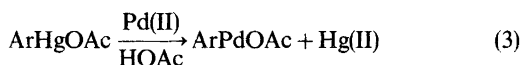
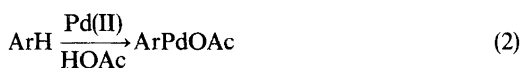
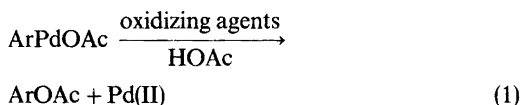


Studies on Electrolytic Substitution Reactions. XV.* Palladium(II) Promoted Anodic Substitution of Arylmercury(II) Acetates

LENNART JÖNSSON

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

Arylpalladium(II) intermediates can be oxidized to aryl acetates, by different oxidants such as dichromate,¹ nitrate,² potassium peroxydisulfate³ and heteropoly acids⁴ (eqn. 1). In these reactions, the arypalladium(II) species were generated *via* two pathways (eqns. 2 and 3), electrophilic palladation of aromatic compounds or transmetallation of arylmercury(II) compounds in acetic acid at 90–110 °C.



In view of our interest in comparing homogeneous and anodic oxidation processes we have now investigated the possibility of oxidizing arypalladium(II) species anodically.⁵ A fundamental difficulty is the low stability of arypalladium(II) species, which causes decomposition to biaryls^{6,7} before they diffuse to the electrode. Arylpalladium(II) species formed *via* reaction (2) (at 90–110 °C in acetic acid) decompose too rapidly to be amenable to

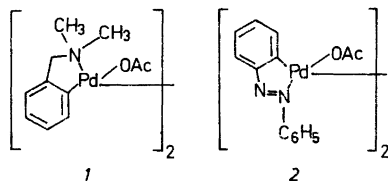
anodic oxidation. Therefore, it is necessary to generate the arypalladium(II) intermediate at room temperature *via* reaction (3), or to use nitrogen stabilized *ortho*-palladated substrates, *e.g.*, the *N,N*-dimethylbenzylamine-palladium(II) acetate complex (1) and the azobenzene-palladium(II) acetate complex (2).⁸ Initially, (1) and (2) were electrolyzed in HOAc/NaOAc solution. These reactions gave, however, no identifiable products, since possible products are oxidized very easily at the anode. On the other hand, anodic oxidation of arylmercury(II) compounds in the presence of palladium(II) acetate in HOAc/NaOAc gave aryl acetates.

The results are presented in Table 1, which shows that the distribution of the aryl acetate isomers is almost the same as that of the starting arylmercury(II) isomers. Note that removal of sodium acetate gave very low yields of aryl acetate, which is in agreement with earlier experience of anodic substitution.⁹ Control experiments showed (exp. 2) that no reaction occurs in the absence of palladium(II) acetate. This was expected since an attempt to run cyclic voltammetry on *p*-anisylmercury(II) acetate showed that no reaction occurred below the anodic limit of the electrolyte (Anodic limit = 3.5 V *vs.* SCE.) Other control experiments showed that if *p*-anisylmercury(II) acetate was treated with palladium(II) acetate at 30 °C, no nuclear acetate was formed.

Thus, the transformation of arylmercury(II) compounds to the corresponding aryl acetates requires both palladium(II) complexes and an oxidizing agent, *e.g.*, anodic oxidation. The same situation has previously been reported for palladium(II) catalyzed acetoxylation in homogeneous solution.^{1–4,10} It was also observed that during the anodic oxidation there was no precipitation of palladium(0).

It is well-known that treatment of arylmercury(II) compounds in acetic acid with palladium(II) complexes gives arypalladium(II) intermediates followed by biaryl formation.⁷ This reaction can be suppressed by adding strong oxidants, which favour the formation of aryl acetates.^{1–4} The present work shows that the biaryl formation can also be suppressed by a heterogeneous oxidant such as an anode.

An attempt to perform a mercury(II)/palladium(II) promoted anodic acetoxylation of aromatic compounds has only been successful with toluene (exp. 11). *tert*-Butylbenzene cannot be acetoxylation by this method, since *tert*-butylphenylmercury(II) acetate cannot be formed *in situ* at 30 °C (exp. 9). Experiment 5 shows that a small amount of anisole gives much less isomer selectivity. This indicates that direct anodic acetoxylation of anisole is much faster than mercuriation at 30 °C.



