

Palladium(II) Catalyzed Aromatic Acetoxylation

I. Factors Influencing the Nuclear Acetoxylation of *p*-Xylene

LENNARTEBERSON* and LUIS GOMEZ-GONZALEZ

*Division of Organic Chemistry 1, Chemical Center,
University of Lund, P.O. Box 740, S-220 07 Lund, Sweden*

The reaction between Pd(II) acetate and *p*-xylene in acetic acid has been studied with the intention of developing an efficient process for preparing the nuclear acetoxylation product, 2,5-dimethylphenyl acetate. This compound can actually be obtained as the main product when *p*-xylene is treated with Pd(II) acetate in refluxing acetic acid in the presence of oxygen; the reaction is catalytic in Pd(II) but is unfortunately too slow for practical use. Addition of alkali metal acetates, *e.g.* sodium acetate, favors the formation of the α acetoxylation product, *p*-methylbenzyl acetate, at the expense of the nuclear acetate. The nature of the alkali metal cation strongly affects the rate of formation of *p*-methylbenzyl acetate. This is probably due to the intervention of binuclear complexes between Pd(II) acetate and the alkali metal acetate as the oxidizing species (as supported by kinetic studies).

Palladium compounds play an important role in organic synthesis,¹⁻³ especially in connection with the chemistry of olefinic compounds. The Wacker process, air oxidation of ethylene in the presence of catalytic amounts of palladium(II) chloride, is a prominent example of such reactions on an industrial scale, whereas Heck's work³ beautifully demonstrates the synthetic applications in the laboratory.

Aromatics can also function as substrates for oxidation by Pd(II) complexes. The most important reaction types hitherto observed are coupling to form biaryls⁴⁻¹² or sometimes diphenylmethane derivatives,⁸ and oxidative substitution by nucleophiles — in most cases acetate ion — in the aromatic nucleus or in the α position of the side-chain of alkylaromatics.^{5,6,8,10,13-16} These reactions are normally effected by stoichiometric amounts of the Pd(II) salt (most often added as the acetate, but sometimes as the chloride,⁴ nitrate¹⁰ or chloride-olefin complex¹¹), but can also be made catalytic in Pd(II) by adding reagents that favor reoxidation of Pd(0) to Pd(II).^{12,14} The

* To whom inquiries should be addressed.

solvent employed is in most cases acetic acid, but it was recently found advantageous in the biaryl coupling reaction to avoid this solvent.¹² The use of acetic acid as solvent also means that the most commonly encountered oxidative substitution process – if observed at all – is acetoxylation, *i.e.* formation of aryl or benzyl acetates. Other oxidative substitutions become possible in acetic acid, however, if other nucleophiles are added.¹⁶

It is at present difficult to make a consistent summary of the influence of experimental conditions on the occurrence of each of these reactions, mainly due to the fact that knowledge about the nature of the oxidizing species is very limited. It is, however, rather well established that biaryl coupling is favored by the addition of perchloric acid,^{5,7,10} by the presence of ligands, *e.g.* chloride ion, that favor formation of binuclear complexes,^{4,11} and by the presence of water,¹⁰ silver nitrate,¹¹ or iron(III).¹¹ Acetoxylation seems to be favored by the presence of acetate ion in large excess over Pd(II),^{5,6,10,14} the use of Pd(NO₃)₂ as a source of Pd(II),¹⁰ and the addition of a co-oxidant such as dichromate ion.¹⁶ Nuclear acetoxylation, but not biaryl coupling¹² or α acetoxylation,^{13,14} is almost suppressed if the reaction is conducted under oxygen pressure.^{6,8}

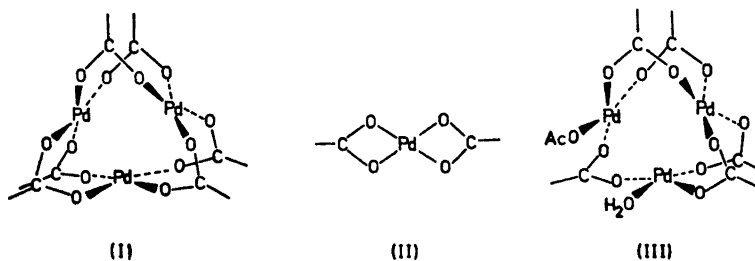
In connection with earlier studies on anodic^{17,20} and Mn(III) acetate¹⁸ acetoxylation processes, we became interested in the possibility of effecting *nuclear* acetoxylation of aromatic substrates *via* a Pd(II) catalyzed reaction. This paper is a report²¹ of an investigation of the Pd(II) mediated acetoxylation of *p*-xylene, considered to be a suitable substrate because of its known tendency¹⁰ to undergo both α and nuclear substitution (in the reported¹⁰ ratio of about 1 : 3). Hence this compound represents a challenge for increasing the relative yield of nuclear acetate. Moreover, only one isomer each of α and nuclear monosubstitution product is possible from *p*-xylene, which simplifies the analytical work. Finally, *p*-xylene undergoes biaryl coupling with difficulty even under the most favorable conditions,¹² presumably for steric reasons,^{4,12} so that this side-reaction would hopefully interfere only to a small extent.

