Benzylic Functionalization of Arene(tricarbonyl)chromium Complexes

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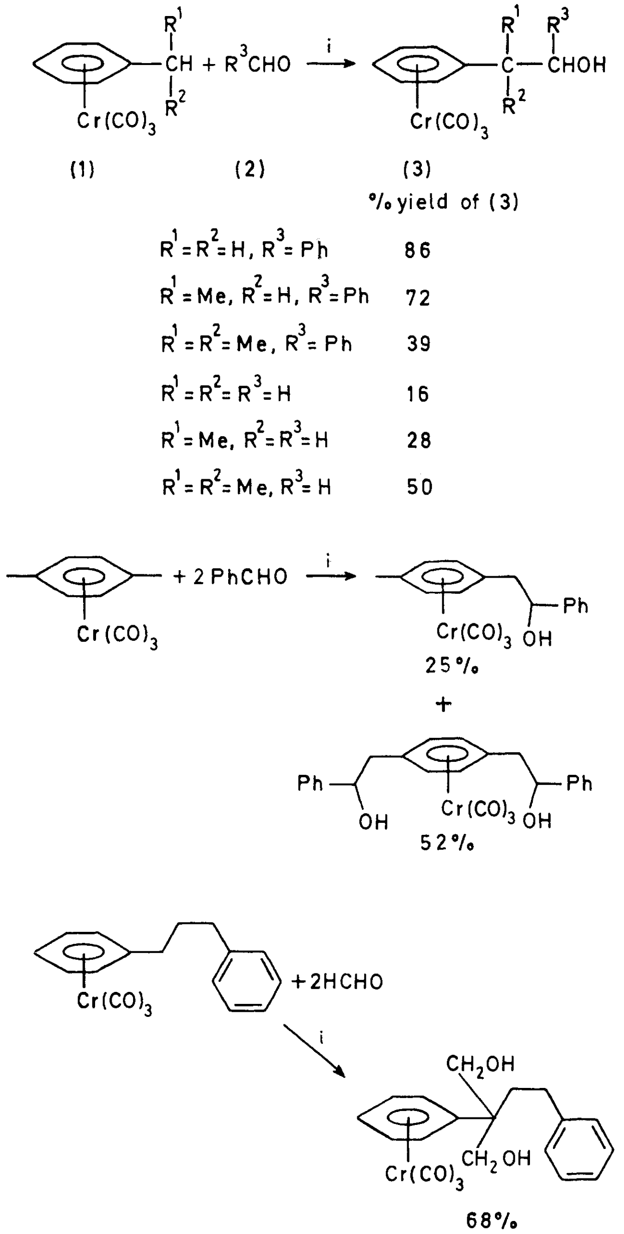
Summary The complexation of a $Cr(CO)_3$ unit to an aromatic hydrocarbon enhances the benzylic position towards attack by base and the resulting carbanion reacts with carbonyl compounds to produce a complexed alcohol; this reaction may be used to functionalize the benzylic position of an aromatic hydrocarbon.

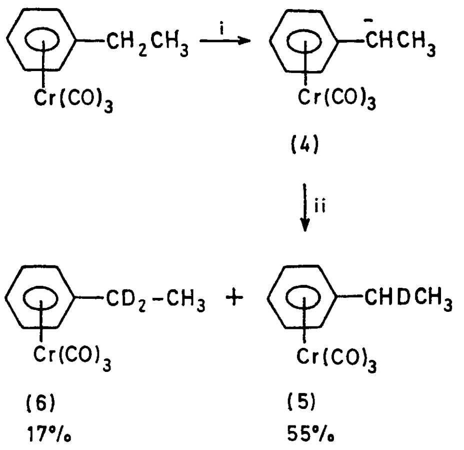
Carbanions are important intermediates in organic synthesis, so any temporary modification of an organic substrate which increases its susceptibility to proton abstraction is of synthetic interest. Thus the strong electron-withdrawing character of the $Cr(CO)_3$ group has been used in synthesis for the 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_2SO with Bu^tOK as base reacts with aldehydes (**2**) to produce the complexed alcohols (**3**) (Scheme 1).



	% yield of (3)
$R^1 = R^2 = H$, $R^3 = Ph$	86
$R^1 = Me$, $R^2 = H$, $R^3 = Ph$	72
$R^1 = R^2 = Me$, $R^3 = Ph$	39
$R^1 = R^2 = R^3 = H$	16
$R^1 = Me$, $R^2 = R^3 = H$	28
$R^1 = R^2 = Me$, $R^3 = H$	50

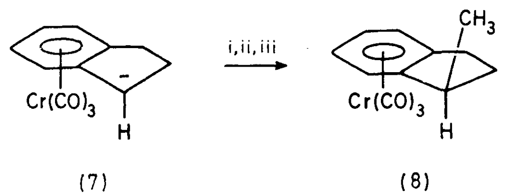
Scheme 1. i, Bu^tOK, Me_2SO.

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 $(CD_3)_2CO$. After isolation a mixture of non-, mono-, and di-deuteriated (tricarbonyl)ethylbenzenechromium (**5**), (**6**) was isolated.



Scheme 2. i, Bu^tOK, Me_2SO. ii, $(CD_3)_2CO$.

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-*p*-sulphonate which was reduced to (tricarbonyl)(1-methylindane)chromium (**8**) (Scheme 3).



Scheme 3. i, HCHO, ii, $MeC_6H_4SO_2Cl$, iii, $LiAlH_4$.

The stereochemistry of (**8**) was assigned from ^1H n.m.r. data (δ_{Me} 1·16). Jackson and coworkers[5] 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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