

Catalysis by Palladium Salts. Part 2.¹ Palladium-catalysed Carboxylation with Carbon Monoxide of Aromatic Compounds Working under Mild Conditions

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The carboxylation with CO of aromatic C-H bonds, catalysed by palladium acetate, occurs with good yields and under mild conditions (1 atm of CO and 20–50 °C), with trifluoroacetic acid as solvent and sodium acetate as co-catalyst. The reaction, which is stoichiometric with respect to palladium, can be transformed into a pseudo-catalytic process by addition of an excess of a specific oxidant, which is consumed stoichiometrically to regenerate palladium(II) continuously. The more efficient oxidants are mercury(II) acetate, thallium(III) trifluoroacetate, and sodium nitrate. With substituted aromatic derivatives, such as toluene and anisole, or condensed aromatic systems such as naphthalene, the pattern of the ring substitution is typical of electrophilic reactions, but in the presence of specific oxidants the regioselectivity of the ring substitution is increased with respect to the stoichiometric reaction.

The carboxylation with CO of non activated C-H bonds of aromatic rings, in the presence of palladium(II) salts, can be carried out stoichiometrically with respect to palladium. However, yields are relatively low and reaction conditions required rather drastic, the competitive reaction being the reduction of palladium(II) to metallic palladium.^{2–4}

Using palladium to catalyse the reaction, better yields are achieved, working under milder conditions, by adding a large excess of an oxidant such as sodium peroxydisulphate⁵ or tertiary butyl hydroperoxide.⁶ The reaction becomes slightly pseudo-catalytic with respect to palladium as a result of the *in situ* regeneration of palladium(II) from metallic palladium.

Recently, the direct one-step carboxylation with CO₂ of aromatic compounds again mediated by palladium(II), was also reported.⁷ In this case the process does not involve a redox mechanism, *via* the palladium(II)–palladium(0) couple, but only simple activation of the aromatic CH bond, mediated by palladium(II).

However, the above mentioned pseudo-catalytic reactions^{5,6} are characterised by poor selectivity. By-products such as phenolic compounds or diaryl derivatives, resulting from coupling of two aromatic rings, are formed in large amounts, sometimes as the major reaction products. Moreover, the carboxylation of substituted aromatic compounds such as toluene and anisole, or of condensed aromatic systems such as naphthalene, is reported to occur with relatively low regioselectivity of the ring substitution. The only exceptions are pseudo-aromatic heterocyclic systems such as furan and thiophene, which are reported to give only the derivatives of the corresponding 2-carboxylic acids.^{2,3} Because of the synthetic interest in the direct carboxylation of non-activated aromatic rings, we have investigated the characteristics of this reaction, and have defined experimental conditions which are not only very mild, but also easily pseudo-catalytic with respect to palladium(II). In addition, the reaction gives the selective formation of derivatives of carboxylic aromatic acids and an interesting regioselectivity of ring substitution.

Results

Carboxylation by a Stoichiometric Reaction with Respect to Palladium.—We have confirmed that this one-step reaction occurs with benzene in low yields (around 10%),^{2,3} either

working in protonic solvents, such as methanol or acetic acid, or in the absence of solvent. Rather drastic conditions are required (100 °C and 10–20 atm of CO), because under normal conditions (room temperature and 1 atm of CO) the reaction does not occur.

Our earlier work on solvent effects in the palladium-catalysed oxidative carbonylation of aryl mercury compounds¹ suggested the use of a strong acid such as trifluoroacetic acid as solvent. In this solvent the reaction occurs with good yields under very mild conditions (20–70 °C and 1 atm of CO), using palladium acetate as catalyst (Table 1). Palladium acetate is a unique system; palladium chloride, for example, even in trifluoroacetic acid as solvent is completely inactive under such mild reaction conditions. Palladium trifluoroacetate is probably generated *in situ*, as it has been reported that in trifluoroacetic acid, palladium acetate is transformed into the corresponding mono- or bis-(trifluoroacetate).⁸

Table 1. Palladium-promoted stoichiometric synthesis of mixed acid anhydrides from aromatic compounds and carbon monoxide (1 atm): concentration of [Pd₃(O₂CMe)₆], 2.38 × 10⁻² mol dm⁻³; NaO₂CMe, 1.4 × 10⁻¹ mol dm⁻³; reaction time 4 h, CF₃CO₂H as solvent (see Experimental)

