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PALLADIUM CATALYZED DECARBONYLATION OF AROMATIC ACYL CHLORIDES

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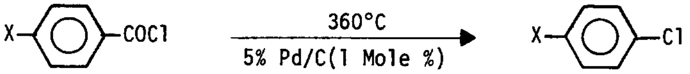
Abstract: A variety of palladium catalysts have been found to effectively promote the decarbonylation of aromatic acyl chlorides at elevated temperatures.

The decarbonylation of aromatic acid chlorides is a well known method for the regioselective introduction of chloride into an aromatic ring (eq.1).[1] Although the decarbonylation of aromatic aldehydes has been reported to be efficiently catalyzed by both rhodium and palladium based catalysts,[2] the corresponding decarbonylation of aromatic acyl chlorides has been reported to be effectively catalyzed by rhodium based catalysts such as $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ but not satisfactorily catalyzed by palladium.[3] In support of this observation, Tsuji has reported that benzoyl chloride yields only 5% chlorobenzene when treated with 5% Pd/C for 24 h at 210°C while $RhCl(CO)(PPh_3)_2$ provides an 85% yield of chlorobenzene at 200°C in 4h.[4] Subsequently, less expensive palladium based catalysts have not been thoroughly investigated as catalysts for accomplishing this transformation.



(1)

1a X = H	2a X = H (92)
1b X = Cl	2b X = Cl (98)
1c X = CN	2c X = CN (63)
1d X = MeO	2d X = MeO (28)
1e X = CH_3	2e X = CH_3 (18)
1f X = NO_2	2f X = NO_2 (7)

Scheme I

We have re-investigated the use of several palladium based catalysts in this regard and wish to report that in the temperature range from 265°-360°C a variety of aromatic acyl chlorides can be successfully and rapidly decarbonylated to the corresponding chlorinated aromatic compounds in the gas phase or in the melt in moderate to excellent yield using 5% Pd/C, $Pd(PPh_3)_4$ or $PdCl_2$ as a catalyst.

Thus, treatment of trimellitic anhydride acid chloride in the melt with 0.30 mole% of 5% Pd/C at 310°C afforded a nearly quantitative yield of 4-chlorophthalic anhydride after 2 h, while at 250°C less than 10% of this product was obtained in the same time period (Table I). Both $PdCl_2$ and $Pd(PPh_3)_4$ were also found to be effective catalysts for this reaction, although in the latter case significant quantities of phthalic anhydride were formed. The amount of phthalic anhydride observed in these reactions was markedly dependent upon the purity of the starting material, the reaction temperature and the catalyst used. No scale dependence was observed in these reactions and the decarbonylation of trimellitic anhydride acid chloride has been run on a 250 gm scale.

TABLE I

Decarbonylations of Trimellitic Anhydride Acid Chloride

Catalyst	Amount (Mol %)	Temp. °C	Time (h)	Products (%) 4-Chlorophthalic Anhydride	Phthalic Anhydride
5% Pd/C	0.30	250	2	<10	0
5% Pd/C	0.30	310	2	100	0
$PdCl_2$	10.0	290	6	99	1
$Pd(PPh_3)_4$	0.10	265	16	79	10

Aromatic acyl chlorides with boiling points below 300°C can be successfully decarbonylated in the gas phase as shown in Scheme I. Most notably, benzoyl chloride <u>1a</u> and 4-chlorobenzoyl chloride <u>1b</u> give excellent yields of chlorobenzene <u>2a</u> and p-dichlorobenzene <u>2b</u> respectively on decarbonylation in the gas phase over 5% Pd/C. The poorest results were obtained in the case of 4-nitrobenzoyl chloride <u>1f</u> which gave appreciable amounts of p-dichlorobenzene and chlorobenzene. Treatment of <u>1f</u> in the melt at 280°C with 5% Pd/C (1 mole %) afforded similar results.

Thus, it has been shown that palladium is an effective catalyst for the decarbonylation of aromatic acyl chlorides at elevated temperatures. Also, the use of palladium based catalysts in this regard provides a less expensive alternative to the conventional rhodium catalysts.

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