RESULTS

Structure of palladium(II) acetate in solution. In order to be able to discuss the reaction mechanism of aromatic acetoxylation *via* Pd(II) acetate, it is necessary to know something about the structure and composition of the Pd(II) complex present under the actual reaction conditions (acetic acid as solvent, in many cases with acetate ion added). In the solid, the structure of Pd(II) acetate has been shown to be a trimeric cluster²³ of the type I. It is trimeric in benzene at 37° but breaks up²³ to the monomer (II) at 80°.

We now postulate that Pd(II) acetate exists as the trimer (I) also in glacial acetic acid at or slightly above room temperature. Support for this assumption stems from the fact that the NMR spectrum of Pd(II) acetate in CDCl₃ displays a singlet at $\delta = 2.22$ ppm, and in CD₃COOD a singlet at $\delta = 2.07$ ppm. If a small amount of water is added, the CDCl₃ spectrum consists of four signals²⁴ with intensities in the ratio 1 : 2 : 2 : 1. A probable structure for this species is III, formed by breaking one Pd-acetate bond in I by a water molecule.

This shows that Pd(II) acetate exists as a trimer also in the absence of water. The similarity between the NMR spectrum of Pd(II) acetate in CDCl_3 and in CD_3COOD , respectively, suggests that also in the latter solvent a trimer exists at room temperature, presumably with structure (I) which would give a one-singlet NMR spectrum.



Further support was obtained by investigating the effect of adding NaOAc to Pd(II) acetate in acetic acid. It is known that oligomeric or polymeric acetates, *e.g.* the Co(III) acetate trimer²⁵ and Cu(II) acetate dimer,²⁶ break down to monomeric species upon the addition of sodium acetate. Acetates of bivalent metals, such as barium and calcium acetate, react with Pd(II) acetate in acetic acid with the formation of binuclear, isolable, Pd-metal-acetate complexes²⁷ of the general formula $\text{MPd}(\text{OAc})_4 \cdot n\text{HOAc}$. For univalent metal acetates, such as KOAc, it was claimed that virtually no reaction was observed.

We now have studied the reaction between Pd(II) acetate and acetates of mono- and divalent metals by UV spectrophotometry and found that all systems behave in an essentially identical manner: A fast decrease in the intensity of the original maximum due to Pd(II) acetate at 397 nm and a shift of the maximum toward shorter wave-lengths with the formation of a new maximum of higher intensity around 360 nm, with two isosbestic points (Table 1). After the fast reaction has subsided, the new maximum grows slowly in

Table 1. Changes in the UV spectrum of Pd(II) acetate in acetic acid observed upon addition of different alkali metal salts.

Salt present ^a	Position of isosbestic points, nm		Position of new ^b λ_{max} , nm
	1	2	
LiOAc	381	322	364
KOAc	397	322	368
NaOAc	403	322	368
RbOAc	393	325	
CsOAc	397	324	
$\text{Ca}(\text{OAc})_2$	397	322	352
$\text{Ba}(\text{OAc})_2$	388	316	356

^a Added as carbonates, except for the K, Na, and Ba salt.

^b Position of λ_{max} for Pd(II) acetate = 389 nm.

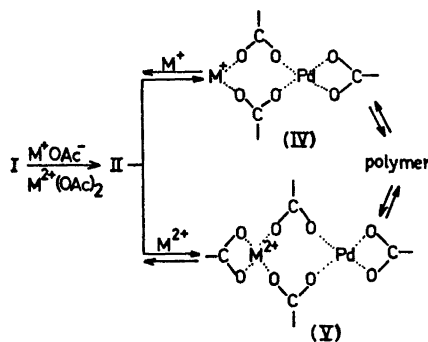
intensity with no isosbestic point, probably due to polymerization of the new complex. The kinetics of two of these reactions (with sodium and barium acetate) were also measured at several temperatures (Table 2) and found to be first order in both Pd(II) acetate and added metal acetate. From these results

Table 2. Rate constants and activation energies ^a for the reaction between Pd(II) acetate and Ba(OAc)₂ or NaOAc.

