Palladium-promoted One-step Carboxylation of Aromatic Compounds with Carbon Monoxide

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Summary The one-step carboxylation of aromatic compounds such as benzene, toluene, anisole, chlorobenzene, furan, and thiophen has been carried out using carbon monoxide and palladium acetate; the reaction does not require oxygen and is electrophilic.

EXTENSIVE studies on the reaction of carbon monoxide with olefins in the presence of transition metals have been carried out.[1] Much less is known about the direct carboxylation of aromatic compounds with carbon monoxide[2] although it is reported that aryl halides and aryl amines give aromatic acid derivatives when treated with palladium compounds and carbon monoxide.[3] We have reported that aromatic compounds undergo palladation to give an intermediate aromatic–Pd σ-complex which further reacts with olefins to give aromatic-substituted olefins.[4] Therefore it was expected that aromatic acid derivatives could be synthesised directly from aromatic compounds and carbon monoxide. We have found that the reaction of carbon monoxide with aromatic compounds in the presence of palladium acetate gives aromatic acids in a single step.

We here report the one-step carboxylation of aromatic compounds such as benzene, toluene, anisole, chlorobenzene, furan, and thiophen with carbon monoxide using palladium acetate. The reaction was carried out using the aromatic compound (20 ml) and carbon monoxide (15 atm) with $Pd(OAc)_2$ (1 mmol) at 100 °C with stirring for 20 h using an autoclave. The resulting mixture was filtered to remove palladium metal and the filtrate was evaporated. The residue (usually crystallised) was analysed by g.l.c. (Table).

Table Palladium-promoted carboxylation of aromatic compounds by carbon monoxide[a]

Aromatic compound	Product	Yield %[b]
Benzene	Benzoic acid	26
Anisole	*o*-Methoxybenzoic acid	5
	p-Methoxybenzoic acid	43
Toluene	*o*-Methylbenzoic acid	12
	m-Methylbenzoic acid	3
	p-Methylbenzoic acid	18
Chlorobenzene	*o*-Chlorobenzoic acid	4
	m-Chlorobenzoic acid	2
	p-Chlorobenzoic acid	8
Furan	Furan-2-carboxylic acid	35
Thiophen	Thiophen-2-carboxylic acid	18

[a] Reactions were carried out at 100 °C with stirring for 20 h using the aromatic compound (20 ml), $Pd(OAc)_2$ (1 mmol) and carbon monoxide (15 atm) in an autoclave. [b] Isolated yields based on $Pd(OAc)_2$.

From the Table it can be seen that not only benzenoid but also non-benzenoid aromatic compounds such as furan and thiophen give the corresponding carboxylic acids. The data in the Table also show that the reactivity of monosubstituted benzenes decreases in the order OMe > Me > H > Cl, and that the reaction proceeds with *ortho–para* orientation when an electron-releasing group is attached to the benzene ring indicating that the reaction is electrophilic. *Ca.* 15 atm of carbon monoxide is the optimum pressure, higher and lower pressures not being so effective. Since common solvents gave lower yields of products, the reactions were carried out using the aromatic compounds themselves as solvents. $PdCl_2$ and $PdCl_2$–NaOAc do not effect the reaction.

Two reaction mechanisms may be considered (using benzene as substrate): one involves benzaldehyde as an intermediate which undergoes oxidation by oxygen dissolved in the benzene, and the other involves a benzoyl–PdOAc σ-complex which undergoes reductive elimination to give the acid anhydride and Pd^0. We favour the latter [equations (1)—(4)] on the basis that (i) no benzaldehyde is detected in the resulting mixture and (ii) benzoic acid was also formed in 30% yield in a control experiment in which deoxygenated benzene† was used under a nitrogen atmosphere.

$$PhH + Pd(OAc)_2 \rightarrow Ph\text{-}Pd\text{-}OAc + AcOH \qquad (1)$$

$$Ph\text{-}Pd\text{-}OAc + CO \rightarrow Ph\text{-}C(:O)\text{-}Pd\text{-}OAc \qquad (2)$$

$$Ph\text{-}C(:O)\text{-}Pd\text{-}OAc \rightarrow Ph\text{-}C(:O)\text{-}OAc + Pd^0 \qquad (3)$$

$$Ph\text{-}C(:O)\text{-}OAc + AcOH \rightarrow Ph\text{-}C(:O)\text{-}OH + Ac_2O \qquad (4)$$

One of the characteristic features of this reaction is that no oxygen is needed to perform the carboxylation of aromatic compounds with carbon monoxide. This reaction may be useful for the synthesis of a variety of aromatic acids.

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† Benzene was refluxed and distilled immediately before use from a dark green solution of sodium benzophenone dianion under nitrogen.

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