A Palladium-Catalyzed Synthesis of Benzyl Esters from Methylbenzenes

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Received May 22, 1968

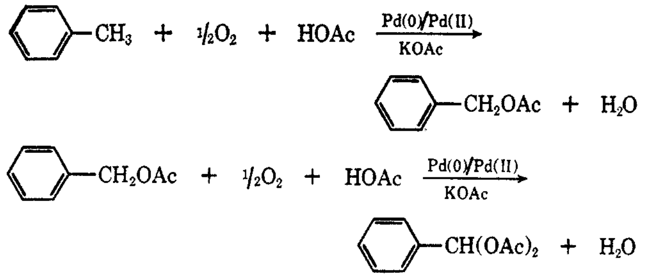
Benzyl esters are produced catalytically at moderate temperatures from methylbenzenes in a liquid phase process employing a homogeneous palladium–stannous acetate catalyst and air (1 atm). Toluene in acetic acid gives benzyl acetate. At high conversions, the secondary oxidation product, benzylidene diacetate, is formed. Other methylbenzenes, *e.g.*, mesitylene, durene, and hexamethylbenzene, give similar oxidation products. Xylenes undergo a selective diacetoxylation reaction in acetic acid, giving α,α'-diacetates in preference to α,α-diacetates.

The catalytic, liquid phase process described herein is an outgrowth of the stoichiometric oxidation of toluene by palladium(II) acetate in acetic acid.[1] The process proceeds at moderate temperatures and pressures with a palladium–stannous acetate catalyst in a carboxylic acid. Air is the ultimate oxidant. The high conversions obtainable from this selective and efficient process make it the method of choice for preparing many benzyl esters from methylbenzenes.

A limited number of metallic oxidants have been used to oxidize methylbenzenes to benzyl esters in carboxylic acids. The best known of these reagents is lead tetraacetate, which gives moderate yields.[2] Several workers have reported the use of ceric salts.[3] Chromic acid in acetic anhydride has yielded benzyl esters in some cases,[4] but further oxidation to benzoyl derivatives is the usual course of the reaction. The stoichiometric oxidation of toluene to benzyl acetate by palladium(II) salts has been reported.[5]

Results and Discussion

In the simplest form of the process, a methylbenzene is dissolved in a carboxylic acid containing a palladium(II) acylate and an alkali metal carboxylate. The solution is stirred at 100° for several hours while air is blown through the reaction flask. A benzyl monoester is efficiently produced. At high conversions small amounts of benzyl diesters are produced. For example, the reaction of toluene is as shown below. Subsequent oxidation of the diacetate is negligible.



In its simplest form, the process is efficient, but not very productive (Figure 1). The palladium metal formed in the reaction is deposited as a mirror which is difficult to oxidize. The addition of a high surface material, such as charcoal (Figure 1), alumina, silica, etc., substantially increases the rate of oxidation by dispersing the palladium metal.

Remarkably, tin salts, such as stannous acetate, increase the rate of benzylic oxidation about 90 times that of the base case (Figure 1 and Table I). To a lesser degree, triphenylphosphine and triethyl phosphite also increase the benzylic oxidation rate.

TABLE I

EFFECT OF CHARCOAL AND COCATALYSTS ON THE OXIDATION OF TOLUENE AT 100°

Expt[a]	Additive	Moles of $C_6H_5CH_2OAc$/ mole of Pd
1	None	0.68
2	Charcoal	6.3
3	$Sn(OAc)_2$	64
4	$Sn(OAc)_2$ and charcoal	96
5	$(C_6H_5)_3P$	31
6	$(C_2H_5O)_3P$	12

[a] Experiments 1–5 were carried out in solutions of 8.0 mol of acetic acid, 1.2 mol of toluene, 1.1 mol of potassium acetate, and 0.008 mol of palladium(II) acetate for 6 hr while air was blown through the flask at a rate of 500 ml/min. Experiment 6 contained the same ratios, but half the amounts of reactants.

If the catalyst is charged as a mixture of palladium(II) acetate, stannous acetate, and charcoal, optimum benzylic oxidation rates result (Figure 1). The fastest rate observed under these conditions was 0.360 mol/(l. hr). This rate may be limited by the mass transfer of oxygen. Faster rates may be possible at higher oxygen partial pressures.

Comparable oxidation rates are obtained by generating the palladium oxidant from 5% palladium(0) on charcoal with air (Figure 1).

Several alkylaromatics were oxidized using the most productive catalyst system described above (Table II).

