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CATALYSIS BY PALLADIUM SALTS

X *. AN INVESTIGATION ON THE FACTORS ACTING ON THE PALLADIUM-CATALYSED OXIDATIVE CARBONYLATION OF ARYLMERCURY COMPOUNDS **

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Summary

The palladium-mediated reaction of oxidative carbonylation of arylmercury compounds to form the derivatives (particularly anhydrides or esters) of the corresponding carboxylic acids has been fully re-investigated in order to establish its synthetic utility. The reaction, which can be accomplished either starting from the preformed mercury compounds or via their preliminary synthesis in situ, is solvent-dependent. Yields can be increased by the carefully controlled addition of a co-catalyst such as a base (sodium acetate) and in the latter case also strong acids ($HClO_4$ or HBF_4). The best yields are obtained in trifluoroacetic acid, which is an ideal solvent for carrying out the reaction; conditions are very mild (room temperature and under 1 atm of CO pressure).

Introduction

The oxidative carbonylation of aromatic hydrocarbons to form various carboxylic acid derivatives, which is catalysed by palladium salts, is a reaction of great potential interest [1]. The direct reaction of oxidative carbonylation of simple aromatic hydrocarbons is reported to occur with relatively low yields, the competitive reaction being the reduction of palladium [2,3]. Better yields have recently been reported to be obtained in acetic acid when an excess of peroxydisulphate anion is added [4].

Good conversions are obtained in a two-step process, which requires the preparation of arylthallium(III) derivatives as active arylation intermediates of the palladium-catalysed oxidative carbonylation reaction [5].

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* For part IX see ref. 11.

** Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.

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In the pioneering work of Henry on the related arylmercury(II) compounds [6], the yields were not particularly high so that this reaction cannot be of synthetic utility. However, since Henry's results are not consistent with other work [5], we have re-investigated in detail the oxidative carbonylation of arylmercury(II) acetates in the presence of different palladium salts as catalysts and under various reaction conditions.

Results and discussion

The oxidative carbonylation of phenylmercury(II) acetate

In the original work of Henry [6], the synthesis of aromatic acid derivatives from arylmercury compounds was reported to occur in solvents such as CH_3CN or CH_3OH (molar ratio of arylmercury acetate to palladium catalyst 1/1) with yields varying from 10 to 30% (yields are referred to the added palladium chloride). We have found that higher yields can be obtained under similar conditions by using $Pd_3(CH_3COO)_6$ as catalyst and that the reaction is quite solvent-dependent (Table 1).

The reaction products are the related anhydrides or esters; the latter are formed in the presence of an alcohol, which is often added to aprotic polar solvents as a prerequisite in order to obtain reasonable yields. We have also found that a coordinating base such as sodium acetate can behave as a good co-catalyst (Table 2); however, another coordinating salt, LiBr, which is reported to be a co-catalyst with arylthallium(III) compounds [5], produces a negative effect under our conditions (in CH_3CN the yields decrease from 57 to 50%; in acetic acid from 18 to 10%). The probable reason why sodium acetate is a good co-catalyst, at least in acetic acid, is the fact that it converts $Pd_3(CH_3COO)_6$ to a more reactive anionic dimer, $Na_2[Pd_2(CH_3COO)_6]$ (see ref. 1, pages 121–124). CF_3COONa, which is formed when sodium acetate is added to trifluoroacetic acid, probably behaves in a similar way. Yields as high as 86% can be attained under our very mild standard conditions (see Tables) in trifluoroacetic acid with $Pd_3(CH_3COO)_6$ as catalyst (CH_3COONa must be added as co-catalyst).

TABLE 1

OXIDATIVE CARBONYLATION OF PHENYLMERCURY ACETATE (0.1 *M*) WITH DIFFERENT PALLADIUM SALTS (0.1 *M*) CARRIED OUT AT ROOM TEMPERATURE AND 1 atm OF CO PRESSURE. YIELDS ARE REFERRED TO THE PALLADIUM SALT

Catalyst	Solvent	Yield (%)
$PdCl_2$	CH_3CN	18
$[Pd(CH_3COO)_2]_3$	CH_3CN	57 [d]
$PdCl_2$	DMF/CH_3OH [a]	27
$[Pd(CH_3COO)_2]_3$	DMF/CH_3OH [a]	70 [d]
$Pd(PPh_3)_2Cl_2$	DMF/CH_3OH [a,b]	8
$Pd(PPh_3)_2Cl_2$	$i\text{-}C_4H_9OH$ [b]	33
$Pd(DPE)Cl_2$	$i\text{-}C_4H_9OH$ [b,c]	37.5

[a] Volume ratio of aprotic polar solvent to CH_3OH 5/1. [b] Under reflux conditions. [c] DPE = 1,2-diphenylphosphinoethane. [d] Yields in other solvents are: CH_3OH (72%), $PhCH_2CN/CH_3OH$ [a] (50%), propylencarbonate/CH_3OH [a] (70%), acetic acid (18%), trifluoroacetic acid (60.5%).

