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HYDROFORMYLATION OF TRICARBONYL(η^6-STYRENE)CHROMIUM AND RELATED COMPOUNDS

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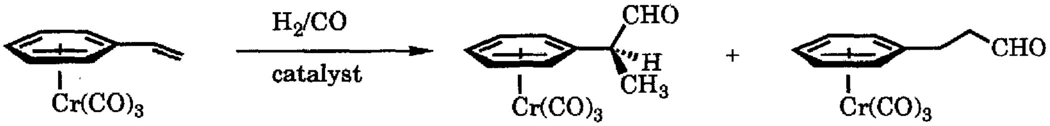
Hydroformylation of the tricarbonylchromium derivatives of styrene, indene, and dihydronaphthalene using rhodium - based catalysts gives α-arylaldehydes with high regioselectivity and, using appropriate chiral catalysts, with enantiomeric excesses of up to 50%.

Asymmetric hydroformylation of alkenylarenes has been used as a key step in enantioselective synthesis of a number of 2-arylpropanoic acids[1,2] which are in wide use as non-steroidal, anti-inflammatory agents.[3]. Enantiomeric excesses of 70-80% were obtained using a platinum catalyst system but the yields of aldehyde were not high and the reactions showed poor selectivity for the desired branch-chain compound[1].

Tricarbonylchromium compounds of alkenylarenes are readily available[4,5] and we have now found that these derivatives can be hydroformylated to give branch chain aldehydes in good yields under mild conditions and with better regioselectivity than the parent aromatics. Results using a range of catalyst systems for the hydroformylation of tricarbonyl(η^6-styrene)chromium (1) are given in the Table.



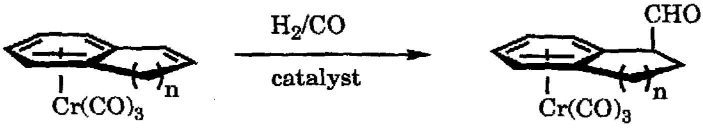
(1) (2) (3)

Reactivity

All hydroformylations of tricarbonyl(alkenylarene)chromiums using rhodium catalysts gave excellent yields (> 90%) of aldehydes. For example, reaction of (1) at 40° under a balloon of H_2/CO gave a high yield (96%) of product isolated as the corresponding alcohols after reduction with sodium borohydride. Under similar conditions styrene itself gave a modest yield of product (30%).

Regioselectivity

The regioselectivity of hydroformylation of styrene using Rh/PPh$_3$ catalysts leads to between 80 and 90% of the branched isomer and this was confirmed under the above conditions. The regioselectivity in the tricarbonylchromium derivatives increased to > 98% using the same reaction conditions. Similarly hydroformylation of the tricarbonylchromium derivatives of indene (4; n=1) and dihydronaphthalene (4; n=2) at 50°C gave virtually quantitative yields of the α-aldehydes(5). Under similar conditions indene and dihydronaphthalene proved to be relatively unreactive giving low yields of aldehydes (< 20%) with significant amounts of hydrogenated material.



(4) (5)

A dramatic change in regioselection was observed in the hydroformylation of α-methylstyrene which, at 100°C, gave aldehydes (33%) in a 9:1 ratio (terminal: to branched). Reaction of the tricarbonylchromium compound under *similar conditions* gave a similar yield of aldehydes but the ratio of linear: to branched isomers was approximately 1:1.

Asymmetric induction

Reactions of tricarbonyl(η^6-styrene)chromium with carbon monoxide and hydrogen in the presence of catalysts containing optically active ligands was next investigated. Reaction in the presence of diop and [Rh(CO)$_2$Cl]$_2$ gave aldehydes (2) and (3) in ratio 90:10 (entry 3) and the aldehyde (2) was formed with an e.e. of ca. 20%. The e.e. value is similar to that reported for hydroformylation of styrene[6] but in that case much less of the branched chain aldehyde was formed. Reactions involving the diphosphines (-) - *bppm and* (-) - *binap* with the rhodium catalyst system gave high yields of branch-chain aldehydes but with disappointingly low e.e.'s (entries 4 and 5).

Best results were obtained using (diop)PtCl$_2$/SnCl$_2$, yielding a 3:1 ratio of branched to linear aldehydes with an e.e. of 46% for the former. These values are a significant improvement over those quoted for reactions of styrene, where the branched to linear aldehyde ratios were approximately 1:2 and the e.e.'s for the branched aldehyde were 4-29%.[7]

Thus the hydroformylation of tricarbonyl(η^6-alkenylarylchromium compounds offers several advantages over reaction with the uncomplexed alkenylarene. These include (i) milder reaction conditions, (ii) better selectivity for branched aldehydes. Whilst the best e.e. obtained for the asymmetric hydroformylation of these complexes was only 46%, the use of a chiral diphosphine / $SnCl_2$ catalytic system appears quite promising.

Acknowledgement

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Table Hydroformylation of tricarbonyl(η^6-styrene)chromium

Entry Number	**Ligand**	**Time (h)**	**Temp (°C)**	**Ratio (2) (3)**	**Yield[c] %**	**Configuration[c] of major enantiomer**	**e.e.[c]**
Rhodium catalysts[a]							
1	PPh_3	20	30	>98:2	90	-	-
2	PPh_3[b]	20	40	>98:2	96	-	-
3	(-)-diop	66	50	90:10	82[e]	R	20[e]
4	(-)-bppm	66	50	95:5	70	S	14
5	(-)-binap	66	50	93:7	89	R	7
Platinum catalysts[d]							
6	(-)-diop	48	50	73:27	73[e]	R	46[e]
7	(-)-bppm	88	50	24:76	84[e]	S	40[e]
8	(-)-binap	66	65	32:68	36[e]	-	0[e]
9	(-)-chiraphos	20	80	65:35	19	R	6

a Reactions 1 and 2 were carried out using $HRhCO(PPh_3)_3$, PPh_3, and alkene in the ratio 1:50:300 with an initial pressure of 400 psi carbon monoxide and hydrogen. Reactions 3,4, and 5 were carried out using $[Rh(CO)_2Cl]_2$, diphosphine, and alkene in the ratio 1:2:300 with an initial pressure of 400 psi carbon monoxide and hydrogen.

b Reaction carried out under a balloon of carbon monoxide and hydrogen.

c The initially formed aldehydes (2) and (3) were reduced to the corresponding alcohols, chromium removed by exposure of a solution to air and light, and yields determined for the resulting alcohols. Configuration of the major enantiomer was determined by optical rotation and e.e. by the formation of an ester with Moshers acid and determining the relative integrals of the CF_3 absorptions in the ^{19}F n.m.r. spectra and the OMe signals in the ^{1}H n.m.r. spectra.

d Reactions were carried out using (diphosphine)$PtCl_2$, $SnCl_2.2H_2O$ and alkene in the ratio 1:2:300 with an initial pressure of 400 psi of carbon monoxide and hydrogen.

e Repeat reactions gave similar values (± 5%).

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