

### Benzylic Acyloxylation of Alkyl Aromatics Using Mixed Palladium Zinc Acetate Catalyst

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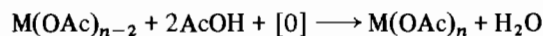
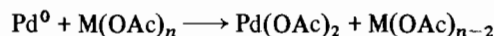
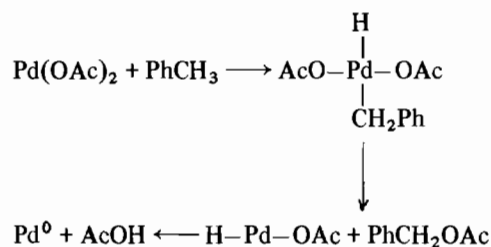
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Production of alcohols by the partial oxidation of alkyl aromatics is economically a very attractive process. However, the direct oxidation results in low yields of alcohols with considerable amounts of undesirable side products (especially CO and CO<sub>2</sub> along with aldehydes and carboxylic acids), due to the higher reactivity of the alcohols toward oxygen than hydrocarbons [1]. Instead of the direct conversion of an alkyl aromatic to the corresponding alcohol, a relatively more stable intermediate compound (such as benzylic carboxylate) is first produced which can be easily converted into alcohol by hydrolysis. We have been involved in the development of a liquid phase catalytic air oxidation process for the conversion of toluene and other alkyl aromatics to the corresponding benzylic alcohols via benzylic carboxylate using homogeneous palladium catalysts. Literature reveals that palladium(II) acetate catalyzed liquid phase oxidation reaction of toluene in acetic acid medium can proceed in different ways including (a) benzylic acetoxylation to give benzyl acetate [2], (b) nuclear acetoxylation to give methyl phenylacetate [3], and (c) coupling to give dimethyl biphenyls [4].

In the course of the development studies, we have found that the palladium(II) acetate catalyzed acyloxylation of alkyl aromatics can significantly be affected by various factors including (a) use of a suitable co-metal acetate salt in conjunction with Pd(OAc)<sub>2</sub>, (b) temperature of the reaction, (c) rate of water removal from the reaction mixture, and (d) availability of oxygen. It has been noticed that the reactions carried out in the temperature range of 160–180 °C function most effectively, and an efficient removal of the water produced in the reaction results in faster reaction rates, giving selectively the benzylic acyloxylation product. It has now been found that the use of zinc acetate in conjunction with Pd(OAc)<sub>2</sub> in the benzylic acyloxylation of toluene in higher boiling carboxylic acid medium (e.g. octanoic, lauric or dodecanedioic acid) at ~170 °C under continuous oxygen stream and azeotropic water removal with toluene, results in an improved catalytic production of benzyl carboxylate compared to that of Pd(OAc)<sub>2</sub> alone.

Thus, when a catalyst system comprising of 12 mmols of Pd(OAc)<sub>2</sub> and 12 mmols of Zn(OAc)<sub>2</sub> was used in the benzylic acyloxylation of toluene [(225 mmols) in lauric acid (552 mmols) at 165–170 °C under continuous oxygen stream (~50 ml/min)], and water produced in the reaction was removed azeotropically with toluene using a Dean Stark type collector, conversion of ~65% of the toluene was noticed in a five-hour reaction period. This yielded 134 mmols of benzyl laurate, along with benzaldehyde (~2 mmols) and benzoic acid (~4 mmols). Results of benzylic acyloxylation of toluene and other alkyl aromatics in various high boiling mono and dicarboxylic acids are given in Table I. The role of a co-metal (usually a redox metal) in the palladium catalyzed oxidation processes of organic substrates has most commonly been considered to be that of an agent to reoxidize the reduced palladium produced in the course of reaction [5] and to regenerate the Pd(OAc)<sub>2</sub> by undergoing a Wacker-type redox cycle as shown in Scheme 1.



Scheme 1.

Since the co-metal (zinc) used in the present studies is not a redox metal, its role cannot be to reoxidize the reduced palladium. Instead, the soluble palladium is probably maintained by forming a bimetallic complex of type shown (eqns. (1), (2)) which is useful in (a) making palladium more electrophilic, thus providing better interaction of toluene or other organic substrates and (b) stabilization of the intermediate palladium hydride complex.