Temperature, °C	Metal	[Metal acetate] ₀ , M	<i>k</i> , m ⁻¹	<i>k'</i> , m ⁻¹ M ⁻¹
20.1	Ba	0.0521	0.0151	0.290
20.1	Ba	0.1042	0.0324	0.311
20.1	Ba	0.1563	0.0524	0.336
25.7	Ba	0.2084	0.1010	0.484
30.9	Ba	0.2084	0.1320	0.633
35.6	Ba	0.2084	0.1580	0.758
35.6	Ba	0.1563	0.1210	0.774
35.6	Ba	0.1042	0.0798	0.766
35.6	Ba	0.0521	0.0361	0.693
20.1	Na	0.1102	0.0117	0.106
20.1	Na	0.2204	0.0246	0.112
25.7	Na	0.2204	0.0338	0.153
30.9	Na	0.2204	0.0422	0.192
35.6	Na	0.2204	0.0610	0.277
44.7	Na	0.2204	0.10	0.45
60.9	Na	0.2204	0.24	1.1

^a Ba salt, *E*_a = 12.3 kcal/mol; Na salt, *E*_a = 11.3 kcal/mol.

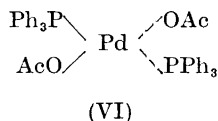
and the derived activation parameters it is obvious that the sodium acetate reaction is of the same type as that taking place with barium acetate. We formulate the processes occurring in these systems at or slightly above room temperature as shown in Scheme 1. The reaction is assumed to be reversible, which would account for the fact that the binuclear complex cannot be isolated in cases of unfavorable solubility relationships.²⁷



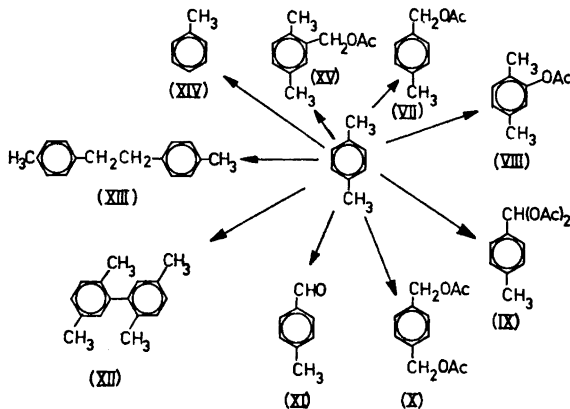
Scheme 1.

As shown in Table 2, the reaction between sodium acetate and Pd(II) acetate is fast even at fairly low temperatures. Around 100°, where most reactions to be described in this paper have been performed, the Pd(II) species prevailing in the presence of sodium acetate should therefore be IV, and II in the absence of sodium acetate. The trimer is not stable above 35° in glacial acetic acid.²⁴

In certain reactions triphenylphosphine was present, and then a complex of structure VI is formed.²³



Palladium(II) acetate oxidation of p-xylene in acetic acid with added acetate ion. At this stage of the investigation, we were mainly interested in determining the dependence of the product distribution upon certain experimental factors, such as solvent, atmosphere, additives, *etc.*, always with the goal in view of maximizing the yield of the nuclear acetoxylation product, 2,4-dimethylphenyl acetate (VIII). Hence the results to be described below have been obtained from runs on the semi-micro or micro scale, using a large excess of *p*-xylene over Pd(II) acetate and analyzing at fairly low conversions in order to avoid further oxidation of primary products as much as possible.



Scheme 2.

The complexity of the problem at hand is amply demonstrated by Scheme 2 which shows the considerable number of products that may be formed — very rarely alone — in the Pd(II) acetate oxidation of *p*-xylene.

Among these products, the acetates VII, VIII, and X, all three together or in pairs, are almost always predominant, and the other compounds either appear in minor amounts (< 5 %) or can be made major components of the

product mixtures only under rather special conditions. We shall here first describe how experimental conditions affect the product distribution in the experiments where acetate products are predominant, and then briefly comment on the side-products. It is only fair to state from the beginning that in very few experiments is it possible to obtain high selectivity in the formation of any single product.

Fig. 1 shows the rate at which VII and VIII form in an argon atmosphere as a function of the $[\text{NaOAc}]/[\text{Pd(II)}]$ ratio (in the following to be abbreviated

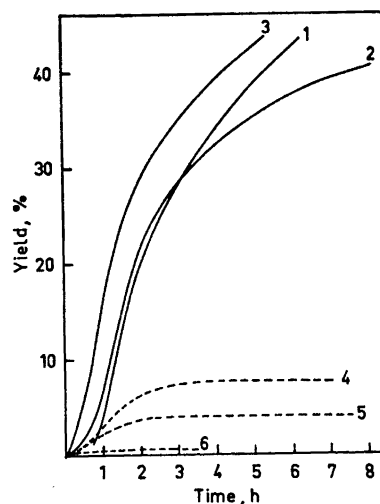


Fig. 1. Yield of VII (solid lines) and of VIII (broken lines) vs. time in the oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 111°C (Ar atmosphere). $[\text{p-Xylene}]/[\text{Pd(II)}] \approx 50$; $[\text{NaOAc}]/[\text{Pd(II)}]$: curves 1 and 4, 0; 2 and 5, 2.1; 3 and 6, 27.7. At the highest ratio, 57, no VIII was detectable.

