ELSEVIER

Journal of Organometallic Chemistry 540 (1997) 185–187

Journal of Organometallic Chemistry

Priority communication

Nickel-promoted coupling of orthomanganated aryl ketones with alkenes as a route to indanols

Warren J. Grigsby, Lyndsay Main, Brian K. Nicholson *

School of Science and Technology, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received 5 December 1996; accepted 21 December 1996

Abstract

Orthomanganated aryl ketones undergo $NiBr_2(PPh_3)_2$-promoted reactions with activated alkenes to give indanol products with higher specificity than similar Pd(II)- or Me_3NO-promoted reactions. © 1997 Elsevier Science S.A.

Keywords: Aryl ketones; Alkenes

Cyclomanganated aryl ketones are proving to be versatile reagents in synthesis [1]. Reactions with alkynes [2], alkenes [3–5], isocyanates [6], SO_2 [7] or PhNSO [8] are well established, generally leading to new compounds arising from reactions at the Mn–C bond.

Previous work with functionalised alkenes has shown that three types of product can be obtained when the reactions are promoted by Pd(II) [1,3–5,9]. These are illustrated in Scheme 1. The distribution of products **1–3** varies somewhat unpredictably depending on the ketone, the alkene, the solvent and the reaction conditions, and the reaction is rarely specific. When the reactions are promoted using Me_3NO as initiator [4,5] they follow a similar course but can also give moderate yields of cyclopentanol-type products such as **4**.

We now report that the corresponding reactions when promoted by Ni(II) can be more specific and in most of the examples described here give indanols of type **4** in near-quantitative yields.

Orthomanganated acetophenone (**5a**) reacts with butenone in the presence of $NiBr_2(PPh_3)_2$ in refluxing acetonitrile over 1 h to form 2-acetyl-1-methyl-1-indanol (**6a**) in essentially quantitative yield. The product **6a** is a mixture of diastereoisomers which may be separated by chromatography. The stereochemistry of each diastereoisomer was unambiguously determined by ^1H NMR and nOe experiments. [1] Coupling **5a** with methyl propenoate under reflux in MeCN similarly gives a mixture of the diastereoisomers of the methyl ester of 1-hydroxy-1-methylindane-2-carboxylic acid

* Corresponding author.

[1] *Experimental.* Employing standard Schlenk techniques $NiBr_2(PPh_3)_2$ (0.218 g, 0.333 mmol) and [2-acetyl-κO-phenyl-κC]-tetra(carbonyl-κC)-manganese(I) **5a** (0.086 g, 0.301 mmol) were dissolved in acetonitrile (6 ml). 3-Buten-2-one (0.6 ml, 7.21 mmol) was added and the solution refluxed for 1 h. Chromatography with ethyl acetate–pet. spirit (3:7) yielded a colourless oil (0.052 g), identified as a mixture (^1H NMR ratio 7:4) of diastereoisomers of 2-acetyl-1-methyl-1-indanol **6a** (0.274 mmol, 91%). Isomer separation was achieved by further chromatography eluting with the same solvent. [1*R**,2*S**]-2-Acetyl-1-methyl-1-indanol has the following spectral characteristics: ^1H NMR($CDCl_3$) δ 7.24 (m, 4H, ArH), 3.24 (m, 2H, CH_2), 3.06 (d of d, $J = 7.8$, 13.4 Hz, 1H, CH), 2.27 (s, 3H, $COCH_3$), 1.71 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 210.1 (s, C=O), 146.5 (s, C7a), 140.4 (s, C3a), 128.6 (d, C4), 127.2 (d, C5), 124.7 (d, C7), 122.5 (d, C6), 81.2 (s, C–OH), 61.2 (d, C2), 32.5 (q, $COCH_3$), 30.8 (t, C3), 27.5 (q, CH_3); MS: *m/e* 172 ($M^+ - H_2O$), 147, 129, 115, 91. [1*S**,2*S**]-2-Acetyl-1-methyl-1-indanol has the following spectral characteristics: ^1H NMR ($CDCl_3$) δ 7.24 (m, 4H, ArH), 2.78 (d of d, $J = 7.2$, 15.8 Hz, 1H, CH), 2.51 (m, 2H, CH_2), 2.30 (s, 3H, $COCH_3$), 1.27 (s, 3H, CH_3); ^{13}C NMR (300 MHz) ($CDCl_3$) δ 208.4 (s, C=O), 148.0 (s, C7a), 140.4 (s, C3a), 128.2 (d, C4), 127.1 (d, C5), 124.8 (d, C7), 122.0 (d, C6), 82.6 (s, C–OH), 66.0 (d, C2), 31.0 (q, $COCH_3$), 30.4 (t, C3), 24.4 (q, CH_3); MS: *m/e* 172 ($M^+ - H_2O$), 157, 129, 115, 102. nOe was observed between the methyl and acetyl protons at δ 2.30 and 1.20 only in this isomer, indicating the cis stereochemistry of the groups. Other reactions, separations and characterisations were performed similarly.

