Tetrahedron Letters No.30, pp. 3371-3373, 1968. Pergamon Press. Printed in Great Britain.

BENZYLIC OXIDATION WITH PALLADIUM(II) ACETATE

David R. Bryant, James E. McKeon, and Bernard C. Ream
(Research and Development Department,
Union Carbide Corporation,
Chemicals and Plastics,
South Charleston, West Virginia 25303)

(Received in USA 8 April 1968; received in UK for publication 29 April 1968)

Sometime ago, we discovered that palladium(II) acetate is an efficient reagent for benzylic oxidation of alkylbenzenes. For example, heating a mixture of 0.10 mole of toluene, 0.20 mole of potassium acetate, and 0.01 mole of palladium(II) acetate in 1.67 moles of acetic acid at 100° for 5 hours gave a 92.5% yield of benzyl acetate (based on palladium(II) acetate), along with 6.0% of benzylidene diacetate and a trace of benzaldehyde.

We were, therefore, somewhat surprised when van Helden and Verberg(1) reported that the reaction of toluene with palladium(II) chloride in acetic acid under strikingly similar conditions gave completely different results. These authors obtained a 75% yield (based on palladium(II) chloride) of a mixture of bitolyls by heating 0.50 mole of toluene, 0.20 mole of sodium acetate, and 0.04 mole of palladium(II) chloride in 2.57 moles of acetic acid at 100° for 5 hours.

More recently, Davidson and Triggs(2) reported that a moderate yield of benzyl acetate is obtained from the reaction of toluene with palladium(II) acetate in acetic acid at 100°. By adding 12% perchloric acid, they obtained a comparable yield of a mixture of bitolyls.

We have developed an efficient, liquid-phase, catalytic process for benzylic oxidation, based on the stoichiometric reaction of toluene with palladium(II) acetate in acetic acid. During our development studies, we resolved the apparent disparity between our results and those of van Helden and Verberg(1). The explanation is found in the data of Tables I and II.

TABLE I[a,b]

REACTIONS OF TOLUENE WITH PALLADIUM(II) ACETATE AND POTASSIUM ACETATE IN ACETIC ACID AT 100° FOR 5 HOURS

Rx #	KOAc (moles)	KOAc/Pd(OAc)$_2$	C_6H_5CHO	$C_6H_5CH_2OAc$	$C_6H_5CH(OAc)_2$	% Benzylic Oxidation	% Isomeric Bitolyls	% Total Yield (Pd(OAc)$_2$)
1	0.05	5	Trace	53.0	6.0	59.0	3.0	62.0
2	0.10	10	Trace	67.4	7.0	74.4	1.2	75.6
3	0.15	15	Trace	69.4	6.2	75.6	<0.2	75.6
4	0.20	20	Trace	92.5	6.0	98.5	<0.2	98.5

a All reactions contained the indicated amount of potassium acetate, plus 1.67 moles of acetic acid, 0.1 mole of toluene, and 0.01 mole of palladium(II) acetate, and were heated at 100° for 5 hours with stirring.

b. Reactions 1 through 4 contained <0.1% of a material with the retention time of bibenzyl. This material could not be detected in the reactions carried out with palladium(II) chloride (Table II). Reaction 1 and all the reactions in Table II contained a small amount of tolyl acetate (by retention time only).

Table I illustrates the effect of increasing the concentration of potassium acetate(*) upon the product from the reaction of toluene and palladium(II) acetate in acetic acid. The yield of benzylic oxidation products increases with the molar ratio of potassium acetate to palladium(II) acetate. The yield of the mixture of bitolyls, small at the lowest ratio, becomes negligible as acetate concentration is increased.

TABLE II[a]

REACTIONS OF TOLUENE WITH PALLADIUM(II) CHLORIDE AND SODIUM ACETATE IN ACETIC ACID AT 100° FOR 5 HOURS

Rx #	* NaOAc (moles)	NaOAc/PdCl$_2$	% C_6H_5CHO	% $C_6H_5CH_2OAc$	% $C_6H_5CH(OAc)_2$	% Benzylic Oxidation	% Isomeric Bitolyls	Total Yield (PdCl$_2$)
5	0.20	5	0	1.7	0	1.7	64.3	66.0
6	0.40	10	0.9	5.0	0.5	6.4	30.0	36.4
7	0.60	15	5.0	50.0	5.0	60.0	7.5	67.5
8	0.80	20	1.5	62.5	4.0	68.0	0.5	68.5

a. All reactions contained the indicated amount of sodium acetate, plus 2.57 moles of acetic acid, 0.5 mole of toluene, and 0.04 mole of palladium(II) chloride, and were heated at 100° for 5 hours with stirring.

---

* Sodium acetate and potassium acetate can be used interchangeably in all of these reactions without any appreciable change in the results.

Table II presents the results of a comparable series of reactions using palladium(II) chloride as the oxidant. Reaction 5 is a repetition of the original coupling reaction as reported.(1) Under the range of conditions studied by van Helden and Verberg, palladium(II) chloride is an effective reagent for coupling aromatic rings. At higher acetate to palladium ratios, benzylic oxidation is the only important reaction.

The sharp decrease in overall yield at intermediate acetate to palladium ratios, e.g., reaction 6, is a reproducible phenomenon. This shows that the increase in acetate concentration does not simply increase the rate of benzylic oxidation relative to coupling. Instead, we must suppose that the palladium species responsible for the coupling reaction is altered as the acetate concentration is increased. There is, in addition, some acceleration of the benzylic oxidation by increased acetate concentrations. We suggest that the coupling reaction requires an aggregate of two or more palladium ions connected by bridging ligands. The bridged structures are easily broken down in the case of palladium(II) acetate, with more difficulty in the case of palladium(II) chloride, since chloride is a more effective bridging ligand than acetate. A palladium species of lower aggregation, possibly mono-nuclear, is the reagent responsible for benzylic oxidation.

Other experiments support this hypothesis. We hope to report on this work in the near future, as well as on the catalytic process and unexpectedly complex interactions which have been identified in our mechanistic studies.

References

1. R. van Helden and G. Verberg, Recueil, 84, 1263-73 (1965); U. S. 3,145,237, August 18, 1964.
2. J. M. Davidson and C. Triggs, Chem. and Ind., March 12, 1966, p. 457.