A Palladium-Catalyzed Synthesis of Xylyl Acetates and Xylylene Diacetates

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Xylenes and xylyl acetates are catalytically oxidized at moderate temperatures with a homogeneous palladium–stannous acetate catalyst and air (1 atm) in acetic acid. *p*-Xylene gives *p*-xylyl acetate, *p*-xylylene diacetate, and *p*-methylbenzylidene diacetate. The α,α'-/α,α-diacetate ratio is 31:1. The other xylenes give similar product mixtures. The selectivity of the diacetoxylation reaction is maintained when the pure xylyl acetates are oxidized under the same conditions.

The catalytic synthesis of several benzyl esters from the corresponding methylbenzenes and a palladium–stannous acetate catalyst in acetic acid was reported earlier.[1] Xylenes give xylyl acetates which on further oxidation preferentially form α,α'-diacetates. The selectivity of the xylene oxidations and kinetic data for both mono- and diacetoxylation are reported herein.

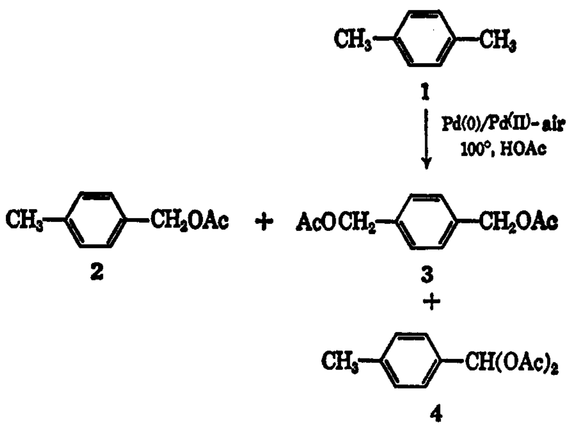
The high conversions of the xylenes into the corresponding xylyl acetates make this procedure the method of choice for preparing these esters. The highly selective diacetoxylation reaction forms the basis of an efficient, catalytic route to xylylene derivatives.

Xylyl acetates and xylylene diacetates have been prepared stoichiometrically from the corresponding xylenes with lead tetraacetate.[2a] Davidson and Triggs[2b] have used palladium (II) acetate to oxidize the xylenes. Acetolysis of the halides[3] and quaternary ammonium salts[4] has also served as a synthetic route. These methods of preparation give moderate to good yields but are not catalytic.

Results and Discussion

Oxidation of the isomeric xylenes was carried out in acetic acid, using a palladium–stannous acetate catalyst and air.

SCHEME I



The reaction of *p*-xylene (**1**) (Scheme I and Table I) gave *p*-xylyl acetate (**2**) and *p*-xylylene diacetate (**3**), along with a small amount of *p*-methylbenzylidene diacetate (**4**). No carboxylic acids were formed in the reaction.

TABLE I[a]

PRODUCT DISTRIBUTIONS FROM THE OXIDATION OF THE XYLENES

Xylene isomer	Time, hr	% conversion of xylene isomer to products	% of product mixture: Xylyl acetate	α,α'-Diacetate	α,α-Diacetate	Others
para **1**	1	14.0	84.1	15.9	0	0
	2	25.1	85.2	14.8	0	0
	3	37.5	85.8	14.2	0	0
	5	55.5	83.0	17.0	0	0
	8	72.0[b]	61.2	34.5	1.1	3.2[c]
ortho **7**	1	4.8	87.5	12.5	0	0
	2	10.5	86.8	13.2	Trace	0
	3	16.1	85.9	14.1	Trace	0
	7	35.5	77.2	18.6	2.5	1.7[d]
meta **13**	1	11.6	85.5	14.5	0	0
	2	19.1	82.4	17.6	0	0
	3	26.3	81.3	18.7	Trace	0
	7	41.3	69.4	22.0	4.5	4.1[e]

[a] Moles of reactants: xylene (isomer), 1.5 (*ortho*), 1.0 (*para*), 1.0 (*meta*), HOAc 8.04, KOAc 1.1, $Sn(OAc)_2$ 0.06, and $Pd(OAc)_2$ 0.016; also present 33.6 g of charcoal. [b] No unreacted *p*-xylene remained; 28% was lost by blowoff in the air flow. [c] Mixture of *p*-acetoxymethylbenzylidene diacetate (**5**) and α-acetoxy-*p*-tolualdehyde (**6**). [d] *o*-Acetoxymethylbenzylidene diacetate (**11**). [e] *m*-Acetoxymethylbenzylidene diacetate (**17**).

