Journal of Organometallic Chemistry, 256 (1983) C35—C36
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PALLADIUM-CATALYZED ONE-STEP SYNTHESIS OF AROMATIC ACIDS FROM AROMATIC COMPOUNDS WITH CARBON MONOXIDE

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(Received June 28th, 1983)

Summary

One-step carboxylation of aromatic compounds such as benzene, anisole, and naphthalene with carbon monoxide giving the corresponding aromatic acids, has been found to proceed catalytically using the $Pd(OAc)_2$/t-BuOOH/CH_2=$CHCH_2Cl$ system.

Recently, we have shown that carbon monoxide reacts with aromatic compounds in the presence of palladium(II) acetate, to give aromatic acids in one step [1,2]. These reactions, however, are not catalyzed by palladium(II). In the hope that palladium would be made to catalyze the reaction, we investigated the reaction conditions using a variety of reoxidizing agents for palladium(0). We now report the palladium-catalyzed one-step synthesis of aromatic acids from aromatic compounds with carbon monoxide by the palladium acetate/t-butyl hydroperoxide/allyl chloride system.

$$ArH \xrightarrow{i} ArCOOH$$

i, $Pd(OAc)_2$, t-BuOOH, CH_2=$CHCH_2Cl$, AcOH, 1 atm CO, 24-72 h, 75°C

In a standard procedure the reaction was carried out using the aromatic compound (12 ml), t-BuOOH (350—500 mol equiv. towards $Pd(OAc)_2$), acetic acid (3 ml), allyl chloride (0.5—10 mol equiv. towards $Pd(OAc)_2$), and carbon monoxide (1 atm) with $Pd(OAc)_2$ (usually 0.1 mmol) at 75°C with stirring for 24—72 h. The reaction of benzene with carbon monoxide gives benzoic acid together with phenol and biphenyl. Since it was made clear that t-BuOOH plus allyl chloride affected the reaction, the addition procedure of t-BuOOH and allyl chloride was studied and it was found that the

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addition of t-BuOOH together with allyl chloride in 2 h intervals gives the best yield*. For example, upon addition of t-BuOOH and allyl chloride with 2 h intervals, benzoic acid is formed in ca. 1200—1300% yield along with biphenyl [3] (ca. 1500%) and phenol** (ca. 200% based on palladium). t-BuOOH reoxidizes the palladium(0) formed in the reaction [1], to palladium(II) which again is active in the reaction process***. The role of allyl chloride may be that it acts as an oxidizing agent by oxidative addition to palladium(0) to form an active divalent palladium(II) species $CH_2{=}CHCH_2{-}Pd^{II}{-}Cl$, since in the absence of allyl chloride the yield is much lower. From the reaction with anisole under similar conditions, *o*-, *m*-, and *p*-anisic acids are obtained in 126, 8, and 123% yields, respectively, together with phenol (ca. 1000%) and a small amount of an unidentified product. Similarly the reaction with naphthalene gives α- and β-naphthoic acids in 105 and 30% yields, respectively. The use of other oxidizing agents such as H_2O_2, *m*-ClC_6H_4COOOH, *p*-benzoquinone, $CuCl_2$, $Cu(OAc)_2$, $Pb(OAc)_4$, $FeCl_3$, and $K_2S_2O_8$ resulted in lower yields.

The present reaction is useful for the direct synthesis of aromatic acids from aromatic compounds with carbon monoxide.

References

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*Control experiments revealed that the concentration of t-BuOOH could be kept about 40% during the reaction by this method.

**Phenol would be formed from t-BuOOH and $Pd(OAc)_2$ via a t-BuO—Pd—OH type intermediate since in the absence of $Pd(OAc)_2$ no phenol is formed.

***Interestingly, the $Pd(OAc)_2$/t-BuOOH system itself without CO causes carboxylation of benzene to give benzoic acid in 39% yield along with biphenyl (227%) and phenol (37%), a COOH group being derived from t-BuOOH or AcOH. Details will be reported elsewhere.