Reactions of toluenes bearing substituents such as nitro, chloro, and acetoxy on the ring are very slow. With a methoxy group present on the ring, benzylic oxidation competes with nuclear oxidation.

When alkylaromatics with side chains greater than methyl are oxidized, undesirable side reactions occur. The benzylic oxidation product, α-methylbenzyl acetate, is formed from ethylbenzene in low yield, along

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[1] D. R. Bryant, J. E. McKeon, and B. C. Ream, *Tetrahedron Lett.*, 3371 (1968).

[2] R. Criegee in "Oxidation in Organic Chemistry," Vol. 5, part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 312.

[3] (a) C. M. Selwitz and E. R. Tucci, U. S. Patents 3,349,117 and 3,346,622 (1967); (b) W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2033 (1966).

[4] (a) T. Nishimura, *Org. Syn.*, **36**, 58 (1956); (b) S. V. Lieberman and R. Connor, *ibid.*, **18**, 61 (1938); (c) W. Triebs and H. Schmidt, *Ber.*, **61**, 459 (1928).

[5] (a) J. M. Davidson and C. Triggs, *Chem. Ind.* (London), 457 (1966). (b) After this manuscript was submitted for publication, J. M. Davidson and C. Triggs [*J. Chem. Soc.*, 1324, 1331 (1968)] expanded their original report. (c) In German Patent 1,262,992, Farbenfabriken Bayer AG discloses the preparation of benzyl acetate from toluene, acetic acid, and oxygen, in the presence of a supported catalyst apparently containing reduced palladium.

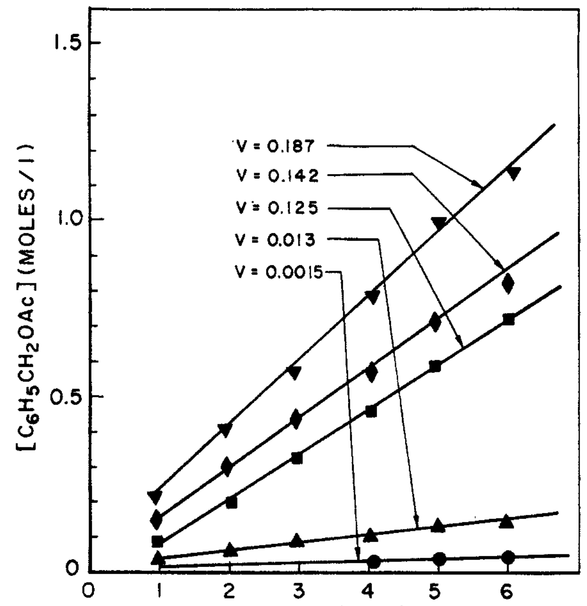

Figure 1.—Effect of catalyst composition on rate of benzyl acetate formation. Reactions contained 8.04 mol of HOAc, 1.10 mol of KOAc, 1.0 mol of toluene, and ●, 0.008 mol of $Pd(OAc)_2$; ▲, 0.008 mol of $Pd(OAc)_2$ and 33.6 g of charcoal; ■, 0.008 mol of $Pd(OAc)_2$ and 0.06 mol of $Sn(OAc)_2$; ◆, 0.008 mol of 5% Pd on charcoal and 0.06 mol of $Sn(OAc)_2$; ▼, 0.008 mol of $Pd(OAc)_2$, 0.06 mol of $Sn(OAc)_2$, and 33.6 g of charcoal. The first hour is excluded because the steady-state $Pd(OAc)_2$ concentration had not yet been established. V = rate in mol/(l. hr).