Na/Pd). The yields given are absolute ones. At a low Na/Pd ratio there is an induction period for the formation of VII, which is diminished at higher ratios. The nuclear acetate (VIII) disappears completely at very high ratios. This behavior is more clearly demonstrated in Fig. 2, which shows the yields of VII and VIII after 20 h as a function of the Na/Pd ratio. Under argon, the yield of VII passes through a maximum at moderate Na/Pd ratios (between 10 and 20).

In an oxygen atmosphere, the over-all behavior with respect to formation of VII and VIII upon varying the Na/Pd ratio is similar, although other major products now appear. These are *p*-methylbenzaldehyde (XI) and *p*-xylylenediol

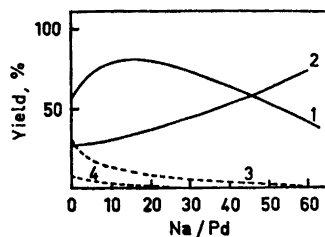


Fig. 2. Yield of VII (solid lines) and of VIII (broken lines) vs. the Na/Pd ratio in the oxidation of *p*-xylene with Pd(II) acetate in glacial acetic acid (as analyzed after 20 h). Temperature, 111°C; curves 1 and 4 in Ar atmosphere; curves 2 and 3 in O_2 atmosphere.

acetate (X). The former compound is present in all product mixtures from experiments conducted under oxygen. The induction period for the formation of VII is still apparent and perhaps even somewhat longer; it gets shorter with higher Na/Pd ratios, and the formation of VIII is strongly suppressed at a high Na/Pd ratio (see Fig. 3). The rate of formation of the aldehyde (XI)

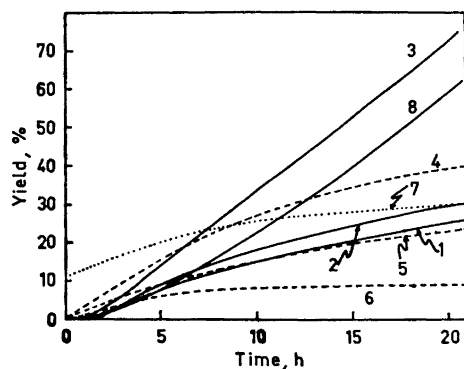


Fig. 3. Yield of VII (solid lines), VIII (broken lines), and XI (dotted lines) vs. time in the oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 111°C (O_2 atmosphere). Na/Pd: curves 1 and 4, 0; curves 2, 5, and 7, 1.9; curves 6 and 8, 13; curve 3, 61 (no VIII is formed at this ratio).

is shown for one ratio (Na/Pd = 1.9); after an initial period of fast formation, the rate is approximately constant. *p*-Xylylenediol diacetate (X) is always formed as a minor product (< 10 % under argon), but becomes a major product when both oxygen and sodium acetate are present. Fig. 4 shows the ratio between the yields of VII and X, plotted vs. time for different Na/Pd ratios. Interestingly enough (*cf.* Ref. 14), X appears in large amounts also at the beginning of the reaction in cases where it is the predominant product (see Fig. 4, curve 4), suggesting that it is formed *via* a separate reaction path directly from *p*-xylene, and not *via* further oxidation of initially formed VII.

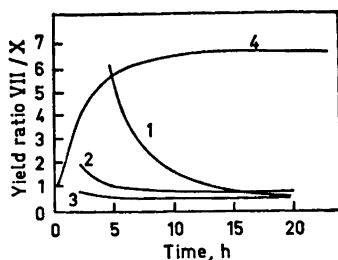
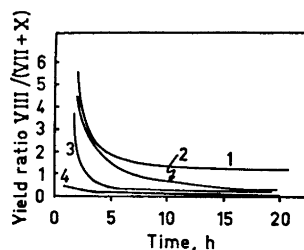


Fig. 4. Variation in the yield ratio of VII to X with time during oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 110° in oxygen (curves 1, 2, and 3) or argon atmosphere (curve 4). Na/Pd: curve 1, 1.9; curve 2, 13; curve 3, 61; curve 4, 27.

