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A NEW SYNTHESIS OF CARBOXYLIC ACIDS BY A Pd(II)-CATALYZED CARBON MONOXIDE INSERTION

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Recently two new syntheses of carboxylic acids from carbon monoxide have been reported. One was via a radical route (1); the other was by CO insertion into certain organomercury compounds under high CO pressure (2). We wish to report a new synthesis of carboxylic acids by a Pd(II)-catalyzed CO insertion which takes place under mild conditions with a variety of metal aryls.

Alkyl and aryl palladium(II) compounds with stabilizing ligands such as phosphines are known to insert CO to form stable acyl compounds (3).

$$\text{[PdXR(PEt}_3\text{)}_2\text{]} + \text{CO} \longrightarrow \text{[XPd(C(=O)R)(PEt}_3\text{)}_2\text{]} \qquad (1)$$

A reaction which presumably proceeds by the reverse of equation 1, the decarboxylation of acid chlorides, has also recently been reported (4). Thus, benzoyl chloride decomposes to give chlorobenzene plus CO.

$$C_6H_5COCl + Pd \longrightarrow [C_6H_5C(=O)PdCl] \longrightarrow C_6H_5Cl + CO + Pd \qquad (2)$$

We have found that a variety of metal aryls react with Pd(II) under a CO atmosphere to give palladium metal and acid chlorides. Thus, phenyl mercuric chloride reacts with palladium(II) chloride in CH_3CN under atmospheric CO pressure at 25°C. to give benzoyl chloride.

$$C_6H_5HgCl + PdCl_2 + CO \xrightarrow{CH_3CN} C_6H_5COCl + Pd + HCl \qquad (3)$$

This reaction probably proceeds by way of an unstable aryl palladium

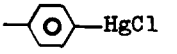
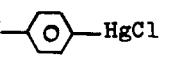
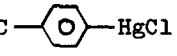
compound which inserts CO (equation 1) followed by decomposition of the aryl compound to give acid chloride (reverse of equation 2).

$$C_6H_5HgCl + PdCl_2 \rightarrow HgCl_2 + [C_6H_5PdCl] \xrightarrow{CO} [C_6H_5\overset{O}{\overset{\|}{C}}PdCl] \rightarrow C_6H_5COCl + Pd \qquad (4)$$

If alcohols are used as solvents, esters are obtained. Anhydrides are produced if $Pd(OAc)_2$ is used in nonhydroxylic solvents. A variety of metal aryls have been shown to give the reaction. The reaction can be made catalytic in Pd(II) by using $CuCl_2$ to regenerate Pd(II). Some examples are given in Table I.

TABLE I

Production of Carboxylic Acids, Acid Chlorides and Esters from Various Metal Aryls[a]

Aryl	mmoles Aryl	mmoles $PdCl_2$	mmoles $CuCl_2$	solvent (25 ml.)	mmoles product
C_6H_5HgCl	2	2	-	CH_3CN	0.2[b]
$(C_6H_5)_2Hg$	1	2	-	CH_3CN	0.42[b]
	10	10	-	CH_3OH	2.7[c]
$(\beta\text{-naphthyl})_2Hg$	10	1	20	CH_3COOH	1.2[d]
	10	1	20	CH_3COOH	3.1[d]
	10	1	20	CH_3COOH	5.6[d]
$(C_6H_5)_4Sn$	6	10	-	CH_3COOH	1.5[d]
$(C_6H_5)_4Pb$	5	5	-	CH_3COOH	1.7[d]

[a] Reactions run at 25°C. under one atmosphere CO pressure.
[b] Acid chloride.
[c] Methyl ester.
[d] Free acid.

Diaryl ketones and coupled products were produced in smaller quantities. For instance, C_6H_5HgCl gave some benzophenone and some biphenyl.

The mercury aryls can be made <u>in situ.</u> In one run, using 120 mmoles $Hg(OAC)_2$ and 1.0 mmoles $PdCl_2$ in 150 ml. of acetic acid containing 100 mmoles toluene and 2 ml. of 70% $HClO_4$, 9 mmoles toluic acid (mainly the p-isomer) were obtained after 8 hours at 150°C. under 1000 psig. CO pressure. The toluic acid could not

have come by direct insertion of CO into an aryl mercury compound (2) since this insertion does not occur under these conditions.

Alkyl metal compounds react to give aliphatic carboxylic acids. For instance, ethyl mercuric chloride gave propionic acid when reacted with $PdCl_2$ under a CO atmosphere.

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