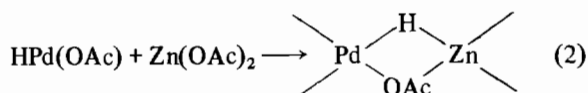
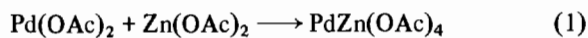


TABLE I. Pd/Zn Catalyzed Benzylic Acyloxylation of Alkyl Aromatics in Carboxylic Acid Medium<sup>a</sup>

Catalyst Pd(OAc) <sub>2</sub> /Zn(OAc) <sub>2</sub>		Carboxylic acid	Substrate	Products (mmol)
(12)	(12)	L.A. (552)	toluene (235)	B.L. (141); Bld. (2); B.A. (4)
(6)	(6)	(550)	(226)	B.L. (118); Bld. (1); B.A. (3)
(6)	(6)	O.A. (700)	(232)	B.O. (116); Bld. (2); B.A. (4)
(6)	(6)	DDA (552)	(217)	MBDD (99); DBDD (8); B.A. (4)
(6)	(6)	L.A. (544)	<i>o</i> -xylene (196)	OMBL (42); OXDL (5); B.A. (4)
(6)	(6)	(545)	<i>m</i> -xylene (216)	MMBL (85); MXDL (14); B.A. (3)
(6)	(6)	(540)	<i>p</i> -xylene (210)	PMBL (73); PXDL (10); B.A. (4)
(6)	(6)	(545)	<i>p</i> -methyl anisole (205)	PMBL (112); B.A. (4)

<sup>a</sup>Reactions were carried out at  $165 \pm 5$  °C under oxygen atmosphere (30–50 ml/min). Products were analyzed by GLC after silylation of the reaction mixture with BSTFA (internal standard method). L.A. = lauric acid; O.A. = octanoic acid; DDA = dodecane dioic acid; B.L. = benzyl laurate; Bld. = benzaldehyde; B.A. = benzoic acid; B.O. = benzyloctanoate; MBDD = mono-benzyl dodecanedioate; DBDD = dibenzyl dodecanedioate; OMBL = *o*-methylbenzyl laurate; OXDL = *o*-xylene  $\alpha, \alpha'$ -dilaurate; MMBL = *m*-methylbenzyl laurate; MXDL = *m*-xylene  $\alpha, \alpha'$ -dilaurate; PMBL = *p*-methylbenzyl laurate; PXDL = *p*-xylene  $\alpha, \alpha'$ -dilaurate.

Formation of such mixed metal complexes of palladium, for instance, palladium thallium acetate complex [6] and hydrido-acetate bridged palladium/copper complex [7] has been proposed in the literature in some other oxidation processes. This postulated role of the co-metal as a complexing agent rather than in a redox cycle can be supported by the fact that the use of a non-redox metal salt, such as potassium acetate with Pd(OAc)<sub>2</sub> results in the formation of K<sub>2</sub>Pd(OAc)<sub>4</sub> with a significant improvement in the catalytic activity of palladium [8].

Evidence for the existence of a similar mixed palladium zinc acetate complex, PdZn(OAc)<sub>4</sub> (I), was observed in UV-Vis studies on the solutions of the reaction of Pd(OAc)<sub>2</sub> and Zn(OAc)<sub>2</sub> in acetic acid which showed the formation of a new absorption band at 335 nm with the disappearance of the band at 400 nm, characteristic of Pd(OAc)<sub>2</sub>. The intensity of this new band at 335 nm was found to be maximum at the point when an equimolar amount of Zn(OAc)<sub>2</sub> was allowed to react with Pd(OAc)<sub>2</sub>. Attempts are being made to isolate this mixed complex in a single crystal form to determine its structure by X-ray crystallographically.

In short, the mixed palladium zinc acetate catalyst system has been found to be quite efficient for the selective benzylic acyloxylation process.

#### References

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