The quotient between the yields of nuclear (VIII) and side-chain (VII + X) acetates has been plotted vs. time at different Na/Pd ratios in Fig. 5. This does not only again serve to emphasize the fact that the formation of VIII is strongly suppressed at high Na/Pd ratios (*cf.* Figs. 1 and 2) but furthermore shows that VIII is the major product at very low conversions, *i.e.* before the induction period for the formation of VII and X has elapsed. The end of the induction

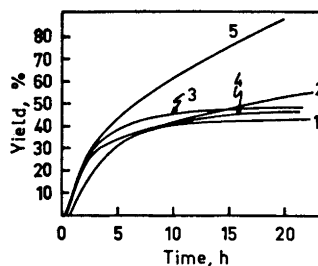
Fig. 5. Variation in the yield ratio VIII/(VII+X) with time during oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 110° in oxygen (curves 1–3) or argon atmosphere (curve 4). Na/Pd: curve 1, 0; curve 2, 1.9; curve 3, 13; curve 4, 0.



period in many cases seems to coincide with the precipitation of black Pd(0) from the solution.

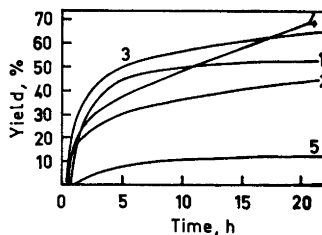
The possibility that binuclear complexes of the type IV might be the kinetically active species in the oxidation process prompted us to study the effect of adding alkali metal acetates other than sodium acetate. These experiments are represented in Figs. 6–8 in the form of yield of VII *vs.* time curves

Fig. 6. Variation in the yield of VII with time during oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 111° with different alkali metal acetates added. Curve 1, Li/Pd = 2.5; curve 2, Na/Pd = 2.1; curve 3, K/Pd = 2.2; curve 4, Rb/Pd = 2.9; curve 5, Cs/Pd = 2.0. Argon atmosphere.



for different alkali metal ions at a low (Fig. 6) and high (Fig. 7) metal/Pd ratio. All these reactions were run under argon. Fig. 8 is a more informative representation of some of the results in Figs. 6 and 7. The strong dependence of the rate of formation of VII upon the nature of the cation supports the assumption that binuclear complexes (IV) are the kinetically active species.

Fig. 7. Variation of the yield of VII with time during oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 111° with different alkali metal acetates added. Curve 1, Li/Pd = 115; curve 2, Na/Pd = 56.7; curve 3, K/Pd = 49; curve 4, Rb/Pd = 48; curve 5, Cs/Pd = 55. Argon atmosphere.



In the experiments with added alkali metal acetates other than sodium acetate, the yield of VIII was always low (about 5%) at low to moderately high metal/Pd ratios (2–20). At high such ratios, VIII is not formed at all except in the presence of Cs(I) ion where a 1% yield was obtained. The yield

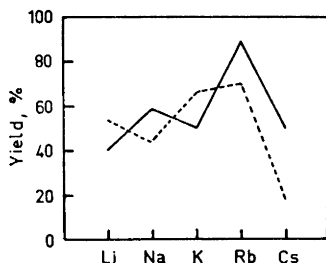


Fig. 8. Schematic representation of the variation of the yield of VII with the nature of the added ion (*cf.* Figs. 6 and 7) in the oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 111° under argon atmosphere. Solid line, metal/Pd ≈ 2; broken line, metal/Pd ≈ 50. Analyses were performed after 22 h.

of *p*-xylylenediol diacetate (X) is fairly low (3–12 %) and does not change significantly with the nature of the added cation.

Among the minor products, *p*-methylbenzylidene diacetate (IX) is of special interest as a possible precursor for the aldehyde (XI). IX is formed only in small amounts under the conditions of the experiments summarized in Figs. 1–7. It is of interest to note that IX is also formed under argon where the aldehyde is not formed. This indicates that the aldehyde is not formed *via* hydrolysis of the diacetate, as previously suggested.¹⁵ Under certain conditions [oxidation with Pd(II) acetate/Cu(II) acetate in a ratio 1 : 10 under oxygen at reflux], IX can be made the major product.

The hydrocarbons in Scheme 2, toluene (XIV) and the two dimers, 2,5,2',5'-tetramethylbiphenyl (XII) and 4,4'-dimethylbibenzyl (XIII), are formed in small amounts (<1 % each) in many experiments. Traces of acetoxylation products of toluene have also been detected. The bibenzyl (XIII) has not been observed before in this type of reactions and commands special interest, since it must be formed *via* coupling of two 4-methylbenzyl radicals. Characteristically, XIII is not formed under oxygen, since then the benzylic radical is trapped efficiently by oxygen and diverted to the aldehyde according to the usual autoxidation mechanism.²⁸ It thus appears probable that benzylic radicals are formed as intermediates in at least one reaction taking place between Pd(II) acetate and *p*-xylene.