Aromatic compound	Concentration (mol dm ⁻³)	T(°C)	Yield (%) ^a	Isomer		
				<i>o</i>	<i>m</i>	<i>p</i>
Benzene	5.6	25	28			
	5.6	50	31.2 (14.5); ^b (36.7, 26, 22) ^c			
	5.6	70	37			
Toluene	4.7	25	41	29	15	56
	4.7	50	52	33	17	50
	4.7	70	64	35	16	49
Anisole ^e	4.6	25	31	44		56
	4.6	50	46	38		62
	4.6	70	50	42		58
Naphthalene	3.3	50	42.5		<i>d</i>	
	<i>f</i>	70	60.5		<i>d</i>	

^a Isolated yields based on [Pd₃(O₂CMe)₆]. ^b Without addition of MeCO₂Na. ^c Concentration of MeCO₂Na, 2.8 × 10⁻¹, 4.3 × 10⁻¹, and 7.1 × 10⁻¹ mol dm⁻³ respectively. ^d Ratio of the 1 to 2 isomer, 81:19. ^e Very minor amounts (less than 1%) of an unknown impurity are formed. ^f Concentration of naphthalene, 1 mol dm⁻³.

We have also found that yields can be dramatically increased by the addition of a co-catalyst such as sodium acetate (Table 1), which participates in the oxidative carbonylation, mediated by palladium salts, of aryl mercury compounds.¹

On the other hand, the addition of 1,2-dibromo- or dichloroethane³ or allyl chloride,⁶ which are reported to be active co-catalysts for this kind of carboxylation, does not produce positive effects under our reaction conditions.

Under our reaction conditions, yields are not only higher than those previously reported from work carried out under much more drastic conditions,²⁻⁴ but the reaction is also more selective, the major and often the only reaction product being the mixed anhydride from trifluoroacetic acid and the carboxylic aromatic acid. By-products, which could result in this solvent by acetoxylation of the aromatic ring⁹ or by coupling of two aromatic rings,¹⁰ occur only to a minor extent and in most cases are completely absent.

We have also found that the reaction is not favoured by high pressures of CO, but instead by an increase of both temperature and the concentration of sodium acetate (Table 1).

The electrophilic character of the reaction is reflected by the higher reactivity, with respect to benzene, of toluene, anisole, and naphthalene, and by the pattern of the ring substitution: a mixture of the *para* and *ortho* isomers in a ratio of about 60:40 is obtained with anisole, while with toluene this ratio is about 50:35, with 15% of the *meta* isomer being formed. With naphthalene the major product is the α -isomer (Table 1).

Carboxylation under Pseudo-catalytic Conditions with Respect to Palladium.—In our investigation of the palladium-mediated oxidative carbonylation of aryl-mercury compounds,¹ we suggested that, with trifluoroacetic acid as solvent, metallic palladium, which separates during the oxidative carbonylation step, could be reoxidised by mercury(II) salts generated *in situ*. As a consequence, the palladium-mediated carboxylation with CO of aromatic compounds could be carried out pseudo-catalytically with respect to palladium in the presence of an excess of an oxidant, for example mercury(II) salts. The catalytic process would be a system in which the palladium(II) salt is continuously regenerated by the excess of oxidant, stoichiometrically consumed in each catalytic cycle.

Two-component oxidation systems are quite common in palladium catalysis,^{11a} in a few cases, even three-component oxidation systems have been used, because the reoxidation process is of paramount importance.¹²

In order to extend our original observation, limited to mercury(II) salts, we studied a series of oxidants, using benzene as the aromatic substrate (Table 2). The choice of oxidants was based on their previous use in oxidation or oxidative couplings of olefins, aromatics, or even carbon monoxide, mediated by palladium.^{11a}

Under our standard reaction conditions (see Experimental section), thallium(III) trifluoroacetate, sodium nitrate, and mercury(II) acetate are the most efficient, the reaction occurring under mild conditions with high selectivity: diphenyl is formed only in few cases as a minor by-product, usually increasing as a result of the temperature. It is worth pointing out that when KNO₃ or HNO₃ are used as oxidant, significant amounts of nitrobenzene are formed in parallel with the mixed anhydride of benzoic acid.

The palladium-catalysed synthesis of nitrobenzene is expected to take place;¹³ however, the lack of significant formation of nitrobenzene when using NaNO₃ as oxidant was unexpected and not in accord with the above results with KNO₃ or HNO₃.