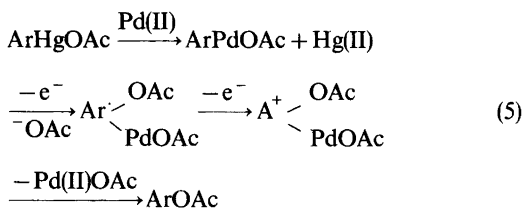
* Part XIV, see Ebersson, L. and Oberrauch, E. *Acta Chem. Scand. B* 33 (1979) 343.

Table 1. Palladium(II) promoted anodic aromatic substitution reactions in acetic acid.^a

| Exp. | Compound | Additive (mmol) | Nuclear acetate | | | |
|-----------------|---|--|-------------------------------|------------------------|----------|----------|
| | | | Current yield ^b /% | Isomer distribution, % | | |
| | | | | <i>o</i> | <i>m</i> | <i>p</i> |
| 1 | Anisole | — | — | 68 | 3 | 29 |
| 2 | <i>p</i> -Anisylmercury(II) acetate | — | No reaction | — | — | — |
| 3 ^c | <i>p</i> -Anisylmercury(II) acetate | Pd(OAc) ₂ (5) | 39 | 2 | <1 | 98 |
| 4 ^d | <i>p</i> -Anisylmercury(II) acetate | Pd(OAc) ₂ (5) | Trace | | | |
| 5 | <i>p</i> -Anisylmercury(II) acetate | Pd(OAc) ₂ (5) Anisole (1) | 10 | 29 | <1 | 71 |
| 6 | <i>tert</i> -Butylbenzene | — | — | 35 | 22 | 43 |
| 7 | <i>m</i> - and <i>p</i> - <i>tert</i> -Butylphenylmercury(II) acetate (35:65) | Pd(OAc) ₂ (5) | 10 | <1 | 35 | 65 |
| 8 | <i>m</i> - and <i>p</i> - <i>tert</i> -Butylphenylmercury(II) acetate (35:65) | Pd(OAc) ₂ (0.25) | 2 | <1 | 35 | 65 |
| 9 | <i>tert</i> -Butylbenzene | Hg(OAc) ₂ (2.5) Pd(OAc) ₂ (5) | 10 | 27 | 28 | 45 |
| 10 | Toluene | — | — | 43 | 11 | 46 |
| 11 ^e | Toluene | Hg(OAc) ₂ (2.5) Pd(OAc) ₂ (5) | 20 | 18 | 11 | 71 |
| 12 | Pentamethylphenylmercury(II) acetate | Pd(OAc) ₂ (5) | Trace | | | |

^a Reaction conditions, unless otherwise noted: anodic oxidation of the substrate (0.05 M) in acetic acid-sodium acetate (1 M) at constant current density (14 mA/cm²). Reaction temperature 30 °C. Reaction conditions in experiments 1, 6, and 10: Anodic acetoxylation of aromatic compounds in HOAc/NaOAc at Pt, data taken from Ref. 11. ^b GLC yield based on initial amount of substrate. ^c Small amounts of *p*-methoxyphenol and anisole were formed. ^d The supporting electrolyte, NaOAc, was replaced by Bu₄NBF₄ [Bu₄NBF₄] = 0.1 M. ^e Side-chain acetate was formed, 18 % of total amount of acetoxylation products.

This work does not permit the proposal of a definite mechanism, but some suggestions can be made (eqn. 5). The first step is the formation of the corresponding arylpalladium(II) intermediate by metal-exchange. The arylpalladium(II) intermediate then undergoes a one-electron transfer to the anode followed by an attack of acetate ion on the palladated carbon atom. The product is formed after a second electron transfer followed by a decomposition of a cationic species. Support for this mechanism comes from the fact that the reaction gives a substitution pattern close to the isomer distribution of the substrates. A similar mechanism has been suggested for anodic nuclear acetoxylation of aromatic compounds.^{9,11}