Palladium(II) acetate oxidation of p-xylene in the presence of various additives. In order to change the nature of the oxidizing species one can in principle add either a Lewis base, which would be expected to lower the oxidation potential of the Pd(II) complex by coordination of its free electron pair with Pd(II), or a Lewis acid which would be expected to increase the oxidizing power by virtue of coordination to Pd(II) and partial electron withdrawal from the metal.

Triphenylphosphine was chosen as a representative Lewis base, since it is known that the prevalent complex will then be of the type VI. This additive causes certain complications in the analytical procedure, though, since it is oxidized itself during the reaction. This results in the formation of triphenylphosphine oxide and products from cleavage of the C–P bond, *viz.*, phenyl acetate, biphenyl, phenol, and diacetoxybenzenes. The formation of biphenyl and phenol indicates that phenyl radicals may be intermediates, an assumption that is supported by the formation of small amounts of a product of phenyl radical attack on *p*-xylene, 2,5-dimethylbiphenyl. The main products from the

Table 3. Changes in the product distribution from the oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 115° at different [triphenylphosphine]/[Pd(II)] ratios; [Pd(II) acetate] = 0.01 – 0.04 M; O₂ atmosphere.

[PPh ₃]/[Pd(II)]	[VIII]/([VII] + [X])		[VII]/[X]	
	30 min	after 4 h	30 min	after 4 h
0	∞	5.0	∞	∞
1	0.025	0.12	0.64	1.1
2	0.028	0.23	1.16	2.0
10	—	0.063	—	2.5

oxidation of *p*-xylene in the presence of triphenylphosphine in an oxygen atmosphere are XI, VII, VIII, and X. In addition, small amounts of toluene are formed together with traces of two isomers corresponding to the formula XV. Table 3 shows the main changes that take place upon addition of triphenylphosphine: α acetoxylation is favored over nuclear, and the formation of X is favored.

The addition of aluminium chloride to a solution of Pd(II) acetate, *p*-xylene, and glacial acetic acid precipitates a red solid, whose IR spectrum differs from that of Pd(II) acetate. The compound is probably a mixed complex between Pd(II) acetate and aluminium chloride. The main effects of conducting the oxidation in the presence of aluminium chloride are demonstrated in Table 4:

Table 4. Changes in the product distribution from the oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 115° at different [AlCl₃]/[Pd(II)] ratios;^a [Pd(II) acetate] about 0.02 M; O₂ atmosphere.

[AlCl ₃]/[Pd(II)]	[VIII]/[VII]	[VIII]/[XII]
0	5.0	> 10
1	0.47	0.59
2	0.55	0.62
10	0.37	1.0

^a Analyzed after a reaction period of 4 h.

α acetoxylation increases, and the yield of biaryl (XII) goes up drastically. The finding that biaryl formation is favored upon addition of a Lewis acid is analogous to the effect of adding a strong protonic acid such as perchloric acid^{5,7,10} which also strongly favors biaryl formation.

The addition of water has no particular influence on the oxidation of *p*-xylene with Pd(II) acetate in glacial acetic acid under conditions of argon atmosphere and high Na/Pd ratio (as already shown, the α acetate (VII) is the major product under these conditions). Table 5 summarizes these experiments. Neither aldehyde (XI) nor nuclear acetate (VIII) is formed.

Table 5. Yield of (VII) after oxidation of *p*-xylene with Pd(II) acetate in acetic acid ^a at different [H₂O]/[Pd(II)] ratios at 111°; Na/Pd = 54; Ar atmosphere; [Pd(II)] about 0.01 M.

[H ₂ O]/[Pd(II)]	Yield, %
0	34
1.2	32
2.5	34
63.2	35

^a Reaction period 5.5 h.

p-Methylbenzoic acid (XVI) was isolated under special conditions only: oxidation in acetic acid at reflux temperature with Pd(II) acetate in the presence of a large excess of sodium nitrite. Furthermore, trace amounts of VII and VIII (3 : 1) were detected. It should be noted that no nitro product was detectable, although these conditions have been known to favor the formation of nitro compounds in other systems.^{10,16}

Tetraalkylammonium acetates occupy a special position among the possible acetate salts, since binuclear complexes cannot form from Pd(II) and a tetraalkylammonium ion. Hence addition of, *e.g.*, tetrabutylammonium acetate (TBA) to the oxidation mixture should cause the monomer (II) to be the oxidizing species.