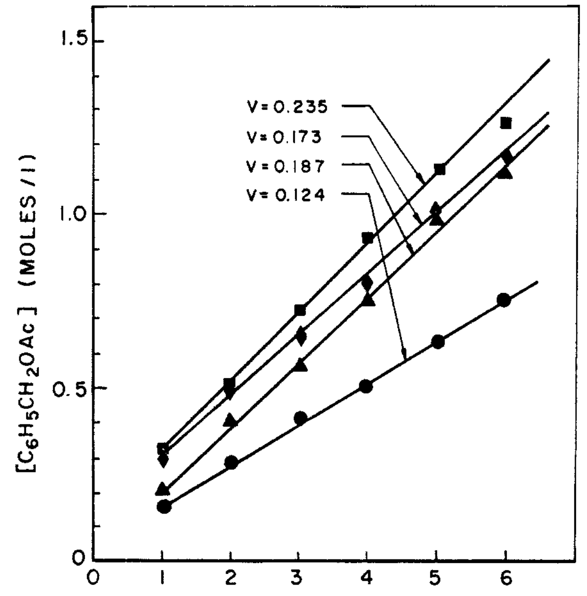

Figure 2.—Effect of [$Pd(OAc)_2$] on rate of benzyl acetate formation: ●, 0.004 mol; ▲, 0.008 mol; ■, 0.016 mol; ◆, 0.032 mol of $Pd(OAc)_2$. Other reactants: 8.04 mol of HOAc, 1.10 mol of KOAc, 1.0 mol of toluene, 0.06 mol of $Sn(OAc)_2$, and 9.33 g of charcoal/0.004 mol of $Pd(OAc)_2$. The first hour is excluded because the steady-state $Pd(OAc)_2$ concentration had not yet been established. V = rate in mol/(l. hr).

with a comparable quantity of several other products (Table II). A similar product mixture can be obtained from styrene under the same oxidation conditions. Tetralin and indane give results similar to those obtained with ethylbenzene.

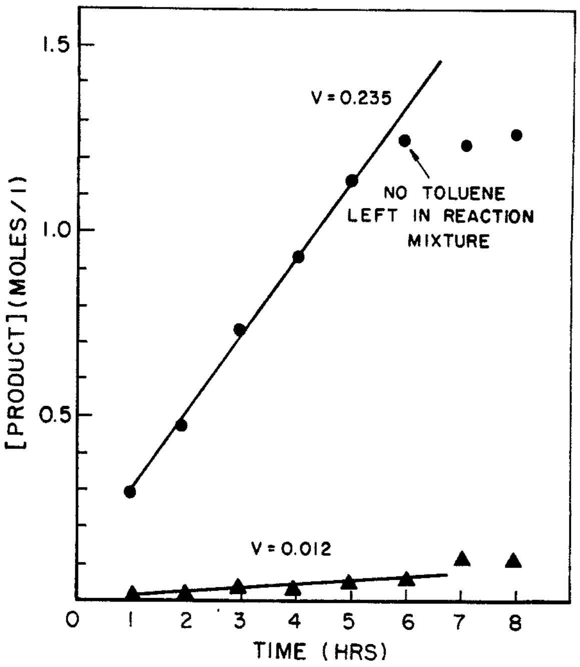

Figure 3.—Complete conversion of toluene: ●, $C_6H_5CH_2OAc$; ▲, $C_6H_5CH(OAc)_2$. Reactants: 8.04 mol of HOAc, 1.1 mol of KOAc, 1.0 mol of toluene, 0.016 mol of $Pd(OAc)_2$, 0.06 mol of $Sn(OAc)_2$, and 33.6 g of charcoal. The first hour is excluded because the steady-state $Pd(OAc)_2$ concentration had not been established. V = rate in mol/(l. hr).

The oxidation of toluene in acetic acid was studied in the most detail. Benzyl acetate is the major product at moderate conversions. Benzylidene diacetate becomes an important product at high conversions and can be made the principal product by employing longer reaction times. Some benzaldehyde is formed from thermal decomposition[6] and hydrolysis of benzylidene diacetate. Only a trace (0.2%) of benzoic acid is formed, even at complete conversion of toluene.

Pure benzyl acetate is oxidized three times more slowly than toluene under comparable conditions. In the presence of toluene, benzyl acetate is oxidized up to 20 times more slowly. This might mean that toluene forms a stronger complex with the catalyst than does benzyl acetate.

The rate of benzyl acetate formation depends on palladium(II) acetate at low concentrations (Figure 2). At high concentrations, other factors limit the rate of oxidation. The availability of oxygen at atmospheric pressure may be important in this respect.

Figure 3 shows the profile of a reaction which was continued until no toluene remained. Of the toluene, 80 mol % was converted into a 15:1 mixture of benzyl acetate and benzylidene diacetate, and 20% was lost by entrainment. With properly designed equipment, complete oxidation is achieved.

In the catalytic reaction (Figure 3), formation of a palladium–toluene complex is not the rate-controlling step of the reaction since the rate is independent of the toluene concentration.

Xylene oxidations are more complex than that of toluene. In addition to mono- and diacetates, tri- and

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(6) N. A. D. Parlee, J. C. Arnell, and C. C. Coffin, *Can. J. Res.*, **18B**, 223 (1940).

