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Benzylic Functionalization of Arene(tricarbonyl)chromium Complexes

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Summary The complexation of a Cr(CO)3 unit to an aromatic hydrocarbon enhances the benzylic position towards attack by base and the resulting carbanion reacts with carbonyl compounds to produce a complexed alcohol; this reaction may be used to functionalize the benzylic position of an aromatic hydrocarbon.

Carbanions are important intermediates in organic synthesis, so any temporary modification of an organic sub-

SCHEME 1. i, ButOK, Me2SO.

strate which increases its susceptibility to proton abstraction is of synthetic interest. Thus the strong electron-withdrawing character of the Cr(CO)3 group has been used in synthesis for the activation of arene substrates^{1,2,3} towards benzylic alkylation and the generation of stabilized benzylic anions.4 We report here the use of tricarbonylchromium complexes to functionalize the benzylic position of an aromatic hydrocarbon. The complex (1) in Me_oSO with Bu^tOK as base reacts with aldehydes (2) to produce the complexed alcohols (3) (Scheme 1).

In the presence of an enolic proton, however, the arene (tricarbonyl)chromium carbanion underwent proton exchange and the unchanged complex was recovered. To demonstrate this proton exchange the experiment outlined in Scheme 2 was conducted. The (tricarbonyl) ethylbenzenechromium carbanion (4) was treated with (CD₃)₂CO. After isolation a mixture of non-, mono-, and di-deuteriated (tricarbonyl)ethylbenzenechromium (5), (6) was isolated.

$$Cr(CO)_3$$
 $Cr(CO)_3$
 $Cr(CO)_3$

SCHEME 2. i, ButOK, Me₂SO, ii, (CD₃)₂CO.

The stereochemical course of the reaction was studied as follows. To the indanechromium(tricarbonyl) carbanion (7) solution formaldehyde was added. After isolation only one (tricarbonyl)(1-hydroxymethylindane)chromium isomer was obtained in 52% yield. Treatment of this alcohol with toluene-p-sulphonyl chloride gave the toluene-psulphonate which was reduced to (tricarbonyl)(1-methylindane)chromium (8) (Scheme 3).

$$Cr(CO)_3 \qquad \qquad Cr(CO)_3 \qquad \qquad Cr(CO)_4 \qquad \qquad Cr(CO)_5 \qquad \qquad Cr($$

SCHEME 3. i, HCHO, ii, MeC₆H₄SO₂Cl, iii, LiAlH₄.

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The stereochemistry of (8) was assigned from ¹H n.m.r. data (δ_{Me} 1·16). Jackson and coworkers report that the syn isomer of (8) has its methyl n.m.r. absorption at lower field (δ 1.28 p.p.m.) than the anti isomer (δ 1.16 p.p.m.). The attack of (7) by formaldehyde is stereospecific at the exo-position.

Similar stereospecificity has been found in the reduction

and alkylation of (tricarbonyl)indanonechromium and in the alkylation of (tricarbonyl)tetralonechromium.6,7

Satisfactory analytical and spectroscopic data have been obtained for all new compounds.

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