TABLE 2

OXIDATIVE CARBONYLATION OF PHENYLMERCURY ACETATE (0.1 M) WITH PALLADIUM ACETATE (0.1 M). YIELDS AND REACTION CONDITIONS AS IN TABLE 1

Solvent	Yield (%) [a]		
CH_3COOH	18	(48.6)	[28.6]
CF_3COOH	60.5	(86.1)	[36.7]
CH_3OH	72	(88)	[40.4] [b]

[a] Values in parentheses refer to reactions with addition of sodium acetate (0.2 M); values in brackets refer to oxidative carbonylation of α-naphthylmercury acetate [7] under similar conditions. [b] Values in brackets refer to oxidative carbonylation of α-naphthylmercury acetate without addition of sodium acetate.

We have extended our investigation briefly to another arylmercury compound, namely the one reported as α-naphthylmercury acetate [7]. With this latter compound we found a lower reactivity and also a low selectivity, because a mixture of α- and β-naphthoic acid derivatives was always obtained (Table 2). However, we also confirmed that the starting compound, reported originally as α-naphthylmercury acetate [7], is in reality a mixture of α- and β-isomers, with the α-isomer prevailing (see Experimental). These discrepancies can be explained by the known observation that naphthylmercury acetates constitute an example of an equilibrium between α- and β-isomers [8].

The direct oxidative carbonylation of aromatic hydrocarbons by a two-step process

It was briefly reported in the original work of Henry [6] that starting from arylmercury compounds made in situ, aromatic hydrocarbons can be transformed into derivatives of aromatic acids by a two-step process, which takes place in the same reaction vessel. We have reconsidered this reaction, which was reported to occur with relatively low yields under rather drastic conditions (150°C and 1000 psig CO pressure).

TABLE 3

OXIDATIVE CARBONYLATION OF BENZENE (0.225 mol DISSOLVED IN 20 ml OF SOLVENT) CARRIED OUT AT ROOM TEMPERATURE AND UNDER 1 atm OF CO PRESSURE BY A TWO-STEP PROCESS (SEE EXPERIMENTAL) [a]; YIELDS AS IN TABLE 1

Acid	Concentration (mol l^{-1})	Solvent	Yield (%)
–	–	CH_3OH	3.4
$HClO_4$	1.5×10^{-2}	CH_3OH	50
HBF_4	1.6×10^{-2}	CH_3OH	43.3
–	–	CH_3COOH [b]	12
$HClO_4$	1.5×10^{-2}	CH_3COOH [b]	46.8
–	–	DMF/CH_3OH [c]	1
$HClO_4$	2.5×10^{-2}	DMF/CH_3OH [c]	5
–	–	CH_3CN	1
$HClO_4$	7.3×10^{-3}	CH_3CN	4

[a] The concentrations of mercury(II) acetate and palladium acetate were both 7.5×10^{-2} M. [b] In the presence of 1.5×10^{-1} M sodium acetate. [c] Volume ratio of DMF to CH_3OH 5/1.

Under our conditions, using methanol as solvent, a large excess of benzene (molar ratio of benzene to palladium 75/1) is converted to methyl benzoate with very low yields (Table 3). However, the addition of small amounts of a strong protonic acid such as $HClO_4$ or HBF_4 causes a substantial increase of the yields (from 3.4 to about 50%). In acetonitrile or in a mixture of DMF/CH_3OH, with a volume ratio of 5/1, the yields are still very low even after addition of strong acids (Table 3).

The co-catalytic action must be attributed to the known relevant catalytic action of strong inorganic acids on the mercuration step, when carried out in protic solvents [9].

We have found that the concentration of the strong acid plays an important role. When the concentration of $HClO_4$ was increased above $3\text{–}4 \times 10^{-2}$ *M*, a parallel significant decrease of the yields occurred (Table 4). At the same time, diphenyl, originally only a very minor by-product of the reaction (see Experimental), becomes the major product. Similar behaviour is found with naphthalene but the total yields are much lower.