No unreacted *p*-xylene (**1**) remained after 8 hr; 72% had been converted into products, while the remainder was lost as blowoff in the air flow. Figure 1 shows the relative rates of formation of *p*-xylyl acetate (**2**) and the diacetates. *p*-Xylyl acetate (**2**), at a rate of 0.178 mol/l. hr, is formed about five times faster than the diacetates. *p*-Xylylene diacetate (**3**) is the only diacetate observed during the first 5 hr of reaction.

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(3) (a) J. Entel, C. H. Ruof, and H. C. Howard, *J. Amer. Chem. Soc.*, **74**, 441 (1952); (b) S. Dev, *J. Indian Chem. Soc.*, **32**, 403 (1955).

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TABLE II[a]

PRODUCT DISTRIBUTIONS FROM THE OXIDATION OF XYLYL ACETATES

Xylyl acetate isomer	Time, hr	% conversion of xylyl acetate to products	% of product mixture α,α′-Diacetate	α,α-Diacetate	Others
para **2**	1	20.2	82.8	7.7	9.5[b]
	2	39.6	79.9	8.1	12.0
	3	52.5	79.3	7.4	13.3
	7	79.3	75.2	4.5	20.3
ortho **8**	1	20.5	94.0	4.3	1.7[c]
	2	38.2	91.8	4.6	3.6
	3	52.3	89.5	4.2	6.3
	4	66.5	86.3	4.1	9.6
meta **14**	1	10.9	92.5	4.3	3.2[d]
	2	20.1	90.9	4.4	4.7
	3	25.7	90.7	3.7	5.6
	7	29.4	90.4	2.9	6.7

[a] Moles of reactants: xylyl acetate 0.25; HOAc 2.00, KOAc 0.27, $Sn(OAc)_2$ 0.06, and $Pd(OAc)_2$ 0.016, also present 8.4 g of charcoal. [b] Mixture of **5**, **6**, and α-acetoxy-*p*-toluic acid (**18**). [c] Mixture of *o*-acetoxymethylbenzylidene diacetate (**11**) and α-acetoxy-*o*-tolualdehyde (**12**). [d] *m*-Acetoxymethylbenzylidene diacetate (**17**).

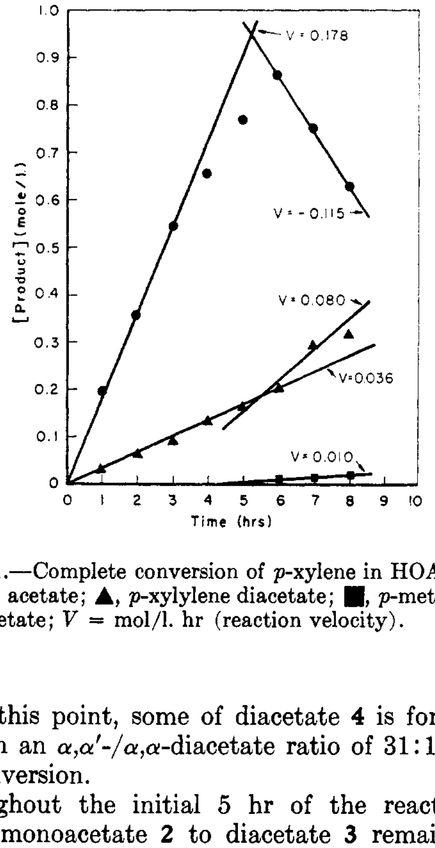

Figure 1.—Complete conversion of *p*-xylene in HOAc at 100°: ●, *p*-xylyl acetate; ▲, *p*-xylylene diacetate; ■, *p*-methylbenzylidene diacetate; V = mol/l. hr (reaction velocity).

Beyond this point, some of diacetate **4** is formed, resulting in an α,α′-/α,α-diacetate ratio of 31:1 at complete conversion.

Throughout the initial 5 hr of the reaction, the ratio of monoacetate **2** to diacetate **3** remains fairly constant, suggesting that coordinated xylene undergoes diacetoxylation before release of a product from the catalyst. After 5 hr, the reaction profile more closely resembles that expected for the sequential oxidation of xylene to xylyl acetate to diacetate.

The change in reaction profile may result from competition between xylene and xylyl acetate for catalyst coordination sites. When xylene is present, it preferentially coordinates with palladium; oxidation may give either mono- or diacetate before release of a product. Later, when xylene is depleted, xylyl acetate competes more favorably for coordination sites. Oxidation of the monoacetate to diacetate can then become significant.

o-Xylene (**7**) (Table I) gave a product mixture similar to that obtained with *p*-xylene, but at a rate about one-third as fast. *o*-Xylyl acetate (**8**), *o*-xylylene diacetate (**9**), and a trace of the α,α-diacetate, *o*-methylbenzylidene diacetate (**10**), were formed. No carboxylic acids were obtained.

m-Xylyl acetate (**14**) and *m*-xylylene diacetate (**15**) were obtained from the oxidation of *m*-xylene (**13**) (Table I). A trace of *m*-methylbenzylidene diacetate (**16**) was formed but carboxylic acids were not. The rate of reaction was comparable to that of *o*-xylene.

