlR' system under mild conditions (1 atm CO, 20–55 °C) can serve as a convenient method of synthesis of asymmetric ketones RCOR' of various classes:[118]

$$RX + \text{iso-}Bu_2AlR' \xrightarrow{1\%\ PdCl_2(MeCN)_2,\ CO} \underset{41\text{–}99\%}{RCOR'}\ .$$

RX = 4-YC_6H_4I (Y = NO_2, NC, Cl, MeO, H), 2-iodothiophen, 4-$NO_2C_6H_4CH_2Br$, MeI
R' = Ph, PhC≡C, CH_2=CH

The reaction of aluminium trialkyls and dialkylaluminium chlorides with aryl iodides and CO (1 atm, 50 °C) takes place in a more complex manner.[119] Alkyl aryl ketones ArCOAlk obtained initially are capable of bineg reduced and alkylated by the initial organoaluminium compounds, affording, ArCH(OH)Alk and $ArC(OH)Alk_2$. Thus the carbonylation of iodobenzene in the presence of Et_3Al leads to a mixture containing the three products indicated in comparable amounts. The use of Et_2AlCl and iso-Bu_3Al as reactants made it possible to direct the process towards the preferential formation of a ketone or secondary alcohol respectively:



The ketones RCOC≡CR' are obtained from the halides RX and terminal acetylenes R'C≡CH (R' = Ph, $PhCH_2CH_2$, or Bu) in a CO atmosphere (20 atm, 80–120 °C).[120] The method is applicable over

a wide range of organic halides: substituted iodo- and bromo-benzenes, 1-bromonaphthalene, 2-bromothiophen, and vinyl bromides. In order to increase the yield of the ketone and to reduce the amount of the side products [$RC{\equiv}CR'$, $(R'C{\equiv}C)_2$], it is recommended that the complex $PdCl_2$ with the bidentate phosphine ligand 1,1'-bis(diphenylphosphino)ferrocene be used:

$$RX + R'C{\equiv}CH \xrightarrow[Et_3N]{1\%\ «Pd»,\ CO} \underset{47-93\%}{RCOC{\equiv}CR'}\ .$$

The reactions of aryl iodides with $RC{\equiv}CH$ at 1 atm CO and approximately 60 °C in the presence of the zinc–copper couple lead mainly to the enone $ArCOCH{=}CHR$ after the hydrolysis of the reaction mixture:[121]

$$ArI + RC{\equiv}CH \xrightarrow[2)\ H_2O]{1)\ cat.,\ CO,\ Zn/Cu} \underset{33-92\%}{ArCOCH{=}CHR} + \underset{0-26\%}{ArCOCH{=}CAr}R + \underset{0-44\%}{ArCOCH_2CHRCOAr} + \underset{0-23\%}{ArC{\equiv}CR}\ .$$

cat. = 2% $PdCl_2(PPh_3)_2$ + 4% $(C_6H_5)_2TiCl_2$

R=Ph, Bu; Ar=YC_6H_4 (Y=H, Me, MeO, Br), 2-thienyl.

The $ArCOC{\equiv}CR$ formed initially is apparently reduced by Zn/Cu to $ArCOCH{=}CRZnI$ whose subsequent interaction with water affords $ArCOCH{=}CHR$.[121]

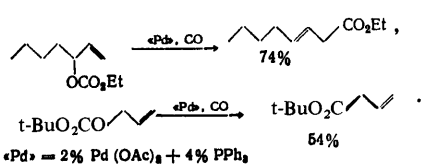
The possibility, in principle of synthesising symmetrical diaryldiketones by carbonylating aryl iodides in the presence of palladium catalysts (8 atm CO, 111 °C) has been demonstrated recently[122] for the conversion of *p*-iodoanisole into *p*-bianisoyl:

$$4\text{-}MeOC_6H_4I + Et_6Sn_2 \xrightarrow{1\%\ «Pd»,\ CO} \underset{71\%}{(4\text{-}MeOC_6H_4CO)_2} + Et_3SnI\ .$$

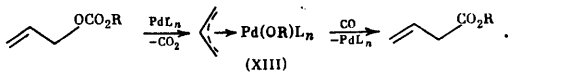
Thus the study of the reactions of organic halides with CO under the conditions of homogeneous catalysis by palladium complexes has led to the development of new convenient methods of synthesis of carboxylic acids and their derivatives, aldehydes, and symmetrical and asymmetrical ketones.

