Palladium-promoted One-step Synthesis of Aromatic Acid Anhydrides from Aromatic Compounds with Carbon Monoxide

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The one-step synthesis of aromatic acid anhydrides from aromatic compounds such as benzene, toluene, anisole, chlorobenzene, furan, and thiophen has been carried out using carbon monoxide, 1,2-dibromoethane, and palladium acetate.

In a previous paper we described the one-step carboxylation of aromatic compounds with carbon monoxide using palladium acetate to give aromatic acids.[1] This reaction is useful for the direct synthesis of a variety of aromatic acids. In related studies we have employed 1,2-dibromoethane as an additive in the reaction of benzene with carbon monoxide using palladium acetate, and found that benzoic acid anhydride was formed instead of benzoic acid.

We report here the one-step synthesis of aromatic acid anhydrides from carbon monoxide and aromatic compounds such as benzene, toluene, anisole, chlorobenzene, naphthalene, furan, and thiophen using palladium acetate and an excess of 1,2-dibromoethane. In a standard procedure the reaction was carried out using the aromatic compound (20 ml), 1,2-dibromoethane [6.7 mol. equiv. of $Pd(OAc)_2$], and carbon monoxide (15 atm) with $Pd(OAc)_2$ (1.5 mmol) at 100 °C with stirring for 20 h in an autoclave. The sole formation of acid anhydrides and the absence of acids in the reaction mixture

$$\mathrm{ArH} \xrightarrow{\text{i}} \mathrm{ArCO.O.COAr}$$

i, $BrCH_2CH_2Br$, $Pd(OAc)_2$, 15 atm CO, 20 h, 100 °C

Table 1. Palladium-promoted synthesis of acid anhydrides from aromatic compounds and carbon monoxide.

Aromatic compound	Acid anhydride yield, %[a]
Benzene	32
Anisole	66[b]
Toluene	36[c]
Chlorobenzene	33[d]
Furan	58[e]
Thiophen	35[f]
Naphthalene	33[g]

[a] Isolated yields based on $Pd(OAc)_2$. [b] Mixture of *o*-, *m*-, and *p*-substituted mixed anhydrides. After $NaHCO_3$ hydrolysis and subsequent treatment with HCl, *p*-, *m*-, and *o*-methoxybenzoic acids were obtained in 53, 6, and 7% yields respectively. [c] Mixture of *o*-, *m*-, and *p*-substituted mixed anhydrides. After hydrolysis *p*-, *m*-, and *o*-methylbenzoic acids were obtained in 16, 9, and 11% yields, respectively. [d] Mixture of *o*-, *m*-, and *p*-substituted mixed anhydrides. Hydrolysis gave *p*-chloro-, *m*-chloro-, and *o*-chlorobenzoic acids in 15, 8, and 10% yields, respectively. [e] A 25% yield of β-furan carboxylic acid was also obtained. [f] A 42% yield of β-thiophen carboxylic acid was also obtained. [g] Mixture of mixed anhydrides of α- and β-naphthoic acids. Hydrolysis gave 23% yield of α-naphthoic acid and 10% yield of its β-isomer.

were confirmed both by n.m.r. spectral analysis and by transformation of the anhydrides into anilide derivatives.† The results are summarized in Table 1 and show that not only benzenoid but also non-benzenoid aromatic compounds such as furan and thiophen give rise to the corresponding carboxylic acid anhydrides. From the reactions with substituted benzenes, mixed anhydrides of *o*-, *m*-, and *p*-substituted benzoic acids are obtained. Both furan and thiophen undergo carbonylation at the β-position regioselectively to give β-furan (58%) and β-thiophen (35%) carboxylic acid anhydrides, respectively, in addition to β-furan and β-thiophen carboxylic acids, which may be formed from hydrolysis of the corresponding (unstable) acid anhydrides. 1,2-Dichloroethane could replace dibromoethane in the reaction. Substitution of other alkyl halides such as $CHBr_2CHBr_2$, CCl_3CCl_3, and CH_3CH_2I resulted in lower yields. The role of the dibromide in the formation of the anhydrides is not yet clear; one possibility is that Pd^0, which is formed in the carboxylic acid formation,[1] undergoes oxidative addition of the dibromide to give an active species like $Br{-}CH_2CH_2{-}Pd{-}Br$, which would react with benzene affording PhCOBr, which further reacts with $PhCO_2H$ to give $(PhCO)_2O$ plus HBr.

The present reaction may be generally useful for the synthesis of aromatic acid anhydrides from aromatic compounds with carbon monoxide.

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References

1 Y. Fujiwara, T. Kawauchi, and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1980, 220.

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† In the case of furan and thiophen, the corresponding β-carboxylic acids were also formed; these may be derived from hydrolysis of the unstable acid anhydrides.