Our best systems are more efficient and work under milder conditions than those previously reported, such as palladium

Table 2. Palladium-promoted pseudo-catalytic synthesis of mixed acid anhydrides from benzene and carbon monoxide (1 atm): concentration of [Pd₃(O₂CMe)₆], 4.7 × 10⁻³ mol dm⁻³; NaO₂CMe, 7.2 × 10⁻² mol dm⁻³; C₆H₆, 5.6 mol dm⁻³; reaction time 4 h; temperature 50 °C; CF₃CO₂H as solvent. Molar ratio of oxidant with respect to [Pd₃(O₂CMe)₆] = 30

Oxidant	Yield (%) ^a	Efficiency of the pseudo-catalytic system (%) ^b
Without oxidant	21	—
Hg(O ₂ CMe) ₂	268 ^c (413) ^{c,d}	44.6 (37.5) ^d
Cu(O ₂ CCF ₃) ₂	199	33
Tl(O ₂ CCF ₃) ₃	680 ^c (1 087) ^{c,d}	61.8 (51.7) ^d
NaNO ₂	208 ^c	34.6
NaNO ₃	721 ^{c,e}	45
C ₅ H ₁₁ ONO	184 ^f	30.6
KNO ₃	392 ^g	24.5
HNO ₃	158 ^h	9.8
MnO ₂	107	9.7
Chloranil	56	5

^a Isolated yields based on [Pd₃(O₂CMe)₆]. ^b Efficiency with respect to the total reoxidation of metallic palladium to palladium(II) by the excess of oxidant. Each cycle corresponds to theoretical 100% yield based on [Pd₃(O₂CMe)₆]. ^c Very minor amounts of diphenyl as by-product (less than 1% yield). ^d Molar ratio of oxidant with respect to [Pd₃(O₂CMe)₆] = 60. ^e Nitrobenzene produced as a minor by-product in a few reaction runs. ^f Solution of C₅H₁₁ONO in trifluoroacetic anhydride added slowly to the reaction mixture. ^g Nitrobenzene produced in 58% yield. ^h Nitrobenzene produced in 47% yield.

Table 3. Palladium-promoted pseudo-catalytic synthesis of mixed acid anhydrides from substituted or condensed aromatic compounds and carbon monoxide (1 atm). Conditions as in Table 2. Concentration of the aromatic compounds: benzene, 5.6 mol dm⁻³; toluene, 4.7 mol dm⁻³; anisole, 4.6 mol dm⁻³; naphthalene, 3.3 mol dm⁻³

Aromatic compound	Oxidant	Yield (%) ^a	Isomer		
			<i>o</i>	<i>m</i>	<i>p</i>
Benzene	Hg(O ₂ CMe) ₂	268			
	NaNO ₃	721			
	Tl(O ₂ CCF ₃) ₃	680			
Toluene	Hg(O ₂ CMe) ₂	187	16.3	14.3	69.4
	NaNO ₃	724	38.5	13.8	47.6
	Tl(O ₂ CCF ₃) ₃	652	22.4	10.1	67.5
Anisole	Hg(O ₂ CMe) ₂	44.8 ^b	58.2		41.8
	NaNO ₃	55.5 ^c	55.5		44.5
	Tl(O ₂ CCF ₃) ₃	63.3 ^b	26.9		73.1
Naphthalene	Hg(O ₂ CMe) ₃	133		<i>d</i>	
	NaNO ₃	695		<i>e</i>	
	Tl(O ₂ CCF ₃) ₃ ^g	132		<i>f</i>	

^a Isolated yields based on [Pd₃(O₂CMe)₆]. ^b Major reaction product dimethoxybiphenyl as a mixture of isomers. ^c Major reaction products, nitroanisole and dimethoxybiphenyl as a mixture of isomers. ^d Ratio of the 1 to 2 isomer 78.7:21.3. ^e Only 1 isomer. ^f Ratio of the 1 to 2 isomer, 81:19. ^g Concentration of naphthalene, 1 mol dm⁻³.

salts in the presence of an excess of Na₂S₂O₈⁵ or Bu'OOH with CH₂=CHCH₂Cl,⁶ and are more selective.

We have extended our investigation, using our best catalytic systems, to a series of substituted aromatic compounds such as toluene, anisole, and naphthalene (Table 3). In contrast with the direct stoichiometric reaction (Table 1), both toluene and naphthalene display a reactivity comparable with that of benzene, suggesting that the reoxidation of metallic palladium could be the important step in the pseudo-catalytic system. With these substrates the reaction is quite clean, as it is with benzene, the dimeric by-products being formed in minor amounts.