It is known that perchloric acid favours the oxidative coupling of aromatic hydrocarbons, catalysed by the palladium-soluble catalysts [10].

In conclusion, these results can be interpreted on the basis of the presence of two competitive catalytic reactions, which are affected quite differently by the $HClO_4$ concentration. Moreover, we have also reported [11] that, under the standard

$$HClO_4 + 4CO \rightarrow HCl + 4CO_2 \qquad (1)$$

reaction conditions used in this work, reaction 1 takes place at high $HClO_4$ concentration, with parallel formation of $PdCl_2$ and partial deactivation of the palladium catalyst corresponding to a decrease of the total catalytic acitivity. However, the negative effect of the water added with the acid (reduction to metallic

TABLE 4

EFFECT OF THE CONCENTRATION OF PERCHLORIC ACID ON THE OXIDATIVE CARBONYLATION OF BENZENE OR NAPHTHALENE IN PROTIC SOLVENTS; YIELDS AND REACTION CONDITIONS AS IN TABLE 1

Hydrocarbon	Solvent	Concentration of $HClO_4 \times 10^{-2}$	Yield (%)
C_6H_6 [a]	CH_3OH	3×10^{-1}	46.2
C_6H_6	CH_3OH	1.5	50
C_6H_6	CH_3OH	4.3	11.5 [d]
C_6H_6	CH_3COOH [c]	1.5	46.8
C_6H_6	CH_3COOH [c]	2.2	43.5
C_6H_6	CH_3COOH [c]	4.3	23.7 [d]
$C_{10}H_8$ [b]	CH_3COOH [e]	1.4	26.3
$C_{10}H_8$	CH_3COOH [e,f]	3	20.8
$C_{10}H_8$	CH_3COOH [e,f]	6	12.2

[a] The concentrations of mercury(II) acetate and palladium acetate were both 7.5×10^{-2} *M*; concentration of benzene was 5.65 *M*. [b] The concentrations of mercury(II) acetate and palladium acetate were both 1.5×10^{-1} *M*; concentration of naphthalene was 1.5 *M*. [c] Sodium acetate (1.5×10^{-1} *M*) was added as co-catalyst. [d] Diphenyl became the major product. [e] Sodium acetate (3×10^{-1} *M*) was added as co-catalyst. [f] The temperature was raised to 60°C.

palladium by CO and H_2O) cannot be disregarded although addition of acetic anhydride does not produce a positive effect. In conclusion, the addition of a strong acid such as $HClO_4$ is beneficial, but only under carefully controlled conditions.

Again, the addition of a large amount of sodium acetate produces a positive co-catalytic effect, particularly in acetic acid.

We have also briefly investigated the effect of temperature and of the CO pressure when the oxidative carbonylation is carried out in acetic acid in the presence of both sodium acetate and perchloric acid (Table 5). The yields are quite independent of the temperature, whilst an increase of the CO pressure produces a significant decrease of the total catalytic activity.

Trifluoroacetic acid is a solvent which under standard reaction conditions shows a high activity of the catalytic system without the addition of strong acids ($HClO_4$ or HBF_4). However, also in this case, the addition of sodium acetate produces a positive co-catalytic effect (Table 6).

It should be pointed out that this solvent effect could be expected in consideration of the solvent effects reported in the first part of this investigation, dealing with the reaction with preformed phenylmercury acetate. Moreover, it is known that both the mercuration of benzene [12] and probably also its direct palladation [13] take place more easily in trifluoroacetic acid. Since we obtained yields higher than 100% (see Table 6), mercury(II) acetate must reoxidize some metallic palladium, probably according to reaction 2. If this reoxidation takes place completely, the yields

$$Pd + 2Hg(CH_3COO)_2 \rightarrow Pd(CH_3COO)_2 + Hg_2(CH_3COO)_2 \qquad (2)$$

expected are 150% under our reaction conditions. The results found are not too far from this value. Again, palladium acetate shows a specific high catalytic activity when compared with other palladium compounds such as $PdCl_2$ or $Pd(PPh_3)_2Cl_2$ (Table 6).

It is reported that in trifluoroacetic acid both mercury(II) and palladium acetate are transformed into the corresponding mono- or bis-(trifluoroacetates) [14,15]; consequently the catalytic activity in trifluoroacetic acid must be ascribed to these new species formed in situ.

