Palladium(II)-catalysed Nitration of Benzene

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SOLUTIONS of Pd^{II} salts in acetic acid are capable of catalysing the oxidation of benzene to mixtures of phenyl acetate[1] and biphenyl[1,2] in which the latter predominates. Added acetate (as LiOAc) raises the proportion of phenyl acetate produced,[1] suggesting that the pathway leading to its formation may involve nucleophilic attack by acetate on an arylpalladium intermediate.

The *direct* introduction of an oxygen function into an unactivated aromatic nucleus is unusual,[‡] and we wondered whether other added nucleophiles could participate in the reaction. The discovery of a novel Pd^{II}-catalysed nitration of benzene during the course of our work on this problem prompts us to communicate our findings.[3]

Very finely divided metallic palladium may be prepared conveniently by the reduction of aqueous solutions of Pd^{II} salts (acetate, chloride, nitrate, *etc.*) using either sodium borohydride or hydrazine hydrate.[4] If the reduction is carried out in the presence of a protective colloid,[4] colloidally dispersed Pd^0 results. In contrast to massive palladium, palladium black prepared in this way was readily attacked and dissolved by the addition of $NaNO_2$, N_2O_4, or $NO–O_2$ mixtures to its suspension in acetic acid.[5] The resulting solutions exhibited u.v. spectra identical with those of solutions of $Pd(OAc)_2$ in acetic acid to which $NaNO_2$, N_2O_4, or $NO–O_2$ mixtures had been added, demonstrating the presence of a common Pd^{II} complex in solution.

All these solutions catalyse the oxidative substitution of benzene to mixtures of phenyl acetate[§] and nitrobenzene.[§] Typical results are presented in the Table. No biphenyl is formed, even when benzene is present in excess. Smaller amounts of deeply coloured crystalline material were also isolated and shown by t.l.c. (silica gel) to consist of at least three compounds. By comparison of R_F factors with those of authentic materials, these by-products were shown to be neither polynitrated benzene derivatives, nitrated biphenyls, nor nitrophenyl acetates; none of them contained palladium (*X*-ray analysis). Ir. spectra of these substances (isolated by preparative scale t.l.c.) were inconclusive.

Pd^{II}-*catalysed oxidation of benzene*[a] *in acetic acid*; *at* 100° *for* 18 *hr.*

Run	Total Pd (mmole)	Oxidant added as	PhOAc (mmole)	$PhNO_2$ (mmole)
1[b]	0·10	$NaNO_2$	0·60	0·80
2[b]	0·00	$NaNO_2$	0·00	0·00
3[b,c]	0·50	$NaNO_2$	(1)[d]	(2)[d]
4[b]	0·30	N_2O_4	0·35	0·60
5	2·20	$NO + O_2$	0·45	0·20

[a] 10 ml. of benzene in 50 ml. of catalyst solution; [b] solution saturated with LiOAc; [c] reaction mixture subjected to exhaustive vacuum-degassing before heating; [d] relative yield.

The truly catalytic nature of the reaction was established by carrying out an experiment of three days' duration in which N_2O_4 was fed continuously at a slow rate to a refluxing mixture of benzene and the catalyst solution. At the end of this period no palladium had precipitated; the solution remained catalytically active. Furthermore, the yield of oxidized products corresponded to a "turnover number" of *ca.* 60 based on the number of moles of palladium present.

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[‡] Known methods include Fenton's reagent, transition-metal and Lewis-acid-catalysed decomposition of peroxydicarbonates, peracid–BF_3 mixtures, anodic oxidation, and enzymic hydroxylation.

[§] Trapped from gas-chromatograph effluent and identified by comparison of i.r. and n.m.r. spectra with those of authentic materials.

[1] J. M. Davidson and C. Triggs, *Chem. and Ind.*, 1966, 457.

[2] R. van Helden and G. Verberg, *Rec. Trav. chim.*, 1965, **84**, 1263.

[3] For a review of nitration reactions, see J. H. Ridd in "Studies on Chemical Structure and Reactivity," ed. J. H. Ridd, Wiley, New York, 1966, ch. 7.

[4] G. Brauer "Handbook of Preparative Inorganic Chemistry," vol. II, 2nd edn., Academic Press, New York, 1965, p. 1581.

[5] R. F. Schramm and B. B. Wayland, *Chem. Comm.*, 1968, 898, report the oxidation of palladium by $NOBF_4$, NO_2BF_4, and N_2O_4.