

Preliminary communication

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

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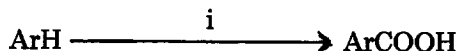
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Summary

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 $\text{Pd}(\text{OAc})_2/\text{t-BuOOH}/\text{CH}_2=\text{CHCH}_2\text{Cl}$ 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.



i, $\text{Pd}(\text{OAc})_2$, t-BuOOH, $\text{CH}_2=\text{CHCH}_2\text{Cl}$, 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 $\text{Pd}(\text{OAc})_2$), acetic acid (3 ml), allyl chloride (0.5–10 mol equiv. towards $\text{Pd}(\text{OAc})_2$), and carbon monoxide (1 atm) with $\text{Pd}(\text{OAc})_2$ (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

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 $\text{CH}_2=\text{CHCH}_2-\text{Pd}^{\text{II}}-\text{Cl}$, 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*- $\text{ClC}_6\text{H}_4\text{COOOH}$, *p*-benzoquinone, CuCl_2 , $\text{Cu}(\text{OAc})_2$, $\text{Pb}(\text{OAc})_4$, FeCl_3 , and $\text{K}_2\text{S}_2\text{O}_8$ 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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- 2 Y. Fujiwara, I. Kawata, T. Kawauchi, and H. Taniguchi, *J. Chem. Soc. Chem. Commun.*, (1982) 132.
- 3 Y. Fujiwara, I. Moritani, K. Ikegami, R. Tanaka, and S. Teranishi, *Bull. Chem. Soc. Japan*, 43 (1970) 863.

*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 $\text{Pd}(\text{OAc})_2$ via a *t*-BuO—Pd—OH type intermediate since in the absence of $\text{Pd}(\text{OAc})_2$ no phenol is formed.

***Interestingly, the $\text{Pd}(\text{OAc})_2$ /*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.