The investigation, in this solvent, has been extended to other hydrocarbons such as toluene, anisole and naphthalene. As expected for reactions that are basically

TABLE 5

EFFECT OF TEMPERATURE AND OF THE CO PRESSURE ON THE OXIDATIVE CARBONYLATION OF BENZENE IN ACETIC ACID [a]; YIELDS AS IN TABLE 1

P (atm)	*T* (°C)	Yield (%)
1	25	27
1	60	18.2
1	80	21.0
3	25	14
50	25	10.5

[a] The concentrations of mercury(II) acetate and palladium acetate were both 0.2 *M*; $HClO_4$ (5×10^{-3} *M*) and CH_3COONa (0.4 *M*) were added as co-catalysts.

electrophilic, toluene and anisole are more reactive than benzene, but the low reactivity of naphthalene is not in agreement with this general trend.

Unfortunately, the reaction with naphthalene needed to be carried out at a higher dilution in order to work under homogeneous conditions; this means that the results cannot be completely compared (see Experimental and Table 6).

In any case, the reactions are not particularly selective because for both toluene and anisole, comparable mixtures of derivatives of *para*- and *ortho*-carboxylic acids are obtained (with toluene a significant amount of the *meta* isomer is also formed); naphthalene gives rise to a mixture of α- and β-isomers.

It is reported that the electrophilic substitution by mercury(II) under acidic conditions of toluene [15] and of naphthalene [7,8] proceeds with good selectivity towards the *para* and α-isomers, respectively. The lower selectivity that we found in the direct oxidative carbonylation under our reaction conditions would suggest a fluxional rearrangement of the bonding of the aryl group to the metal probably in the transfer to the coordination sphere of palladium.

However, this suggestion must be verified carefully since it is known that the mercurations of toluene and naphthalene are slow equilibrium reactions [8,15]. Work is in progress on this point. It is relevant that under our mild reaction conditions side-chain reactions are not observed, while they occur, although to a rather small degree, in the acetoxylation of toluene [17].

Moreover, under our reaction conditions we could not detect any by-product due to the direct acetoxylation of the aromatic rings. Only with anisole did we observe the formation of a significant amount of *para*-methoxyacetophenone, which was characterized by MS-GC and also by gas chromatography by comparison with a pure sample.

TABLE 6

OXIDATIVE CARBONYLATION OF DIFFERENT AROMATIC HYDROCARBONS IN TRIFLUOROACETIC ACID. YIELDS AND REACTION CONDITIONS AS IN TABLE 1 [a]; YIELDS HIGHER THAN 100% ARE DUE TO REOXIDATION OF METALLIC PALLADIUM BY MERCURY(II) ACETATE (SEE RESULTS AND DISCUSSION)

Palladium catalyst	Hydrocarbon	Yield (%)
$Pd_3(CH_3COO)_6$	C_6H_6 [b]	133 (102.3) [c]
$PdCl_2$	C_6H_6	19
$Pd(PPh_3)_2Cl_2$	C_6H_6	16
$Pd_3(CH_3COO)_6$	$CH_3C_6H_5$ [d]	150
$Pd_3(CH_3COO)_6$	$CH_3OC_6H_5$ [e]	139
$Pd_3(CH_3COO)_6$	$C_{10}H_8$ [f]	72

[a] The concentrations of mercury(II) acetate and the palladium catalyst (referred to palladium) were both 7.5×10^{-2} *M*; sodium acetate (1.5×10^{-1}) was added as co-catalyst. [b] Concentration of benzene 5.6 *M*. [c] The reaction was carried out without the addition of sodium acetate as co-catalyst. [d] Concentration of toluene 4.6 *M*; distribution of isomers: *ortho* 33%, *meta* 31%, *para* 36%. [e] Concentration of anisole 4.6 *M*; distribution of isomers: *ortho* 50%, *meta* 4%, *para* 46%; *para*-methoxyacetophenone was always obtained as a significant by-product. [f] Concentration of naphthalene 1.5 *M*; the concentrations of mercury(II) acetate and palladium acetate were 1.5×10^{-1} *M*; sodium acetate (3×10^{-1} *M*) was added as co-catalyst; distribution of isomers of naphthoic acids: α 73%, β 27%.

Conclusions

In our investigation we have found that the direct stoichiometric oxidative carbonylation of a series of aromatic hydrocarbons results in very high yields when carried out in trifluoroacetic acid. The catalytic system is an equimolecular mixture of mercury(II) acetate and palladium acetate in the presence of an excess of sodium acetate. Both the yields and the conditions are better than those reported previously [6].