PII S0022-328X(97)00025-9

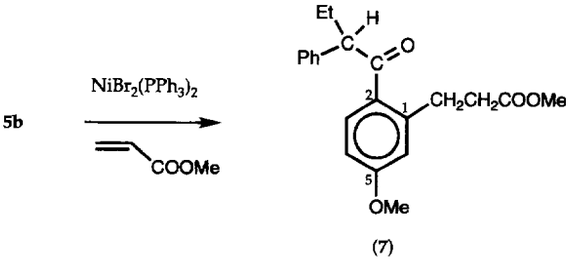
(**6b**) in 78% yield, together with 14% of the arylalkane methyl 3-(1-acetylphenyl)propanoate.

5a R' = Me R'' = H
5b R' = CH(Ph)Et R'' = OMe

6a R' = Me R'' = H R = C(O)Me
6b R' = Me R'' = H R = C(O)OMe
6c R' = CH(Ph)Et R'' = OMe R = C(O)Me

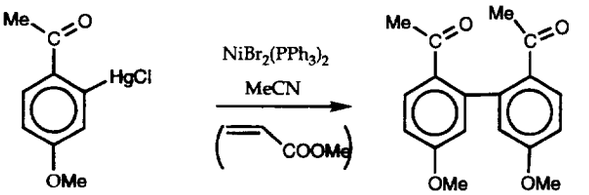
When the analogous manganacycle **5b**, which contains the bulky 1-phenylpropyl substituent, was reacted under the same conditions with butenone in the presence of $NiBr_2(PPh_3)_2$ the cyclised indanol product **6c** was isolated as a mixture of diastereoisomers in quantitative yield after 30 min.

Surprisingly, when **5b** was coupled with methyl propenoate in acetonitrile in the presence of $NiBr_2(PPh_3)_2$ it gave only 12% of a mixture of the corresponding indanol stereoisomers with methyl 3-(5-methoxy-2-(2-phenylbutanoyl)phenyl)propanoate **7**, as the major product (66%). As with the Pd(II)-promoted system, the course of the reaction is obviously sensitive to small changes in the reactants.



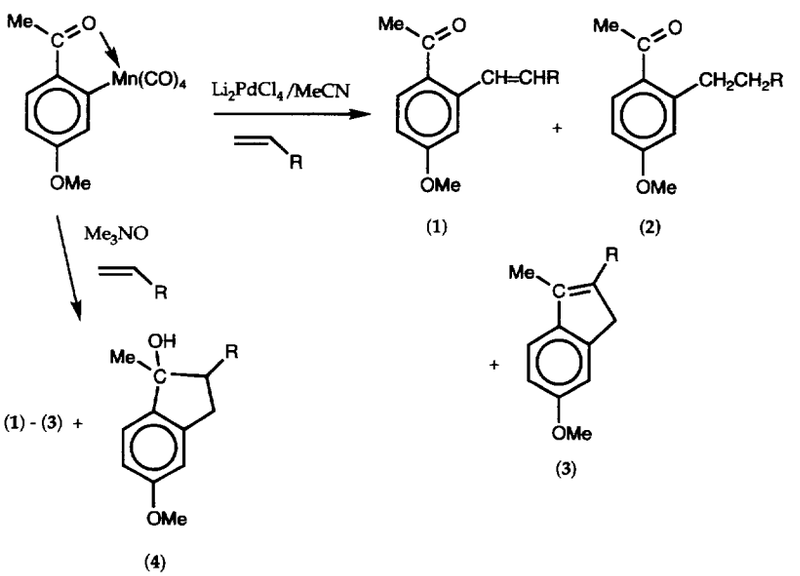
(7)

When the analogous coupling reaction was attempted in acetonitrile using the orthomercurated compound **8** as a substrate, with methyl propenoate in the presence of Ni(II), no species incorporating the alkene was found; rather the major product was the cross-coupled dimer **9**, in 46% yield.