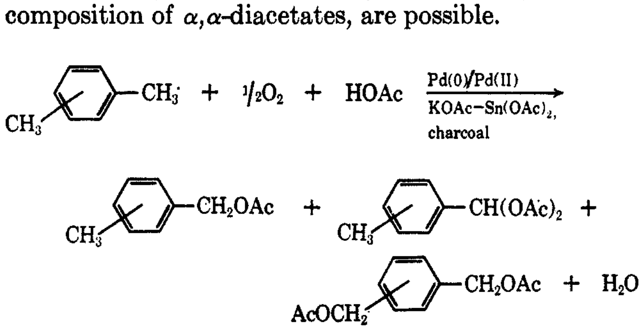
TABLE II[a]

BENZYLIC OXIDATIONS OF ALKYLAROMATICS WITH A PALLADIUM CATALYST AND AIR AT 100°

Alkylaromatic	Acid	Time, hr	% conversion of alkylaromatic into products[b]	Products	% of product mixture[c]
Toluene	Acetic	9	79.7	C_6H_5CHO	6.7 (9.1)
				$C_6H_5CH_2OAc$	91.4 (89.4)
				$C_6H_5CH(OAc)_2$	1.9 (1.1)
				$C_6H_5CO_2H$	... (0.4)
Toluene[d]	Propionic	6	22.3	C_6H_5CHO	0.6
				$C_6H_5CH_2OAc$	2.0
				$C_6H_5CH_2O_2CC_2H_5$	92.0
				$C_6H_5CH(O_2CC_2H_5)_2$	5.4
p-Xylene	Acetic	8	50.6	*p*-$CH_3C_6H_4CHO$	Trace
				p-$CH_3C_6H_4CH_2OAc$	58.0
				p-$CH_3C_6H_4CH(OAc)_2$	4.7
				p-$C_6H_4(CH_2OAc)_2$	37.3
o-Xylene	Acetic	24	38.2	*o*-$CH_3C_6H_4CH_2OAc$	57.4
				o-$CH_3C_6H_4CH(OAc)_2$	4.6
				o-$C_6H_4(CH_2OAc)_2$	38.0
m-Xylene	Acetic	24	43.5	*m*-$CH_3C_6H_4CHO$	10.0
				m-$CH_3C_6H_4CH_2OAc$	33.1
				m-$CH_3C_6H_4CH(OAc)_2$	6.9
				m-$C_6H_4(CH_2OAc)_2$	50.0
Mesitylene	Acetic	24	8.0	3,5-$(CH_3)_2C_6H_3CH_2OAc$	62.5
				20 minor unidentified products	37.5
Durene	Acetic	96	(28.0)	2,4,5-$(CH_3)_3C_6H_2CH_2OAc$	... (98.9)
				2,4,5-$(CH_3)_3C_6H_2CO_2H$	... (1.1)
Hexamethylbenzene	Acetic	96	(21.9)	2,3,4,5,6-$(CH_3)_5C_6CH_2OAc$	... (100.0)
Hexamethylbenzene	Propionic[e]	96	(26.5)	2,3,4,5,6-$(CH_3)_5C_6CH_2O_2CC_2H_5$	... (100.0)
Ethylbenzene	Acetic	25	8.3	$C_6H_5CH{=}CH_2$	13.6
				$C_6H_5CH(OAc)CH_3$	39.0
				$C_6H_5(CH_2)_2OAc$	13.2
				cis-$C_6H_5CH{=}CHOAc$	13.2
				trans-$C_6H_5CH{=}CHOAc$	16.7
				$C_6H_5CH_2CHO$	1.4
				$C_6H_5COCH_3$	2.9

[a] All experiments were carried out in solutions of 1.1 mol of alkali metal carboxylate in 8.0 mol of the corresponding carboxylic acid, with air being blown through the flask at a rate of 500 ml/min. In reactions using acetic acid, the catalyst was charged as a mixture of $Pd(OAc)_2$, $Sn(OAc)_2$, and charcoal. In reactions using propionic acid, the catalyst was charged as a mixture of 5% Pd on charcoal and $Sn(OAc)_2$. Ratio of $Sn(OAc)_2$:Pd was 3.75:1; the amount of alkylaromatic ranged from 0.15 to 1.0 mol. [b] This figure represents the amount of alkylaromatic oxidized. In the case of toluene, 15–20% of the starting material was lost by entrainment in the air flow. Entrainment also caused loss of starting material in the xylene reactions. The numbers in this column in parentheses were determined from isolated material; all others were determined by glpc after addition of an internal standard. [c] Numbers in parentheses are based on isolated material, while the others were determined by glpc, using an internal standard. [d] The benzyl acetate formed in this reaction results from the $Sn(OAc)_2$ present in the catalyst. [e] Reaction temperature was 145°, and $Sn(OAc)_2$:$Pd(OAc)_2$ ratio was 7.5:1.

tetraacetates, as well as aldehydes resulting from decomposition of α,α-diacetates, are possible.