In the case of anisole, however, the system shows a very low selectivity, the carboxylation reaction becoming a minor component of a complex series of parallel reactions. The major reaction products are mixtures of isomeric dimethoxybiphenyls with substitution in both rings [using $\text{Hg}(\text{O}_2\text{CMe})_2$ or $\text{Ti}(\text{O}_2\text{CCF}_3)_3$ as oxidants] or mixtures of isomeric nitroanisoles and isomeric dimethoxybiphenyls, as above, when using NaNO_3 . This is the only case in which NaNO_3 gave significant nitration of the aromatic ring under these conditions. However, the low selectivity of the pseudo-catalytic carboxylation of anisole is not unexpected. A similar characteristic was found in the palladium-catalysed oxidative carbonylation of mercury derivatives of anisole.¹

We also found that the *para* substitution of toluene using $\text{Hg}(\text{O}_2\text{CMe})_2$ or $\text{Ti}(\text{O}_2\text{CCF}_3)_3$ as oxidant, is higher than in the simple stoichiometric oxidation (see Tables 3 and 1, respectively), although this is not the case with NaNO_3 as oxidant. Also, with anisole the regioselectivity of the ring substitution is affected by the nature of the oxidant. In particular *ortho* substitution is predominant with $\text{Hg}(\text{O}_2\text{CMe})_2$ or NaNO_3 (Table 3), again in contrast with the distribution of isomers observed in the direct stoichiometric reaction (Table 1). However, with $\text{Ti}(\text{O}_2\text{CCF}_3)_3$, the extent of *ortho* substitution of anisole is low, even when compared to the direct stoichiometric reaction (Tables 3 and 1 respectively).

These observations would suggest that the excess of oxidant does not behave as a separate reagent, necessary only for the continuous reoxidation of metallic palladium, but probably also interacts with the palladium catalyst, producing *in situ* specific new palladium species. These have a slightly different catalytic behaviour from palladium trifluoroacetate, in particular with respect to the selectivity of the reaction and the regioselectivity of the ring substitution.

Although the nature of the *in situ* interactions between palladium trifluoroacetate and some oxidants is at the moment not understood, our observations would suggest that by a careful choice of the oxidant, it could be possible to achieve high regioselectivity of the ring substitution of various aromatic compounds.

In agreement with this, we have found that the carboxylation of naphthalene occurs selectively only in the α -position with NaNO_3 as oxidant (Table 3). With other oxidants or in the stoichiometric reaction with palladium acetate, the ring substitution is not so selective, the α -isomer produced being contaminated by some β -isomer (Tables 1 and 3).

Discussion and Conclusions

We have found that, contrary to previous reports,²⁻⁴ the carboxylation with CO of the C-H bond of an aromatic ring, which is stoichiometric with respect to palladium salts, can be carried out in good yield and high selectivity under very mild conditions, with trifluoroacetic acid as solvent, a co-catalyst such as sodium acetate, and palladium acetate as catalyst.

The use of such a solvent for oxidative carbonylation reactions has been reported,¹⁴ but its application to aromatic systems has only recently been described by us.¹

The mechanism of the reaction under investigation probably requires first palladation of the aromatic ring to generate an aryl-palladium intermediate, in common with other related reactions such as aromatic hydrocarbon acetoxylation⁹ or coupling.¹⁰ Carbon monoxide insertion followed by nucleophilic attack and internal electron transfer, corresponding to reduction of palladium, concludes the cycle.

The typical electrophilic character of the palladium-mediated oxidative carbonylation reaction, that we have confirmed, would suggest that the palladation of the aromatic ring is the relevant step. This probably accounts for the positive effect of a

strong protonic solvent such as trifluoroacetic acid, because it is well known that strong acidity favours the formation of cationic electrophilic palladium species, particularly when starting from palladium carboxylates.¹⁵

The co-catalytic action of a slight excess of NaO_2CMe is quite unexpected, however, because it has been reported that in the presence of CO, addition of a nucleophile such as NaO_2CMe favours, in acetic acid, a fast reduction to metallic palladium of $[\text{Pd}_3(\text{O}_2\text{CMe})_6]$ with parallel formation of acetic anhydride.¹⁶