IV. CARBONYLATION OF OTHER ORGANIC SUBSTRATES

Not only organoelemental compounds and organic halides but also other substrates, capable of interacting with zerovalent palladium or palladium(II) complexes to form σ-organopalladium compounds, can serve as donors of organic groups in the carbonylation reaction. Thus, as early as the 1960's, it was shown[42,50] that ethers and esters of allyl alcohols react with CO in the presence of palladium catalysts. However, the severe conditions under which the process takes place and the low yields of the products precluded a wide-scale application of this synthetic method. Only much later was it found[123] that the readily available alkyl allyl carbonates exhibit a high reactivity: their carbonylation takes place under mild conditions (1–10 atm, 50 °C) and leads to βγ-unsaturated acid esters in satisfactory yields, for example:

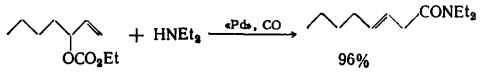


The carbonylation is regioselective: only one product is formed in which the alkoxycarbonyl group is bound to the least substituted carbon atom of the allyl fragment. π-Allyl complexes of palladium (XIII), obtained as a result of the oxidative addition of allyl carbonates to zerovalent palladium on subsequent decarboxylation, are intermediates in the reactions considered:



(XIII)

When diethylamine is introduced into the reaction mixture as a nucleophilic coreactant, amides can be synthesised:[123]

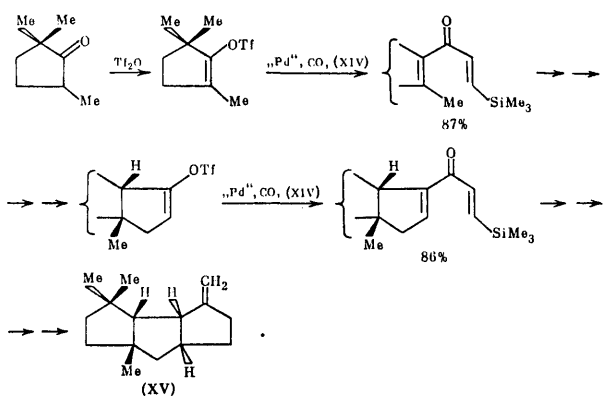


The vinyl esters of trifluoromethanesulphonic acid (vinyl triflates) interact with CO and various organotin compounds (alkyl-, aryl-, vinyl-, ethynyl-, and allyl-trialkylstannanes) to form αβ-ketones (1–4 atm CO, 20–75 °C):[124]

$$RCH{=}CR'OSO_2CF_3 + R''SnAlk_3 \xrightarrow[70-95\%]{3\%\ Pd(PPh_3)_4,\ CO} RCH{=}CR'COR''\ .$$

It is important to note that both the (*Z*)- and (*E*)-configurations of the alkenyl group in the initial vinyl stannanes are retained in the reaction. This constitutes an undoubted advantage of the given method compared with the analogous method of synthesis based on the carbonylation of vinyl halides[112] (see above). The ready availability of vinyl triflates, the methods of synthesis of which from the anhydride of trifluoromethanesulphonic acid and the corresponding ketones have now been thoroughly developed, is also important from the preparative point of view.

There has been an interesting communication about the synthesis of compound (XV) using (*E*)-1-trimethylsilyl-2-trimethylstannylethylene (XIV) (Tf = CF_3SO_2):[124]



(XV)

The carbonylation of alcohols in the presence of palladium catalysts is of very limited importance and is applicable only to allyl derivatives.[41,42,50] The reaction proceeds with low yields at high CO pressures. Homogeneous catalytic systems based on rhodium compounds proved to be much more promising. Thus, in the presence of small amounts of added HI, certain carbonyl rhodium complexes are capable of catalysing the conversion of methanol into acetic acid at relatively low CO pressures (30–40 atm) (the active substrate is not the alcohol itself but the methyl iodide formed *in situ* by the reaction of methanol with HI; the interaction of MeI with CO and H_2O leads to acetic acid with the simultaneous regeneration of HI). This highly selective reaction served as the basis of a large-scale industrial process developed by the Monsanto Company.[8]

The wide scale synthetic possibilities of the reactions involving the carbonylation of arenediazonium salts have been demonstrated.[125-128] The interaction of arenediazonium tetrafluoroborates with sodium

carboxylates at 9 atm CO and 25 °C yields mixed anhydrides of the carboxylic acids:[125,126]

$$ArN_2BF_4 + RCO_2Na \xrightarrow{1\text{–}2\%\ Pd(OAc)_2,\ CO} \underset{28\text{—}86\%}{ArCOCR} \quad (\text{O, O})$$