The data in Table I show that in the early stages of the reactions (1–3 hr) the monoacetate to diacetate ratio is sufficiently high to make these reactions of interest for preparing xylyl acetates. At higher conversions, the amount of diacetate increases, so that by employing longer reaction times, a route to α,α′-diacetates is also available.

To show the selectivity of the diacetoxylation reaction in the absence of the xylenes, the pure monoacetates were subjected to the oxidation conditions. *p*-Xylyl acetate (**2**) gave mainly *p*-xylylene diacetate (**3**), along with a much smaller amount of the α,α-diacetate (Table II). A small amount of α-acetoxy-*p*-toluic acid (**18**), and minor amounts of two other oxidation products were obtained.

o-Xylyl acetate (**8**) (Table II) was oxidized at about the same rate as *p*-xylyl acetate (**2**). As in the reaction of the latter, a trace of a carboxylic acid, α-acetoxy-*o*-toluic acid (**19**), was formed.

The oxidation of *m*-xylyl acetate (**14**) was the slowest of the xylyl acetates, giving only 29.4% conversion in 7 hr (Table II). No carboxylic acids were formed.

A comparison of xylene and xylyl acetate oxidation rates shows that if compensation is made for the different relative amounts of palladium catalyst and reactant, the rates of xylene oxidations are approximately four times those of the corresponding xylyl acetates.

The data in Table II show that the selectivity of the diacetoxylation reaction is maintained in the absence of the corresponding xylenes.

The reactions described herein provide an efficient route to xylyl acetates. In addition, a highly selective route to α,α′-xylylene diacetates is available. Pure α,α-diacetates decompose on heating to tolualdehydes and acetic anhydride.

Experimental Section

A. General Procedure.—The reactants were charged to an appropriately sized flask, fitted with a thermometer, a stirrer, a high-capacity condenser, and a sampling port with a rubber septum for removal of samples by hypodermic syringe. The resulting mixture was stirred at 100° while air was blown over its surface at a rate of 500 ml/min.

Periodically, a sample was removed and internal standards were added. After thorough mixing, the sample was centrifuged to separate the solids, and diluted with 15 ml of water. The resulting solution was extracted with three 25-ml portions of 1:1 $Et_2O-CH_2Cl_2$. The extracts were combined, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), concentrated, and analyzed by glpc. Analyses were carried out on a 10 ft × 0.25 in. column, packed with 5% SE-30 on Chromosorb G, at a He flow of 70 ml/min, and programmed from 100 to 200°.

At the end of the reaction time, the cooled reaction mixture was filtered through diatomaceous silica. The filtrate was diluted with an equal volume of water and continuously extracted with Et_2O for 24 hr for all reactions except that of *p*-methylbenzyl acetate (**2**), which is described separately. The Et_2O extract was washed successively with water, saturated $NaHCO_3$ solution, water, and saturated NaCl solution, then dried ($MgSO_4$) and concentrated. The products were isolated as noted.

To determine if carboxylic acids were among the products, the aqueous layers were combined, acidified, and extracted with benzene. The extracts were dried ($MgSO_4$), concentrated, and treated with BF_3–MeOH[5] to obtain the methyl esters for glpc analysis.

B. Oxidation of *p*-Xylene (1) in Acetic Acid.—A charge of 482.0 g (8.04 mol) of acetic acid, 107.9 g (1.10 mol) of potassium acetate, 106.0 g (1.00 mol) of **1**, 14.2 g (0.06 mol) of stannous acetate, 3.6 g (0.016 mol) of palladium acetate, and 33.6 g of charcoal was stirred at 100° for 8 hr. Hourly aliquots, containing benzyl acetate and **9** as internal standards, were analyzed by glpc.

The usual work-up gave (by glpc) 72.5 g of **2**, 40.9 g of **3**, 1.3 g of **4**, 0.6 g of **5**, and 3.2 g of **6**. Distillation yielded 62.6 g (38.2%) of pure **2**, bp 170–172° (200 mm) [lit.[2] bp 227–230° (760 mm)]. The pot residue (49.2 g) solidified on cooling. Crystallization from petroleum ether (bp 60–70°) afforded 37.9 g (17.1%) of **3**, mp 48–50° [lit.[6] mp 45–49°].