In particular, the reaction conditions are so mild that secondary reactions such as the coupling of the aromatics or the acetoxylation of the aromatic rings are irrelevant. Moreover, we have observed that this carbonylation reaction is not particularly favoured by high temperatures or high CO pressures. On the contrary, when the reaction temperature is increased, the competitive reaction of coupling of aromatics becomes important. We have also observed a low reactivity of naphthalene, a result which is not in agreement with the known classical electrophilic attack of the mercuration step [18].

The observation that metallic palladium, which separates in the oxidative carbonylation step, can be easily reoxidized in situ by mercury(II) suggests that the direct activation of aromatic hydrocarbons can be carried out in a pseudo-catalytic way.

In agreement with this expectation, we have found that the addition of an excess of mercury(II) acetate or other simple oxidants causes a real pseudo-catalytic reaction (with respect to palladium acetate), under reaction conditions which are much milder [19] than those reported by Henry for a similar pseudo-catalytic reaction [6].

In conclusion, the direct activation of the C–H bond of the aromatic rings by oxidative carbonylation in order to prepare the corresponding carboxylic acid can be carried out conveniently under mild reaction conditions, which are typical of standard synthetic organic chemistry.

Therefore it is expected that this reaction will soon become a standard laboratory synthetic method, which, in addition, does not require the isolation of organometallic intermediates.

Experimental

Materials

The aromatic hydrocarbons were of reagent grade and were used without further purification. Solvents were of reagent grade and were distilled before use when necessary.

Mercury(II) acetate and dry sodium acetate were of reagent grade; they were kept dry by treatment with acetic anhydride followed by distillation to dryness. $Pd_3(CH_3COO)_6$ was synthesized by the method of ref. 15. $Pd(PPh_3)_2Cl_2$ and $Pd(DPE)Cl_2$ (DPE stands for 1,2-diphenylphosphinoethane) were kindly supplied by Prof. Cenini. Phenylmercury acetate and naphthylmercury acetate were prepared by literature methods [7,9]. The naphthylmercury derivative was reported to be the pure α-isomer [7]; however, when it was treated with bromine [8], we always obtained a mixture of α- and β-bromonaphthalene (about 70/30); the rough composition of the mixture was obtained by HPLC or capillary column gas chromatography.

The methyl esters of the acids, which were of reagent grade, were used as gas chromatographic standards; they were prepared by esterification with methanol under acidic conditions. In the case of benzene, the isobutyl ester (Table 1) was prepared in a similar way. The esters were carefully purified by distillation or crystallization.

Analytical methods

The mixtures of methyl esters produced under our reaction conditions were analysed by gas chromatography on a Hewlett–Packard 5700 A instrument with a flame detector. The analytical conditions were the following: (a) starting from benzene the internal standard was naphthalene, a steel column of 3.1 m (Chromosorb W 100/120 mesh, methylsilicone SE 30 5% in weight) was used at 160°C; (b) starting from toluene the internal standard was *ortho*-dichlorobenzene, a copper column of 3.2 m (Chromosorb W silanised 80/100 mesh, fluorinated silicone DC FS 1265 10% in weight) was used at 130°C; (c) starting from anisole the internal standard was methylnaphthalene, the column was that used for toluene derivatives used at 160°C; (d) starting from naphthalene the internal standard was methylnaphthalene, the column was that used for benzene derivatives working at 190°C. The injection temperature was always 200°C and the flux of nitrogen was 10 ml/min.

In the case of isobutyl benzoate, the internal standard was naphthalene and the column was that used for benzene derivatives. The analysis was carried out by programmed temperature: initial isotherm 150°C for 4 min, programmed temperature increase of 16°C/min, final isotherm 170°C.

Analysis of the mixture of α- and β-bromonaphthalene (obtained by simple bromination in CS_2 of the mixture of naphthylmercury acetates) was carried out on a Perkin–Elmer Series 3B Liquid Chromatograph. The solvent was a mixture of methanol and water (flux 1 ml/min): gradient 2 from 55 to 62% of methanol for 30 min and then 10 min at constant ratio (retention times: α-isomer 33 min, β-isomer 35 min).

Analysis of this mixture could also be done with a capillary column (OV 1) of 15 m (isotherms at 80°C, injection temperature 70°C, flux of helium 2 ml/min) on a Carlo Erba HRGC Fractovap 4160 instrument.