Ar = YC_6H_4 (Y = H, Me, MeO, Cl, Br, I, NO_2), 1-naphthyl

R = H, Me, Et, t-Bu, Ph

Heating of the mixed anhydrides to 100–120 °C *in vacuo* induces their disproportionation to $(ArCO)_2O$ and $(RCO)_2O$ in nearly quantitative yields.[126] It is of interest that substituents in ArN_2BF_4 such as chlorine, bromine, and even iodine are hardly involved during the carbonylation reaction. Thus an anhydride has been obtained from *p*-iodobenzoic acid in 86% yield relative to the initial diazonium salt.[125]

The reaction of PhN_2BF_4 with CO and alcohols ROH (R = Me, Et, Bu, or t-Bu) results in the formation of $PhCO_2R$ (0–21%) and $PhCO_2H$ (7–66%).[125]

In the presence of triethylsilane or better poly(methylhydrosiloxane), CO, and a palladium catalyst, the conversion of ArN_2BF_4 into ArCHO can be readily achieved (9 atm CO, 25 °C).[127] The formation of diazonium salts is a more chemo-selective process than the analogous reaction of halogenoarenes (see Section III): chlorine, bromine, and iodine atoms and acyl, alkoxycarbonyl, and nitro-groups are not reduced under the conditions used for the synthesis of aldehydes.

Asymmetric ketones can be obtained from ArN_2X and tetra-organostannanes in a CO atmosphere (9 atm CO, 25 °C):[128]

$$YC_6H_4N_2X + R_4Sn \xrightarrow[40\text{—}90\%]{2\%\ Pd(OAc)_2,\ CO} YC_6H_4COR + R_3SnX .$$

X = BF_4, PF_6; Y = H, 2-, 3- and 4-Me, 2- and 4-Cl, 4-Br, 4-F, 3- и 4-NO_2; R = Me, Et, Ph

We may note that the possibility of using arenediazonium salts ArN_2X as the substrates in various carbonylation reactions catalysed by palladium compounds is due to the ease of formation of the σ-organopalladium complexes $ArPdL_2X$:[125]

$$ArN_2X + PdL_n \rightarrow ArPdL_2X + N_2 + (n-2)\,L.$$

Diaryliodonium halides exhibit a high reactivity in the reactions with CO. Thus the alkoxycarbonylation of $[Ar_2I]X$ and their conversion into amides proceed under extremely mild conditions (1 atm CO, 20 °C) in the presence of 2 mole% of $PdCl_2$ and lead to quantitative yields of esters and amides respectively:[129]

$$[Ar_2I]X + ROH \xrightarrow[Bu_3N]{«Pd»,\ CO} \underset{\sim 100\%}{ArCO_2R} + ArI ,$$

$$[Ar_2I]X + PhNH_2 \xrightarrow[Bu_3N]{«Pd»,\ CO} \underset{\sim 100\%}{ArCONHPh} + ArI ,$$

X = Cl, Br, I; R = Me, Bu; Ar = YC_6H_4 (Y = H, 4-MeO, 4-Me, 4-t-Bu, 4-Cl, 3-NO_2), 2,4,6-$Me_3C_6H_2$.

The steric hindrance generated by the substituents in the aromatic ring does not prevent their reaction. For example, methyl 2,4,6-trimethylbenzoate has been obtained in 100% yield.

Symmetrical diaryl ketones are formed in the presence of reductants—copper or tin powder or best of all zinc dust (1 atm CO, 20 °C):[130,131]

$$[Ar_2I]X + Zn \xrightarrow[38\text{—}68\%\ \ 90\text{—}100\%]{5\%\ Pd(OAc)_2,\ CO} Ar_2CO + ArI + ZnX_2 .$$

X = Cl, Br, I, BF_4; Ar = 4-YC_6H_4 (Y = H, Me, t-Bu, Cl, Br), 2,4,6-$Me_3C_6H_2$

The main side products are α-diketones $(ArCO)_2$ (up to 24%) and biaryls Ar_2 (up to 49%). The presence of electron-donating substituents in the initial diaryliodonium salt increases and that of electron-accepting groups decreases the yield of carbonyl-containing compounds. The catalytic cycle proposed by Uchiyama et al.[131] is presented schematically below:

$$[Ar_2I]X \xrightarrow[-ArI]{Pd(0)} ArPdX \xrightarrow[-ZnX_2]{Zn} Ar_2Pd + Pd(0) ,$$

$$\begin{array}{ccccc} Ar_2Pd & \xrightarrow{CO} & ArCOPdAr & \xrightarrow{CO} & (ArCO)_2Pd \\ \downarrow & & \downarrow & & \downarrow \\ Ar_2 + Pd(0) & & Ar_2CO + Pd(0) & & (ArCO)_2 + Pd(0) \end{array} ,$$