The major products are the methylbenzyl acetates (Table II). Further oxidation of the monoacetates gives α,α'-diacetates in preference to α,α-diacetates. *p*-Xylene shows a higher selectivity toward the α,α'-diacetate than the other isomers. The selective diacetoxylation reaction forms the basis of a novel route to xylylene derivatives which will be discussed in greater detail in a separate paper. Under the conditions reported in Table II, only traces of tri- and tetraacetates are formed.

Methylbenzenes with greater than two methyl groups are also oxidized by this process, but reaction rates are slower than those obtained with toluene and the xylenes, *i.e.*, toluene > *p*-xylene > *o*- and *m*-xylene > mesitylene > durene > hexamethylbenzene. The formation of the monoesters of durene and hexamethylbenzene, though slow, is very selective. Increased reaction rates might be attainable by using higher reaction temperatures and greater partial pressures of oxygen.

Progress has been made in identifying the unexpectedly complex interactions involved in the mechanism of this oxidation process. Our results cannot be adequately described here; we hope to describe them in detail in the near future.

Experimental Section

I. **Typical Rate Determination.**—To an appropriately sized flask, fitted with a thermometer, a stirrer, a high-capacity condenser, and a sampling port equipped with a rubber septum for removal of liquid samples by hypodermic syringe, were charged 482.0 g (8.04 mol) of acetic acid, 107.9 g (1.10 mol) of potassium acetate, 109.3 g (1.20 mol) of toluene, 14.2 g (0.06 mol) of stannous acetate, and 1.8 g (0.008 mol) of palladium(II) acetate. The resulting mixture was stirred at 100° while air was blown over its surface at a flow rate of 500 ml/min.

Periodically, a 3-ml aliquot was removed and *n*-butyrophenone, the internal standard, was added. Glpc analyses were carried out on a 9.5 ft × 0.25 in. aluminum column, packed with 10% trimer acid on a Teflon-6 support, at 172° and a helium flow of 70 ml/min.

Anal. Time (hr) for $C_6H_5CH_2OAc$ (mol/l.) by glpc: 1, 0.075; 2, 0.216; 3, 0.331; 4, 0.461; 5, 0.598; and 6, 0.720.

Rate with $(C_6H_5)_3P$ Present.—The procedure described under I was followed using 15.7 g (0.06 mol) of $(C_6H_5)_3P$ instead of stannous acetate. The final sample represents an 18.5% yield, based on toluene.

Anal. Time (hr) for $C_6H_5CH_2OAc$ (mol/l.) by glpc: 1, 0.000; 2, 0.056; 3, 0.133; 4, 0.209; 5, 0.276; and 6, 0.352.

Rate with $(EtO)_3P$ Present.—The procedure described under I was followed using 4.9 g (0.03 mol) of triethyl phosphite instead of stannous acetate and halving the amounts of the other reactants. The final sample represents a 7.0% yield, based on toluene.

Anal. Time (hr) for $C_6H_5CH_2OAc$ (mol/l.) by glpc: 3, 0.107; and 6, 0.153.

II. Preparative Reactions. General Procedures.—Melting and boiling points are uncorrected. All yields are based on alkylbenzene charged. The reactants were charged to an appropriately sized flask, fitted with a stirrer, a condenser, a thermometer, and an air-inlet tube. The reaction mixture was stirred at 100° for the specified time, while air was blown over its surface at a rate of 500 ml/min.

The cooled reaction mixture was filtered through diatomaceous silica. The filtrate was diluted with an equal volume of water and extracted with 1:1 Et_2O–pentane. The extracts were combined, washed successively with a saturated $NaHCO_3$ solution, water, and a saturated NaCl solution, then dried ($MgSO_4$). The products were isolated by distillation, sublimation, or column chromatography, as noted.

To determine if carboxylic acids were present, the aqueous layers were combined, acidified, and extracted with benzene. The extracts were dried ($MgSO_4$), concentrated, and treated with BF_3–MeOH reagent[7] to obtain the methyl esters for glpc analysis.

