

### Preliminary communication

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

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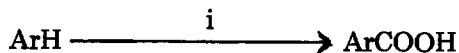
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### Summary

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 Pd(OAc)<sub>2</sub>/t-BuOOH/CH<sub>2</sub>=CHCH<sub>2</sub>Cl system.

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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, Pd(OAc)<sub>2</sub>, t-BuOOH, CH<sub>2</sub>=CHCH<sub>2</sub>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 Pd(OAc)<sub>2</sub>), acetic acid (3 ml), allyl chloride (0.5–10 mol equiv. towards Pd(OAc)<sub>2</sub>), and carbon monoxide (1 atm) with Pd(OAc)<sub>2</sub> (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  $\alpha$ - and  $\beta$ -naphthoic acids in 105 and 30% yields, respectively. The use of other oxidizing agents such as  $\text{H}_2\text{O}_2$ , *m*- $\text{ClC}_6\text{H}_4\text{COOOH}$ , *p*-benzoquinone,  $\text{CuCl}_2$ ,  $\text{Cu}(\text{OAc})_2$ ,  $\text{Pb}(\text{OAc})_4$ ,  $\text{FeCl}_3$ , 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

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

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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  $\text{Pd}(\text{OAc})_2$  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.