

## Acetoxylation of Aromatic Compounds by Potassium Peroxydisulphate in Acetic Acid with Palladium(II) Complexes as Catalysts

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**Summary** Aromatic compounds undergo a clean, predominantly *meta*-directing acetoxylation with potassium peroxydisulphate in glacial acetic acid, using Pd<sup>II</sup> complexes with amines as catalysts.

THE palladium(II)-mediated acetoxylation of aromatic compounds in glacial acetic acid is known to be favoured by the addition of certain co-oxidants, *e.g.*, dichromate<sup>1</sup> or nitrate ion.<sup>2,3</sup> We have recently found<sup>4</sup> that isolable amine-nitrate-acetate complexes of Pd<sup>II</sup>, such as acetate-(2,2'-bipyridine)nitratopalladium(II), act as efficient catalysts for this process, the previously described<sup>5</sup> anomalous *meta* selectivity being retained to some extent. Concurrent nitration is, however, a troublesome side-reaction with activated aromatic compounds.<sup>4,6</sup>

We now report that potassium peroxydisulphate<sup>7,8</sup> acts as a co-oxidant in a remarkably clean acetoxylation. Some results for the acetoxylation of aromatic substrates are

given in the Table. Generally, potassium peroxydisulphate is added to a solution of substrate, additive, and palladium (II) acetate in glacial acetic acid and the heterogeneous mixture stirred at 110 °C until all the peroxydisulphate has been consumed (after 4 h). No precipitation of Pd<sup>0</sup> occurs, except in one case (expt. No. 7).

Without added palladium acetate, no reaction takes place, showing that the role of peroxydisulphate ion is to assist at some stage of the process after a palladium species has attacked the aromatic ring<sup>4</sup> (the reaction is much slower in the absence of co-oxidant<sup>5</sup>). The reaction is clearly catalytic in palladium, as shown by the more than stoichiometric yields obtained in most cases. Yields based on the amount of peroxydisulphate salt used are low in most cases, although experiment 9 shows that a yield of up to 35% can be obtained. Since optimization experiments have not so far been performed, it is too early to judge this aspect.

The *meta* selectivity is retained in most cases, although

TABLE. Acetoxylation of some aromatic compounds with a Pd<sup>II</sup> complex as a catalyst in the presence of potassium peroxydisulphate

Experiment	Compound	Amount of K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , mmol	Additive, mmol	Yield <sup>b</sup> (%)	Nuclear acetates			Other products <sup>b</sup>
					Isomer distribution			
					<i>ortho</i>	<i>meta</i>	<i>para</i>	
1	Benzene	20	2,2'-Bipyridine	292				Unidentified compounds, 44
2	Toluene	10	—	71	20	50	30	PhCH <sub>2</sub> OAc, 22
3	Toluene	10	2,2'-Bipyridine, 1.0	100	3	60	37	PhCH <sub>2</sub> OAc, 22
4	Anisole	20	2,2'-Bipyridine, 0.5	193	3	61	36	PhOCH <sub>2</sub> OAc, 33
5	<i>p</i> -Xylene	10	2,2'-Bipyridine, 1.0	Trace				<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OAc, 45
6	Chlorobenzene	20	2,2'-Bipyridine, 0.5	191	7	49	44	
7 <sup>c</sup>	Chlorobenzene	10	Pyridine, 1.3	80	39	60	1	
8	Chlorobenzene	20	Isoquinoline, 1.0	137	43	34	24	
9 <sup>d</sup>	Chlorobenzene	10	2,2'-Bipyridine, 0.5	350	5	51	44	Traces of diacetoxy-chlorobenzenes

\* Conditions used in all experiments, unless otherwise noted: substrate (10.0 mmol), Pd(OAc)<sub>2</sub> (1.0 mmol), glacial acetic acid (50 ml), 110 °C, 4 h reaction. <sup>b</sup> Based on Pd(OAc)<sub>2</sub>. <sup>c</sup> Pd<sup>0</sup> precipitated towards the end of the reaction. <sup>d</sup> 30 mmol of chlorobenzene.

the very high selectivity reported under somewhat different conditions<sup>5</sup> is not obtained. Finally, it is important to note that the acetoxylation is remarkably clean when potassium peroxydisulphate is used as a co-oxidant; this is a distinct advantage over using nitrate ion. On the other hand, with peroxydisulphate it is not possible to have a catalytic

system with oxygen as the ultimate oxidant.<sup>4</sup>

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<sup>5</sup> L. Ebersson and L. Gomez-Gonzalez, *Acta Chem. Scand.*, 1973, **27**, 1249; *Chem. Comm.*, 1971, 263.

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<sup>7</sup> Similar chlorinations *via* peroxydisulphate-copper(II) chloride systems were recently described: A. Ledwith and P. J. Russell, *J.C.S. Chem. Comm.*, 1974, 291.

<sup>8</sup> For a survey of peroxydisulphate reactions, see: A. Ledwith and P. J. Russell, *J.C.S. Perkin II*, 1974, 582.