This co-catalytic action can not be explained by increased formation of electrophilic palladium species, because a similar co-catalytic action has been reported for the oxidative carbonylation of aryl mercury(II) compounds mediated by $[\text{Pd}_3(\text{O}_2\text{CMe})_6]$ or $[\text{Pd}_3(\text{O}_2\text{CCF}_3)_6]$.¹ This does not require the activation of a C-H bond of an aromatic ring by direct attack of an electrophilic palladium species to form an aryl-palladium intermediate. In addition, it is known that on adding NaO_2CMe to a solution of $[\text{Pd}_3(\text{O}_2\text{CMe})_6]$ in acetic acid, the anion $[\text{Pd}_2(\text{O}_2\text{CMe})_6]^{2-}$ is generated *in situ*.^{11b} Probably the corresponding anion $[\text{Pd}_2(\text{O}_2\text{CCF}_3)_6]^{2-}$ is generated in our case, although not extensively, when NaO_2CCF_3 (formed *in situ* from NaO_2CMe) is added to a trifluoroacetic acid solution of $[\text{Pd}_3(\text{O}_2\text{CCF}_3)_6]$ (formed *in situ* from $[\text{Pd}_3(\text{O}_2\text{CCF}_3)_6]$).⁸ Obviously such an anionic species will not enhance the electrophilic properties of the palladium catalytic system.

In agreement with this, when the reaction is carried out with high molar ratios of NaO_2CMe to $[\text{Pd}_3(\text{O}_2\text{CMe})_6]$ a sudden decrease of the reaction yields occurs (Table 1), probably because the *in situ* concentration of $[\text{Pd}_2(\text{O}_2\text{CMe})_6]^{2-}$ becomes too high.

The anionic species $[\text{Pd}_2(\text{O}_2\text{CCF}_3)_6]^{2-}$ can not be involved even in the terminal part of the catalytic cycle, namely the CO insertion and the reductive electron transfer step. CO insertion is favoured by oxidation of the metal and the presence of a positive charge, because both effects destabilise the aryl-carbonyl intermediates, by reducing the degree of back bonding to the CO group.¹⁷

In conclusion, we suggest that the positive effect of the formation *in situ* of anionic species by addition of NaO_2CMe could be only that of stabilising the catalytic system, with respect to palladium reduction by CO. Such a reduction requires a preliminary nucleophilic attack, before electron transfer, which is not very likely to occur easily on anionic species, although it has been reported that addition of NaO_2CMe to an acetic acid solution of $[\text{Pd}_3(\text{O}_2\text{CMe})_6]$ saturated with CO produces the separation of metallic palladium.¹⁶ In our case, however, NaO_2CMe is added before CO admission (see Experimental section). Thus, the co-catalytic action of NaO_2CMe has not been clearly rationalised.

Finally, the mild conditions used in this work ensure that the direct carboxylation of aromatic hydrocarbons by palladium(II) carboxylates¹⁸ or by palladium(II) salt in the presence of NaO_2CMe ¹⁹ does not occur. These reactions require a temperature of at least 100 °C for about 10 h to take place. In addition, we have established that the carboxylation reaction does not take place under our reaction conditions in the absence of a pressure of CO.

We have also found that the reaction can be carried out pseudo-catalytically with respect to palladium, by the addition of an excess of an oxidant (Table 3). In this respect, the selective formation of the naphthalene-1-carboxylic acid mixed anhydride from naphthalene, when using NaNO_3 as oxidant, or the increased *para* substitution of toluene, when using $\text{Hg}(\text{O}_2\text{CMe})_2$ or $\text{Ti}(\text{O}_2\text{CCF}_3)_3$ as oxidant, are worth emphasising as results of high synthetic interest.

It is possible that when the many palladium species formed *in situ* in such complex catalytic systems, and their specific roles

are better understood, other reaction conditions, characterised by unusually high regioselectivities, may be suggested. Our systems are far from being optimised from a synthetic point of view. A real catalytic Wacker-type process should be investigated using oxygen as the final oxidant. Preliminary investigations suggest that this is possible.

In conclusion, our investigation suggests that the activation of the C-H bonds of aromatic rings, by direct carboxylation with CO, can be carried out conveniently in one step under very mild conditions, which are commonly used in standard synthetic organic chemistry. In addition, even the formation of stable organometallic intermediates, such as aryl-mercury or -thallium species, can be avoided. Moreover, our preliminary results show that these reactions can be highly selective and even regioselective.

Therefore, it is expected that the palladium-mediated direct carboxylation of aromatic rings can become a standard synthetic method.