III. Oxidation of Toluene in Acetic Acid.—A charge of 482.0 g (8.04 mol) of acetic acid, 107.9 g (1.10 mol) of potassium acetate, 92.0 g (1.00 mol) of toluene, 14.2 g (0.06 mol) of stannous acetate, 3.6 g (0.016 mol) of palladium(II) acetate, and 33.6 g of charcoal was stirred at 100° for 9 hr. After the usual work-up, distillation gave 66.0 g of a liquid, bp 103–105° (20 mm) [lit.[8] bp 222–223° (760 mm)], containing 4.5 g (4.2%) of benzaldehyde and 61.5 g (41.0%) of benzyl acetate.

Benzaldehyde was identified by its 2,4-dinitrophenylhydrazone, mp 233–235° (lit.[9] mp 237°). A purified sample of benzyl acetate had the correct ir spectrum.

Trituration of the distillation residue (4.9 g) with petroleum ether (bp 60–70°) gave 1.3 g of crude solid. Recrystallization gave 1.0 g (0.5%) of benzylidene diacetate, mp 44–45° (lit.[10] mp 43.5–44°), identified by its ir and nmr spectra.

Acidification of the aqueous layers, followed by extraction and esterification, gave 0.28 g of methyl benzoate, which corresponds to a 0.2% yield (based on toluene).

Oxidation of *p*-Xylene in Acetic Acid.—The procedure described under III was followed using 106.0 g (1.0 mol) of *p*-xylene instead of toluene. After 8 hr, the usual work-up gave (by glpc) [compound, wt (g), % yield] *p*-xylene, 0.2, 0.2; *p*-tolualdehyde, trace, . . . ; *p*-methylbenzyl acetate, 54.2, 33; *p*-methylbenzylidene diacetate, 4.4, 1.9; and *p*-xylylene diacetate, 34.8, 15.7.

Distillation gave 44.3 g (27.0%) of *p*-methylbenzyl acetate, bp 170–174° (200 mm) [lit.[8] bp 227–230° (760 mm)], identified by its ir spectrum.

The pot residue (41.6 g) solidified upon cooling. Crystallization from petroleum ether (bp 60–70°) afforded 23.1 g (10.4%) of *p*-xylylene diacetate, mp 49–51° (lit.[11] mp 45–49°), identified by its ir and nmr spectra.

p-Tolualdehyde and *p*-methylbenzylidene diacetate were identified by their glpc retention times. No carboxylic acids were found by the usual procedure.

Oxidation of Durene in Acetic Acid.—The procedure described under III was followed using 50.0 g (0.36 mol) of durene instead of toluene. After 4 days, the reaction mixture was worked up, and 20.6 g (41.2% recovery) of durene, mp 77.5–79.5° (lit.[12] mp 79–80°), was obtained by sublimation. Distillation of the sublimation residue gave 19.1 g (27.7%) of 2,4,5-trimethylbenzyl acetate: bp 95° (1 mm) [lit.[13] bp 141–150° (9 mm)]; ir (neat) 5.77 (ester C=O) and 8.10 μ (acetate); nmr ($CDCl_3$) δ 5.04 ppm ($ArCH_2OAc$).

Acidification of the aqueous layers gave 0.2 g (0.34%) of 2,4,5-trimethylbenzoic acid, mp 154–156° (lit.[14] mp 150°).

Oxidation of Hexamethylbenzene in Acetic Acid.—The procedure described under III was followed using 25.0 g (0.15 mol) of hexamethylbenzene instead of toluene and a reaction time of 4 days. After the usual work-up, the residue was chromatographed in 2-g portions on 100 g of 28–200 mesh silica gel. Elution with petroleum ether (bp 60–70°) gave 7.4 g (32.6% recovery) of hexamethylbenzene, mp 164–165° (lit.[15] 165–166°); elution with chloroform gave 7.0 g (21.9%) of 2,3,4,5,6-pentamethylbenzyl acetate, recrystallized from methylcyclohexane, mp 82–84° (lit.[16] mp 83–85°), identified by its ir and nmr spectra.

Oxidation of Ethylbenzene in Acetic Acid.—The procedure described under III was followed using 106.0 g (1.00 mol) of ethylbenzene instead of toluene. After 25 hr the usual work-up gave (by glpc) 17.6 g (16.6% recovery) of ethylbenzene and [compound, wt (g), % yield] styrene (I), 1.67, 1.6; α-methylbenzyl acetate (II), 4.81, 2.9; β-phenylethyl acetate (III), 1.62, 1.0; *cis*-styryl acetate (IV), 1.63, 1.1; *trans*-styryl acetate (V), 2.06, 1.3; phenylacetaldehyde (VI), 0.16, 0.1; acetophenone (VII), 0.36, 0.3; and two unknowns (1.54 g).