The metallation of arenes by palladium(II) salts affords the σ-diorganopalladium compounds ArPdX,[132] which, as shown previously, are key intermediates in various carbonylation reactions catalysed by palladium complexes. The direct palladisation of aromatic compounds thus opens a pathway to their use as the initial substrate in the synthesis of carbonyl-containing products. The possibility of the practical realisation of this idea has been demonstrated in a number of studies.[36,133-140] It has been shown[133] that substituted benzenes as well as thiophen and furan react with palladium acetate and CO at 15 atm and 100 °C to form the corresponding carboxylic acids [the yields of the mixture of regio-isomers are given relative to $Pd(OAc)_2$]:

$$ArH + Pd(OAc)_2 \xrightarrow{CO} \underset{14\text{—}48\%}{ArCO_2H} + Pd .$$

ArH = C_6H_6, PhOMe, PhMe, PhCl, thiophen, furan

The sequence of the reactivities of the aromatic compounds (PhOMe > PhMe > C_6H_6 > PhCl) and the preferential *ortho-*, *para*-directing effect in the carboxylation reaction in the presence of *ortho, para*-directing substituents in the initial benzene (MeO, Me, Cl) indicates the electrophilic character of the process. The proposed mechanism of the carboxylation of arenes[133] is shown schematically below:

$$ArH + Pd(OAc)_2 \rightarrow ArPdOAc + HOAc ,$$
$$ArPdOAc + CO \rightarrow ArCOPdOAc ,$$
$$ArCOPdOAc \rightarrow ArCOOAc + Pd ,$$
$$ArCOOAc + HOAc \rightarrow ArCO_2H + Ac_2O .$$

It is of interest that, in the presence of certain organic halides, for example, 1,2-dibromoethane, the interaction of ArH with CO and $Pd(OAc)_2$ does not lead to carboxylic acids but affords their anhydrides $(ArCO)_2O$.[134]

According to the scheme presented above, in order to make the reaction catalytic it is essential to add an oxidant capable of converting the inactive zerovalent palladium into a palladium(II) salt. It has been suggested that $FeCl_3$,[135] $Tl(O_2CCF_3)_3$ (in this case the substrate may be an organothallium compound formed *in situ* and not the arene itself—see Section II),[36] $CuCl_2$,[136] $Na_2S_2O_8$,[137,138] and t-BuOOH[139] be used as the oxidants. However, the yield of the carbonylation product and the selectivity of the catalytic process are usually low, for example:[135,139]

$$C_6H_6 \xrightarrow[75\ ^\circ C\ t\text{-}BuOOH]{Pd(OAc)_2,\ 1\ atm\ CO} \underset{1300\%}{PhCO_2H} + \underset{1500\%}{Ph_2} + \underset{200\%}{PhOH} ,$$

$$MePh \xrightarrow[125\rightarrow 175^\circ C,\ FeCl_3]{PdCl_2,\ 48\ atm\ CO} \underset{520\%}{4\text{-}MeC_6H_4CO_2H} .$$

The yields are quoted relative to the palladium(II) salt.

The reaction of substituted arenes frequently yields mixtures of regioisomeric acids which are difficult to separate (1 atm CO, 75 °C):[139]

$$PhOMe \xrightarrow[t\text{-}BuOOH]{Pd(OAc)_2,\ CO} MeOC_6H_4CO_2H .$$

The yields, calculated relative to $Pd(OAc)_2$, of the *ortho*-, *meta*-, and *para*-products are 126, 8, and 123% respectively.

The interaction of substituted benzenes with palladium acetates in a CO_2 atmosphere also leads to aromatic acids.[140] In the presence of t-BuOOH, the reaction becomes weakly catalytic with respect to palladium (1 atm CO_2, 70 °C):

$$RPh \xrightarrow[t\text{-}BuOH]{Pd(OAc)_2,\ CO_2} RC_6H_4CO_2H\ .$$

R=Me (125%), H (127%), Cl (40%)

[the yields are quoted relative to $Pd(OAc)_2$]

Thus the carbonylation of arenes, which is of considerable interest because of the ready availability of the initial reactants, encounters major difficulties. The main problem is the low yield of the products and the low selectivity of the reaction.

Apart from arenes, the hydrogen atom can be replaced by CO only in the 1-position in terminal acetylenes (1 atm CO, 20 °C):[141]

$$RC{\equiv}CH + R'OH \xrightarrow[CuCl_2,\ NaOAc]{cat.\ Pd,\ CO} \underset{58-74\%}{RC{\equiv}CCO_2R'}\ .$$

R = n-C_5H_{11}, Ph, $PhOCH_2$; R'=Me, iso-Pr

The reaction is catalysed by 6 mole% of $PdCl_2$ using copper dichloride or *p*-benzoquinone as the oxidants.

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