Experimental

Palladium acetate was prepared according to Wilkinson and co-workers.⁸ The aromatic hydrocarbons were of reagent grade and were used without further purification; dry sodium acetate and all the oxidant reagents used were of reagent grade. Trifluoroacetic acid and trifluoroacetic anhydride were reagent grade and were distilled before use.

Analysis of the reaction mixture was carried out by vapour-phase gas chromatography according to the experimental conditions reported in detail in reference 1. The detection of the original presence of the mixed anhydride of trifluoroacetic acid with the carboxylic aromatic acids, formed as the major reaction product of the oxidative carboxylation, was achieved by direct mass spectroscopy investigation of the reaction mixture using a Varian Mat 112 mass spectrometer.

Reactions under Stoichiometric Conditions.—To a solution of $[\text{Pd}_3(\text{O}_2\text{CMe})_6]$ (448 mg) and NaO_2CMe (328 mg) in trifluoroacetic acid (14 cm³) the aromatic hydrocarbon (ca. 14 cm³) was added. The hydrocarbon concentrations under standard conditions were benzene, 5.6 mol dm⁻³; toluene, 4.5 mol dm⁻³; and anisole 4.6 mol dm⁻³. With naphthalene, a suspension was obtained with final concentration ca. 3.3 mol dm⁻³, while a solution was obtained when the concentration was ca. 1 mol dm⁻³.

The solutions so obtained were maintained under reflux, under 1 atm of CO. CO was bubbled through the solution for 4 h,* with vigorous stirring and at 25, 50, and 70 °C, respectively. At the end of the reaction, metallic palladium eventually separated, and was filtered off, and the resulting solution was refluxed for 1 h after H₂O (4 cm³) and concentrated H₂SO₄ (0.2 cm³) had been added. Finally the solvent was evaporated to dryness under reduced pressure and the residue was extracted twice with 30 and 10 cm³ of CCl₄, respectively. The organic layer was evaporated again to dryness and treated with a few cm³ of dry methanol. Esterification was carried out with an excess of CH₂N₂ in dry ether. The final solution was analysed by vapour-phase gas chromatography after addition of the internal standard.¹

Reaction in the Presence of an Excess of Oxidant.—The reaction was carried out as above except that the excess of

oxidant was added to the initial solution before admission of the CO atmosphere. In a few cases, the excess of oxidant did not dissolve completely so the reaction was carried out in suspension. The amount of oxidant was usually a molar ratio of 10:1 or 20:1 with respect to palladium atoms (see Table 2).

Reactions carried out under Non-standard Conditions.—The carbonylation could also be carried out under CO pressure. In this case palladium acetate was added to the cool solution containing the aromatic hydrocarbons and NaO₂CMe. 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 solid CO₂, the required carbon monoxide pressure was applied. After 4 h the reaction was stopped, the resulting mixture was filtered and the autoclave washed with CCl₄ (20 cm³) which was added to the reaction mixture. The latter was treated as above. Yields were always much lower than those obtained under 1 atmosphere of CO.¹

By-products formed under the Reaction Conditions.—Usually the reactions were quite clean. However, at temperatures above 50 °C or in the presence of particular oxidants (see Tables 2 and 3), other products were formed, and detected as peaks in the gas chromatographic analysis of the reaction mixtures. These peaks were characterised by GC-MS on a Varian Mat 112 mass spectrometer equipped with a Varian Aerograph Series 1400 connected to a 2-m glass column (Chromosorb 80-100 mesh, SE 30 2.5%), at 150 °C with a flux of helium of 10 ml min⁻¹.

The products from coupling of the original hydrocarbon (biphenyls) or from one molecule of the hydrocarbon with one molecule of the corresponding carboxylic acid (mono-carboxylated biphenyls) or, very rarely, from dicarboxylation of the original hydrocarbon (dicarboxylated phenyls) were detected as very small peaks with high retention time. Their formation was observed only at temperatures around 70 °C and/or in the presence of particular oxidants (see Tables). Other by-products such as those derived from nitration or other substitutions of the aromatic ring, also occurred in the case of anisole (see Tables 2 and 3).

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* The reaction time was chosen because, on increasing it above 4 h, the yield of hydrocarbon conversion was not noticeably increased. In the case of benzene, working at 50 °C, the yields referred to palladium acetate were, respectively, 31.3% after 4 h, 36.2% after 13 h, and 38.5% after 48 h.

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