Table 6. Changes in the product distribution from the oxidation of *p*-xylene with Pd(II) acetate in acetic acid at 115° at different [TBA]/[Pd(II)] ratios; [Pd(II)] 0.02 M; O₂ atmosphere.

[TBA]/[Pd(II)]	[VIII]/([VII] + [X]) after		[VII]/[X] after	
	30 min	4 h	30 min	4 h
0	∞	5.0	∞	∞
1	1.8	0.13	3.0	0.77
2	2.4 ^a	0.32		0.63 ^b
10		3.1		

^a Value at the same ratio with sodium acetate = 1.4.

^b Value at the same ratio with NaOAc = 5.4.

Table 6 shows the effect of the addition of TBA in the oxidation of *p*-xylene with Pd(II) acetate at different ratios of TBA/Pd in an oxygen atmosphere. The ratio of VIII/(VII + X) goes through a minimum with a change in the TBA/Pd ratio from 1 to 10. The ratio VII/X is smaller at small TBA/Pd ratios than at small Na/Pd ratios, showing that the addition of acetate favors formation of the α, α' -diacetate (X) as long as it is not coordinated as a ligand to Pd(II).

Preparative oxidations. Some preparative runs have also been performed in order to establish the usefulness of Pd(II) acetate oxidation for nuclear aromatic acetoxylation (no excess acetate, O₂). Thus Pd(II) acetate (10 mmol) in *p*-xylene and acetic acid (100 ml) was kept at 110° with a slow stream of oxygen bubbling through for 150 h, resulting in an isolated yield of 450 % of VII + VIII in a 30 : 70 ratio. A similar result was obtained from an experiment identical to the one above except that triphenylphosphine (10 mmol) was also added. A 480 % yield of VII + VIII (ratio 46 : 56) was isolated. In both cases the solutions were still catalytically active at the discontinuation of the experiment. From these experiments it is obvious that the sluggishness of the reaction seriously hampers its preparative use. We are presently working on the problem of speeding it up to useful rates.

The discussion of the results described in this paper is deferred to Part III of this series.²⁹

EXPERIMENTAL PART

Materials. The following starting or reference chemicals were purchased in the highest quality available: *p*-Xylene (Schuchardt AG, München, Germany, 99.85 % purity), XI (Fluka AG, Buchs, Switzerland), triphenylphosphine (Merck AG, Darmstadt, Germany), and palladium(II) acetate (Engelhard, also prepared according to a literature method²³). Solvents and inorganic reagents were of analytical grade quality. The following reference compounds were synthesized according to well-known methods: VII,³⁰ VIII³¹, IX,³² X,³³ XII,³⁴ and XIII.³⁵ The identity and purity of all compounds used were checked by mass, IR, and NMR spectral analysis as well as by gas chromatography. Retention times (min) for the reference compounds (4 m × 0.3 cm 5 % neopentylglycolsuccinate on Chromosorb W, temperature programming between 120 and 210° at a rate of 2°/min, Perkin-Elmer 880 gas chromatograph equipped with a disc or electronic integrator) were: XI (15.6), VIII (20.8), VII (23.2), *m-t*-butylphenyl acetate¹⁷ (used as internal standard; 25.6), XII (33.0), IX (43.2), XIII (46.4), and X (57.2 min).

Kinetic procedure. Stock solutions of accurately known concentrations of Na, Ba, and Pd acetate in acetic acid were made up and mixed to give kinetic samples of appropriate concentrations (see Table 2). Solutions of the same concentrations in Na or Ba acetate were used in the reference cell. The kinetics were followed by recording (Unicam SP 800B UV spectrophotometer) the change in extinction at 356 nm. First-order rate constants were evaluated *via* Guggenheim plots.³⁶

Analytical oxidation experiments. The oxidation experiments were performed according to one of the following methods:

A. Solutions of Pd(II) acetate (0.02 M) and substrate (40–80 times in excess over Pd(II) acetate) in acetic acid, together with additive if applicable, were filled (2 ml) into 5 ml ampoules, through which a slow stream of either argon or oxygen was passed for 30 min at room temperature. The ampoules were sealed and kept in a thermostated bath at the appropriate temperature. Analyses were then performed after approximately 30 min, 1, 2, 4, 8, and 20 h.

B. The reaction mixture (50–100 ml) was kept in a jacketed reaction vessel which could be kept at a suitable temperature by circulating triethylene glycol from an ultrathermostat. Argon or oxygen was slowly passed through the solution *via* a glass frit inlet tube. An efficient condenser was attached to the vessel which was also provided with an opening covered by a rubber septum. Analytical samples were withdrawn by use of a hypodermic syringe.