Compounds I–V were isolated by preparative glpc and identified by their ir spectra. Compounds VI and VII were identified by their glpc retention times.

IV. Oxidation of *o*-Xylene in Acetic Acid.—A charge of 482.0 g (8.04 mol) of acetic acid, 106.0 g (1.0 mol) of *o*-xylene, 107.9 g (1.10 mol) of potassium acetate, 28.4 g (0.12 mol) of stannous acetate, 7.2 g (0.032 mol) of palladium(II) acetate, and 33.6 g of charcoal was stirred at 100° for 24 hr. The usual work-up gave (by glpc) [compound, wt (g), % yield] *o*-xylene, 1.6, 1.5; *o*-methylbenzyl acetate, 40.5, 24.7; *o*-methylbenzylidene diacetate, 3.2, 1.4; and *o*-xylylene diacetate, 26.8, 12.1.

Fractionation gave 33.9 g (22.6%) of *o*-methylbenzyl acetate, bp 94° (5 mm) [lit.[17] bp 119–121° (15 mm)], and 24.4 g (11.0%) of *o*-xylylene diacetate, bp 151° (5 mm), which crystallized on standing. Recrystallization from petroleum ether (bp 30–60°) gave a white powder, mp 33.5–34.5° (lit.[18] mp 35–36°). The products were identified by their ir and nmr spectra.

Oxidation of *m*-Xylene in Acetic Acid.—The procedure described under IV was followed using 106.0 g (1.0 mol) of *m*-xylene instead of *o*-xylene. The usual work-up gave (by glpc) [compound, wt (g), % yield] *m*-tolualdehyde, 8.0, 6.8; *m*-methylbenzyl acetate, 26.5, 16.2; *m*-methylbenzylidene diacetate, 5.6, 2.5; and *m*-xylylene diacetate, 40.0, 18.0.

Fractionation yielded 22.3 g (13.6%) of *m*-methylbenzyl acetate, bp 94° (5 mm) [lit.[19] bp 226° (760 mm)], and 36.3 g (16.4%) of *m*-xylylene diacetate, bp 158° (5 mm).

m-Tolualdehyde and *m*-methylbenzylidene diacetate were identified by their glpc retention times. *m*-Methylbenzyl acetate and *m*-xylylene diacetate were identified by their ir and nmr spectra.

m-Xylylene diacetate was prepared independently from *m*-xylylene glycol and acetyl chloride and had bp 154° (5 mm); ir (neat) 5.87 (ester C=O) and 8.12 μ (acetate); nmr ($CDCl_3$)

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δ 1.97 (s, 6, CH_3CO—), 5.03 (s, 4, $ArCH_2O$—), and 7.25 ppm (m, 4, aromatic).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.9; H, 6.4. Found: C, 65.1; H, 6.5.

Oxidation of Mesitylene in Acetic Acid.—The procedure described under IV was followed using 60.0 g (0.50 mol) of mesitylene instead of *o*-xylene and half of the amounts of the other reactants. After the usual work-up, distillation gave 25.0 g (41.6% recovery) of mesitylene and 4.5 g (5.0% based on mesitylene charged) of 3,5-dimethylbenzyl acetate, bp 154° (35 mm) [lit.[20] bp 99–105° (4 mm)], identified by its ir spectrum. The pot residue (2.7 g) contained 20 unknown peaks by glpc.

V. Oxidation of Toluene in Propionic Acid.—A charge of 250.0 g (3.34 mol) of propionic acid, 36.8 g (0.46 mol) of lithium propionate, 36.8 g (0.40 mol) of toluene, 7.1 g (0.03 mol) of stannous acetate, and 17.2 g (0.008 mol) of 5% palladium on charcoal was stirred at 100° for 6 hr. The usual work-up gave (by glpc) [compound, wt (g), % yield] toluene, 4.8, 13.0; benzaldehyde, 0.1, 0.2; benzyl acetate, 0.3, 0.5; benzyl propionate, 13.7, 20.8; and benzylidene dipropionate, 0.8, 0.8.

Distillation gave 11.3 g (17.3%) of pure benzyl propionate, bp 87–88° (1 mm) [lit.[21] bp 222° (760 mm)], identified by its ir spectrum. The other products were identified by their glpc retention times.