(8) (9)

The reaction of **5a** with butenone was repeated in the presence of PPh_3 rather than $NiBr_2(PPh_3)_2$, but only a



Scheme 1.

slow reaction leading to a multiplicity of minor products took place, showing that it is the Ni(II) that is promoting the reaction and not free PPh_3 which could conceivably have induced reactions by carbonyl-displacement from **5a**.

While the types of product obtained from the Ni(II) reactions of the orthomanganated complexes **5a** and **5b** with alkenes have been described previously, the results reported here are significant since:

1. the reactions so far examined indicate higher product specificity than the corresponding Pd(II) or Me_3NO initiated ones, and would be the method of choice if indanol products were sought;
2. $NiBr_2(PPh_3)_2$ is less expensive than the corresponding Pd(II) reagents;
3. there are mechanistic implications.

With respect to the last point we note that it is usually assumed that transmetallation of the arene from manganese to palladium is a key initial step in Pd(II)-promoted reactions. We have previously demonstrated by comparing parallel reactions with orthomanganated and orthomercurated substrates that the role of the manganese is more than just as a source of the organic fragment in Pd(II)-promoted reactions [1,9], and the results with Ni(II) for the manganese substrate **5a** and the corresponding mercury substrate **8** extend this conclusion to Ni(II)-promoted reactions. Transmetallation for **8** from mercury to Ni(II) is probable since the product **9** is that expected from such a process, based on the well-established use of $NiBr_2(PPh_3)_2$ as a cross-coupling centre for Grignard reagents [10]. However the role of the manganese is obviously more complex.

Further discussion of reaction pathways is deferred to a full paper.

References

[1] L. Main, B.K. Nicholson, Adv. Metal Org. Chem. 3 (1994) 1.
[2] L.S. Liebeskind, J.R. Gasdaska, J.S. McCallum, S.J. Tremont, J. Org. Chem. 54 (1989) 669. N.P. Robinson, L. Main, B.K. Nicholson, J. Organomet. Chem. 364 (1989) C37. R.C. Cambie, M.R. Metzler, P.S. Rutledge, P.D. Woodgate, J. Organomet. Chem. 429 (1992) 41.
[3] (a) L.H.P. Gommans, L. Main, B.K. Nicholson, J. Chem. Soc. Chem. Commun. (1987) 12. (b) R.C. Cambie, P.S. Rutledge, D.R. Welch, P.D. Woodgate, J. Organomet. Chem. 467 (1994) 237.
[4] R.C. Cambie, M.R. Metzler, P.S. Rutledge, P.D. Woodgate, J. Organomet. Chem. 429 (1992) 59.
[5] R.C. Cambie, M.R. Metzler, C.E.F. Rickard, P.S. Rutledge, P.D. Woodgate, J. Organomet. Chem. 426 (1992) 213.
[6] L.S. Liebeskind, S.A. Johnson, J.S. McCallum, Tetrahedron Lett. 31 (1990) 4397.
[7] J.M. Cooney, C.V. Depree, L. Main, B.K. Nicholson, J. Organomet. Chem. 515 (1996) 109. C.V. Depree, L. Main, B.K. Nicholson, K. Roberts, J. Organomet. Chem. 517 (1996) 201.
[8] J.M. Cooney, L. Main, B.K. Nicholson, J. Organomet. Chem. 516 (1996) 191.
[9] J.M. Cooney, D. Phil. Thesis, University of Waikato, 1994.
[10] H.M. Colquhoun, J. Holton, D.J. Thompson, M.V. Twigg, in: New Pathways for Organic Synthesis, Plenum, New York, 1984.