The samples obtained either from method A or B were neutralized with saturated sodium bicarbonate solution. The organic components were extracted by ether and the extracts washed with water. After the addition of an internal standard (*m-t*-butylphenyl acetate), the product composition and yield were determined by gas chromatographic analysis (see above). In doubtful cases the combination gas chromatography/mass spectrometry (LKB 9000 system) was used for checking the identity of the components.

Preparative oxidations. See text.

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REFERENCES

1. Maitlis, P. M. *The Organic Chemistry of Palladium*, Vols. 1 and 2, Academic, New York 1971.
2. Hüttel, R. *Synthesis* **1970** 225.
3. Heck, R. F. *Fortschr. Chem. Forsch.* **16** (1970/71) 221.
4. Van Helden, R. and Verberg, G. *Rec. Trav. Chim.* **84** (1965) 1263.
5. Davidson, J. M. and Triggs, C. *Chem. Ind. (London)* **1966** 457.
6. Davidson, J. M. and Triggs, C. *Chem. Ind. (London)* **1967** 1361.
7. Davidson, J. M. and Triggs, C. *J. Chem. Soc. A* **1968** 1324.
8. Davidson, J. M. and Triggs, C. *J. Chem. Soc. A* **1968** 1331.
9. Unger, M. O. and Fouty, R. A. *J. Org. Chem.* **34** (1969) 18.
10. Ichikawa, K., Uemura, S. and Okada, T. *Nippon Kagaku Zasshi* **90** (1969) 212; Tisue, T. and Downs, W. J. *Chem. Commun.* **1969** 410.
11. Fujiwara, Y., Moritani, I., Ikegami, K., Tanaka, R. and Teranishi, S. *Bull. Chem. Soc. Japan* **43** (1970) 863.
12. Itatani, H. and Yoshimoto, H. *Chem. Ind. (London)* **1971** 674.
13. Bryant, D. R., McKeon, J. E. and Ream, B. C. *Tetrahedron Letters* **1968** 3371.
14. Bryant, D. R., McKeon, J. E. and Ream, B. C. *J. Org. Chem.* **33** (1968) 4123.
15. Bushweller, C. H. *Tetrahedron Letters* **1968** 6123.
16. Henry, P. M. *J. Org. Chem.* **36** (1971) 1886.
17. Ebersson, L. *J. Am. Chem. Soc.* **89** (1967) 4669.
18. Ebersson, L. and Nyberg, K. *J. Am. Chem. Soc.* **88** (1966) 1686.
19. Bernhardson, E., Ebersson, L., Nyberg, K. and Rietz, B. *Acta Chem. Scand.* **25** (1971) 1224.
20. a. Ebersson, L. and Sternerup, H. *Acta Chem. Scand.* **26** (1972) 1431; b. Dirlam, J. P. and Ebersson, L. *Acta Chem. Scand.* **26** (1972) 1454; c. Dirlam, J. P., Ebersson, L. and Sternerup, H. *Chem. Ingr. Tech.* **44** (1972) 178; Ebersson, L. and Wilkinson, R. G. *Acta Chem. Scand.* **26** (1972) 1671.
21. A preliminary account of this work has been published; Ebersson, L. and Gomez-Gonzalez, L. *Chem. Commun.* **1971** 263.
22. Skapski, A. C. and Smart, M. L. *Chem. Commun.* **1970** 658.
23. Stephenson, T. A., Morehouse, S. M., Powell, A. R., Heffer, J. P. and Wilkinson, G. *J. Chem. Soc.* **1965** 3632.
24. Campbell, P. G. C. and Wolfe, S. *Private communication*.
25. Lande, S. S. and Kochi, J. K. *J. Am. Chem. Soc.* **90** (1968) 5196.
26. Kochi, J. K. and Subramanian, R. V. *Inorg. Chem.* **4** (1965) 1527.
27. Brandon, P. W. and Claridge, D. V. *Chem. Commun.* **1968** 677.
28. See, for example, Morimoto, T. and Ogata, Y. *J. Chem. Soc. B* **1967** 62.
29. Ebersson, L. and Gomez-Gonzalez, L. *Acta Chem. Scand.* **27** (1973) 1255.
30. Carill, G. W. K. and Solomon, D. H. *J. Chem. Soc.* **1954** 3943.
31. von Auwers, K., Bundesmann, H. and Wieners, F. *Ann.* **447** (1926) 162.
32. Claussner, P. *Ber.* **38** (1905) 2860.
33. Murray, R. W. and Tazzolo, A. M. *J. Org. Chem.* **29** (1964) 1268.
34. Ullmann, F. *Ann.* **332** (1904) 47.
35. Farthing, A. C. *J. Chem. Soc.* **1953** 3261.
36. Guggenheim, E. A. *Phil. Mag.* **2** (1920) 538.

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