VI. Oxidation of Hexamethylbenzene in Propionic Acid.—A charge of 592.0 g (8.00 mol) of propionic acid, 88.0 g (1.10 mol) of lithium propionate, 36.6 g (0.226 mol) of hexamethylbenzene, 28.4 g (0.12 mol) of stannous acetate, and 34.4 g (0.016 mol) of 5% palladium on charcoal was stirred at 145° for 4 days. After the usual work-up, 17.8 g (48.6% recovery) of hexamethylbenzene was obtained by sublimation. Distillation of the sublimation residue gave 14.1 g (26.5%) of 2,3,4,5,6-pentamethylbenzyl propionate, bp 170° (5 mm). The distillate solidified on standing and after crystallization from petroleum ether (bp 60–70°) had mp 78–79°; ir (KBr) 5.80 (ester C═O) and 8.40 μ (propionate); nmr ($CDCl_3$) δ 1.14 (t, 3, J = 7.5 Hz, $CH_3CH_2CO_2$—), 2.24 (m, 17, $CH_3CH_2CO_2$— and $ArCH_3$), and 5.29 ppm (s, 2, $ArCH_2O$—).

Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.9; H, 9.5. Found: C, 77.2; H, 9.8.

Registry No.—Toluene, 108-88-3; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; mesitylene, 108-67-8; durene, 95-93-2; hexamethylbenzene, 87-85-4; ethylbenzene, 100-41-4; $Pd(OAc)_2$, 3375-31-3; $Sn(OAc)_2$, 638-39-1; $(C_6H_5)_3P$, 603-35-0; $(C_2H_5O)_3P$, 122-52-1; $C_6H_5CH_2OAc$, 140-11-4; *m*-xylylene diacetate, 17604-82-9; 2,3,4,5,6-pentamethylbenzyl propionate, 17604-83-0.

Acknowledgment.—We wish to thank Mr. John R. Morrison for his excellent technical assistance in the development of these procedures.

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The Photorearrangements of 2,4-Disubstituted Phenyl Esters[1-3]

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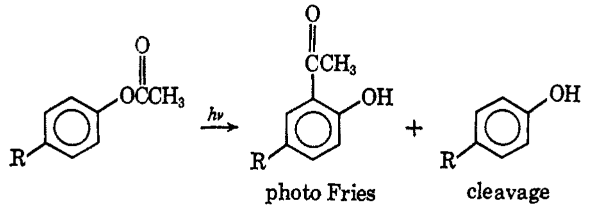
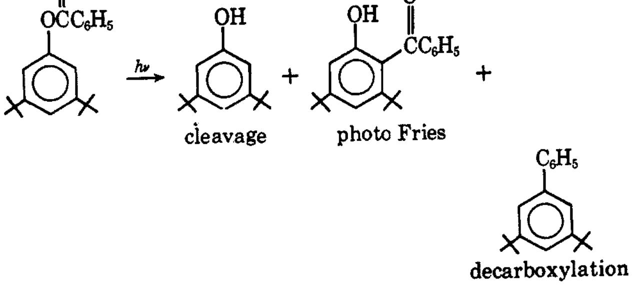
Received March 26, 1968

Various 2- and 2,4-disubstituted phenyl esters have been irradiated by ultraviolet light, and the products have been isolated and characterized. The relative large numbers of products obtained (up to six) showed that at least five different reactions were taking place: (1) photo Fries rearrangements resulting in *o*-hydroxyacetophenones, (2) photo Fries rearrangements in which methoxy groups were displaced resulting in *o*- and *p*-hydroxyacetophenones, (3) cleavage reactions resulting in phenols and in one case benzaldehyde, (4) decarboxylation reactions resulting in methylbenzene and biphenyl compounds, and (5) phototransposition of the ring carbon atoms resulting in rearranged methylbenzene and biphenyl compounds. Mechanisms for the various reactions are discussed.

The photochemical reactions of aryl esters have drawn considerable interest in recent years.[4-8] The photo Fries rearrangement of these esters to yield hydroxyaceto- and hydroxybenzophenone was first reported by Anderson and Reese[4] and Kobsa.[5] Along with the photo Fries, these workers also observed a considerable amount of cleavage products. More recently some attention has been given to the mechanisms of this reaction.[6,7]



With sterically hindered aryl esters, the normal photo Fries and cleavage reactions are accompanied by decarboxylation[8] and, in some cases, decarbonylation[8d] reactions. For example, the photolysis of 3,5-di-*t*-butylphenyl benzoate gave 3,5-di-*t*-butylbiphenyl



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[1] Supported by the Research Division, Brigham Young University, and the United Fund of Utah County.

[2] Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837.

[3] Presented in part by E. L. Loveridge at the student section of the Pacific Northwest Regional American Chemical Society Meeting, Richland, Wash., June 1967.

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