

SUBSTITUENT EFFECTS IN BENZYLIC OXIDATION BY PALLADIUM(II) ACETATE

C. Hackett Bushweller*
Mobil Chemical Company
Edison, New Jersey, U.S.A. 08817

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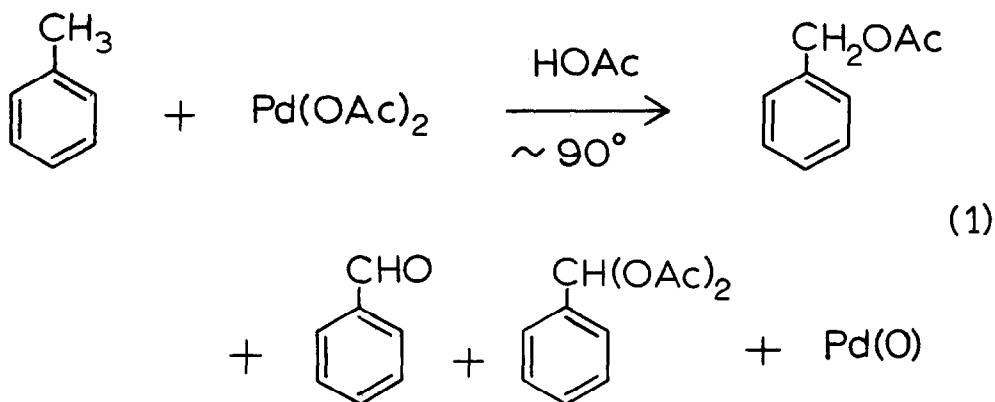
A variety of reagents are effective in oxidizing the benzylic position of alkylaromatic compounds (1). Depending upon the oxidizing agent, substrate, and solvent, the isolated products may be carboxylic acids, aldehydes, alcohols, or esters. Relatively few reagents are available which can effect a direct, highly selective oxidation of a methylaromatic substrate to an aldehyde, alcohol, or ester (2,3,4,5).

In a number of the cases studied to date, a pronounced substituent effect has been observed. Electron-donating substituents generally increase the reactivity of the benzylic position toward oxidation. Such an effect has been observed in oxidations by permanganate (1), chromium(VI) (2,6), cerium(IV) (3), and lead(IV) (4). Although such data suggest the intermediacy of cationic species, there is much evidence that the reactions may have some radical character. Manganese(VII) catalyzes the autoxidation of benzylic positions (7) as well as induces coupling reactions between benzylic sites (1). The oxidation of ethylbenzene and tetralin by lead tetraacetate is accelerated by benzoyl peroxide, but no coupling products, i.e., dibenzyls, have been observed in the absence of peroxide (8).

* Present address: Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts, U.S.A. 01609.

Little work has appeared concerning the reaction of palladium acetate with alkylaromatic substrates (9). This report concerns the reaction of palladium acetate in acetic acid with a variety of ring-substituted toluenes. The reaction exhibits the generally observed sensitivity to electronic effects with electron-donating groups effecting excellent yields of the corresponding benzyl acetates.

In a representative reaction, toluene (5.0 g, 0.054 mole) and palladium acetate (12.1 g, 0.054 mole) in 100 ml of glacial acetic acid were heated at 90° for 13 hours after which time Pd(0) had precipitated essentially quantitatively. Upon work-up, benzyl acetate (6.5 g, 80%), benzaldehyde (0.2 g, 4%), and benzylidene diacetate (0.7 g, 6%) were isolated by preparative glpc (equation 1). The benzaldehyde results presumably from the hydrolysis of benzylidene diacetate by a small amount of water in the acetic acid solvent. Some evidence for this



hypothesis was obtained by reacting toluene with two molar equivalents of palladium acetate in 7% aqueous acetic acid to give a substantial increase in the yield of benzaldehyde (28%) and no detectable benzylidene diacetate.

The dramatic effect of electron-donating substituents is illustrated in the reaction of p-methoxytoluene to give a 96% yield of p-methoxybenzyl acetate (equation 2). p-Nitrotoluene gave a 2% yield of p-nitrobenzaldehyde and p-nitrobenzyl acetate. The results obtained for a number of other substrates are compiled in Table I.

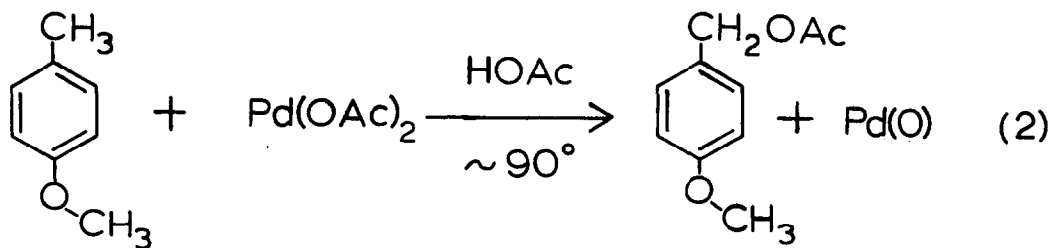


TABLE I

Products and Yields from the Reaction of Various
Methylaromatics with $\text{Pd}(\text{OAc})_2$ in Glacial Acetic Acid^a

<u>Substrate</u>	<u>Product(s)</u>	<u>% Yield</u>
toluene	benzyl acetate	81
	benzaldehyde	4
	benzylidene diacetate	6
toluene ^b	benzaldehyde	28
	benzyl acetate	32
p-methoxytoluene	p-methoxybenzyl acetate	96
o-methoxytoluene	o-methoxybenzyl acetate	85
p-chlorotoluene	p-chlorobenzyl acetate	25
p-nitrotoluene	p-nitrobenzaldehyde	1
	p-nitrobenzyl acetate	1
o-xylene ^c	o-methylbenzyl acetate	45
	o-xylyleneglycol diacetate	21
	benzyl acetate	4
	toluene	4
p-xylene ^c	p-methylbenzyl acetate	38
	p-xylyleneglycol diacetate	16
	benzyl acetate	5
	toluene	6
β -picoline	no reaction	

(a) Reaction conducted using equimolar quantities of substrate and palladium acetate for 12-13 hours at 90°. (b) Reaction conducted using two molar equivalents of palladium acetate in 7% aqueous acetic acid. (c) Reaction conducted using two molar equivalents of palladium acetate in glacial acetic acid.

The substantial amounts of toluene and benzyl acetate observed in the oxidation of o- and p-xylene (Table I) suggest the possibility of a decarbonylation catalyzed by palladium (10).

The pronounced substituent effects for the reactions reported here are intriguing and are being investigated from a mechanistic as well as synthetic approach.

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