Experimental. The arylmercury derivatives were prepared according to known procedures.^{12,13} *p*-Anisylmercury(II) acetate was recrystallized twice from ethanol/water (50/50), m.p. 176–177 °C. *m*- and *p*-*tert*-butylphenylmercury(II) acetates were synthesized by the following method: A solution of 2 g (15 mmol) of *tert*-butylbenzene and 0.8 g (2.5 mmol) of mercury(II) acetate in glacial acetic acid (10 ml) was heated at 85 °C for 20 h. After reaction, the acetic acid and excess unreacted *tert*-butylbenzene was removed by evaporation *in vacuo* at 50 °C, and the residue (*m*- and *p*-*tert*-butylphenylmercury(II) acetate *m*:*p* = 35:65)¹⁴ was used in the electrolysis experiments. The *ortho*-palladation products were prepared by known methods.⁸ All other chemicals and reference compounds were of the quality and origin described in earlier work.^{3,11}

Electrolysis conditions. The reaction was carried out in a divided cell equipped with a platinum foil anode, and a platinum wire cathode. The separation of the anode compartment and the cathode was achieved by a ceramic cylinder. All reactions were run at a constant current density of 14 mA/cm². The substrate (2.5 mmol) and palladium(II) acetate (and

mercury(II) acetate (5 mmol)) and a 1 M sodium acetate solution in acetic acid (50 ml) were added to the anode compartment and the electrolysis was run till 2 F/mol had passed. The electrolyte was stirred vigorously using a magnetic stirring bar. The temperature during the electrolysis was 30 °C. The reaction mixture was worked up by the addition of sodium bicarbonate solution followed by ether extraction.

Analysis. Yields and isomer distributions were determined using a Varian 1400 gas chromatograph, equipped with an electronic integrator (Hewlett-Packard 3380 A) on a 2 m × 3 mm 5% NPGS on Chromosorb W column. The yield was determined using an internal standard calibrated against authentic samples. The identification of the products was based on GLC/MS comparison (LKB 9000 system) with authentic samples.

Acknowledgements. This work was supported by grants from the Swedish Natural Science Research Council and the Royal Physiographic Society in Lund. The author thanks Jeanette Schlaucher for technical assistance.

14. Brown, H. C. and Gianlorenzo, M. J. *Am. Chem. Soc.* 81 (1959) 5611.

Received August 7, 1980.

1. Henry, P. M. *J. Org. Chem.* 36 (1971) 1886.
2. Ebersson, L. and Jonsson, E. *Acta Chem. Scand. B* 28 (1974) 771.
3. Ebersson, L. and Jönsson, L. *Justus Liebigs Ann. Chem.* (1977) 233; *Chem. Commun.* (1974) 885.
4. Mennenga, G. U., Rudenkov, A. J., Matveev, K. L. and Kozhevnikov, J. V. *React. Kinet. Catal. Lett.* 5 (1976) 401; *Chem. Abstr.* 86 (1977) 105719.
5. Ebersson, L. and Wistrand, L.-G. *Justus Liebigs Ann. Chem.* (1976) 1777; Nyberg, K. and Wistrand, L.-G. *J. Org. Chem.* 43 (1978) 2163; Jönsson, L. and Wistrand, L.-G. *J. Chem. Soc. Perkin Trans. 1* (1979) 669; Ebersson, L. and Wistrand, L.-G. *Acta Chem. Scand. B* 34 (1980) 349.
6. Tsuji, J. In *Organic Synthesis with Palladium Compounds, Reactivity and Structure*, Springer, New York 1980, Vol. 10, Chapter III.
7. Unger, M. O. and Fouty, R. A. *J. Org. Chem.* 34 (1969) 18.
8. Thompson, J. M. and Heck, R. F. *J. Org. Chem.* 40 (1975) 2667.
9. Ebersson, L. and Nyberg, K. *Tetrahedron* 32 (1976) 2185.
10. Ebersson, L. and Gomez-Gonzalez, L. *Acta Chem. Scand.* 27 (1973) 1162, 1249, 1255.
11. Ebersson, L. *J. Am. Chem. Soc.* 89 (1967) 4669.
12. Dimroth, O. *Ber. Dtsch. Chem. Ges.* 35 (1902) 2853.
13. Smith, L. J. and Taylor, F. L. *J. Am. Chem. Soc.* 57 (1935) 2370.