Compounds **4**, **5**, and **6** were identified by their glpc retention times. No carboxylic acids were found by the usual procedure.

Oxidation of *o*-Xylene (7) in Acetic Acid.—The procedure described in B was followed using 159.0 g (1.50 mol) of **7** instead of **1** and a reaction time of 48 hr. Aliquots containing benzyl acetate and **3** as internal standards were analyzed by glpc.

The usual work-up gave (by glpc) 10.7 g of **7**, 75.0 g of **8**, 26.4 g of **9**, 4.2 g of **10**, and 3.8 g of **11**. Distillation yielded 60.8 g (24.7%) of pure **8**, bp 143–144° (37 mm) (lit.[7] bp 119–121°). The pot residue (43.6 g) crystallized on standing. Recrystallization from petroleum ether (bp 30–60°) gave pure **9**, mp 34–35° (lit.[3a] mp 35–36°).

Compound **10** was identified by its glpc retention time. No carboxylic acids were found by the usual procedure.

Oxidation of *m*-Xylene (13) in Acetic Acid.—The procedure described in B was followed using 106.0 g (1.00 mol) of **13** instead of **1** and a reaction time of 7 hr. Aliquots containing benzyl acetate and benzyl benzoate as internal standards were analyzed by glpc.

The usual work-up gave (by glpc) 31.4 g of **13**, 50.5 g of **14**, 16.0 g of **15**, 3.3 g of **16**, and 3.0 g of **17**. Distillation yielded 47.6 g (29.0%) of pure **14**, bp 95° (5 mm) [lit.[8] bp 226° (760 mm)], and 13.8 g (6.2%) of pure **15**, bp 156° (5 mm) [lit.[1] bp 158° (5 mm)]. Both **14** and **15** were identified by their ir spectra. Compounds **16** and **17** were identified by their glpc retention times. No carboxylic acids were found by the usual procedure.

C. Oxidation of *o*-Xylyl Acetate (8) in Acetic Acid.—A charge of 120.0 g (2.00 mol) of acetic acid, 41.0 g (0.25 mol) of **8**, 27.1 g (0.27 mol) of potassium acetate, 14.2 g (0.06 mol) of stannous acetate, 3.6 g (0.016 mol) of palladium acetate, and 8.4 g of charcoal was stirred at 100° for 7 hr. Aliquots containing **3** as internal standard were analyzed by glpc.

The usual work-up gave (by glpc) 3.3 g of **8**, 21.7 g of **9**, 1.4 g of **10**, 2.7 g of **11**, and 0.2 g of **12**. The aqueous layers were combined, extracted, and concentrated to yield 0.3 g (0.6%) of α-acetoxy-*o*-toluic acid (**19**): mp 119–121°; ir (KBr) 3.90 (acid –OH), 5.75 (ester C=O), 5.97 (acid C=O), and 8.00 μ (acetate); nmr ($CDCl_3$) δ 2.17 (s, 3, CH_3CO–), 5.61 (s, 2, $ArCH_2O$–), 7.58 (m, 3, aromatic), 8.18 (d, 1, aromatic *ortho* to CO_2H), and 11.14 ppm (–CO_2H). *Anal.* Calcd for $C_{10}H_{10}O_4$: C, 61.9; H, 5.2. Found: C, 62.1; H, 5.2.

Oxidation of *m*-Xylyl Acetate (14) in Acetic Acid.—The procedure described in C was followed using **14** instead of **8**. Aliquots containing benzyl benzoate as internal standard were analyzed by glpc.

The usual work-up gave (by glpc) 20.8 g of **14**, 11.7 g of **15**, 0.4 g of **16**, and 0.8 g of **17**. No carboxylic acids were found by the usual procedure.

Oxidation of *p*-Xylyl Acetate (2) in Acetic Acid.—The procedure described in C was followed using **2** instead of **8**. Aliquots containing **9** as internal standard were analyzed by glpc.

The work-up procedure was the same except that 100 ml of a saturated NH_4F solution was added before the addition of water to prevent emulsion formation. Using this technique, batchwise extraction, followed by the other usual steps of the work-up yielded (by glpc) 8.5 g of **2**, 33.1 g of **3**, 2.0 g of **4**, 5.4 g of **5**, and 1.4 g of **6**. The aqueous layers were acidified, extracted, and concentrated to give 2.6 g (1.3%) of α-acetoxy-*p*-toluic acid (**18**), mp 125–127° [lit.[9] mp 127.5–128.0°].

Registry No.—**1**, 106-42-3; **2**, 2216-45-7; **7**, 95-47-6; **8**, 17373-93-2; **13**, 108-38-3; **14**, 17369-57-2.

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