Reactions

Case (A): In 50 ml of the dry solvent (or of a mixture of solvents), phenyl- (or naphthyl)-mercury acetate and palladium acetate were added (for concentrations see Tables 1–6). The solution was stirred under a stream of dry CO for 3.5 h (we found that the yields do not increase above 3-4 h of reaction). After filtration of metallic palladium, the resulting solution was maintained for 1 h under reflux (after addition of 5 ml of H_2O and a few drops of concentrated H_2SO_4). Finally the solvent was evaporated under vacuum and the residue was extracted twice with 30 and 10 ml of CCl_4, respectively. The organic layer was evaporated again to dryness and treated with a few milliliters of dry methanol. Esterification was then carried out with an excess of a solution of CH_2N_2 in dry ether. The final solution was analysed by gas chromatography after addition of the internal standard.

If the reaction is carried out in the presence of an alcohol, the final product is already the corresponding ester so that the steps of hydrolysis of the anhydride and of esterification are not necessary.

Co-catalysts such as strong acids or LiBr or sodium acetate can be added initially, before CO admission. Their concentrations are reported in Tables 1–6.

We found that in acetic acid in the case of addition of concentrated strong acids ($HClO_4$, HBF_4, etc.) the presence of acetic anhydride (10–20% in excess to the water added) did not produce a significant effect.

Case (B): An excess of hydrocarbon (20–30 ml of benzene, toluene or anisole, or 3.9 g of naphthalene) was added to about 20 ml of the dry solvent. Then 3 mmol of mercury acetate was added together with the strong acid acting as co-catalyst (when necessary, for concentration see Tables 3 and 4). The mixture was refluxed for 2 h. After cooling, sodium acetate could be added (concentrations are reported in the Tables; usually about 0.5 g). After admission of a stream of dry carbon monoxide, palladium acetate (about 0.67 g) was added (see Tables for exact concentration). The mixture was stirred at room temperature for 3.5 h in a stream of dry CO. After filtration of metallic palladium, the resulting solution was treated under reflux with 5 ml of H_2O containing 3–4 drops of concentrated sulphuric acid. After cooling, the solvent was evaporated under vacuum and the residue was treated twice with 30 and 20 ml of CCl_4, respectively. The organic layer was then separated and evaporated to dryness. The residue was treated with a few milliliters of dry methanol and esterification was carried out with an excess of a solution of CH_2N_2 in dry ether. The final solution was analysed by gas chromatography after addition of the internal standard.

If the reaction is carried out in the presence of methanol, the final products are already the methyl esters so that the steps of hydrolysis of the anhydrides and of esterification are not necessary.

Details of reactions carried out under non-standard conditions

(a) When other Pd catalysts were used ($PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(DPE)Cl_2$), they were added in the same way as palladium acetate.

(b) The carbonylation reaction could be carried out at temperatures higher than room temperature (Table 5) or under reflux (Table 3); the reaction time was still 3.5 h and the work-up of the reaction mixture was the same as that of cases A en B.

(c) The carbonylation reaction could be carried out under pressure. In this case, palladium acetate was added to the cool solution containing the organo-mercury product; the resulting mixture was introduced into a glass autoclave (3 atm of CO) or into a steel bomb (50 atm of CO); after evacuation at the temperature of dry ice, the required carbon monoxide pressure was introduced. After 3.5 h, the reaction was stopped, the resulting mixture was filtered, and the autoclave was washed with 10 ml of benzene or CCl_4 which was added to the reaction mixture. The latter was then treated as in the above-mentioned methods.

By-products formed under the reaction conditions

In the gas chromatographic analysis of the reaction mixtures, we could always detect small peaks due to the presence of very small amounts of several by-products. In the case of benzene, they were characterized by GC-MS on a Varian Mat 112 mass spectrometer equipped with a Varian Aerograph Series 1400 connected to a glass column of 2 m (Chromosorb 80-100 mesh, SE 30 2.5%) working at 150°C with a flux of helium of 10 ml/min.

Diphenyl, monocarboxylated diphenyls, dicarboxylated phenyls and fluorenone were definitively characterized; under certain conditions diphenyl can become the major product (see Results and discussion). In the case of anisole, a peak of medium intensity was always present in the gas chromatographic analysis; it was characterized as *para*-methoxyacetophenone by GC-MS (conditions as above); this assignment was confirmed (both by GC-MS and simple GC) by comparison with a pure sample purchased commercially.

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