Substituent Effects in Benzylic Functionalization of Arene(tricarbonyl) Chromium Complexes

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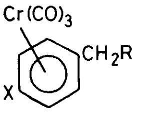
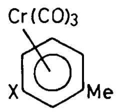
Effects of a *meta*- or *para*-electron withdrawing substituent on benzylic functionalization of arene–chromium–tricarbonyl complexes have been studied; tricarbonyl{η^6-(t-butyl 3,4-dimethylbenzoate)}chromium promoted the attachment of the CRHOH group exclusively at the 4-methyl group, while the 3-methyl group remained unchanged.

Several reports have appeared in the literature on substituent effects in electrophilic[1,2] and nucleophilic addition[3—5] to the aromatic ring of arene–chromium–tricarbonyl complexes. The dominance of conformational effects in directing the attack of both electrophilic and nucleophilic reagents has been established.[6,7]

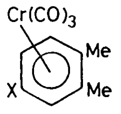
In tricarbonyl(methoxybenzene)chromium the $Cr(CO)_3$ unit adopts an eclipsed conformation[8,9] for electronic reasons.



(1) R = H
(2) R = Me



(3)



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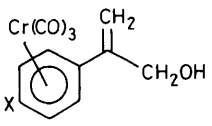

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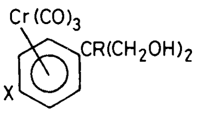
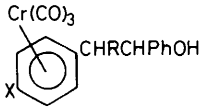
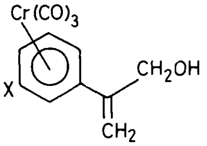


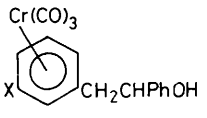
(6) R = CH₂OH
(7) R = Me



(8) R = H
(9) R = Me



(10)



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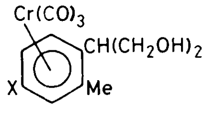
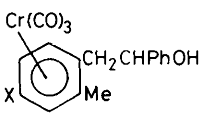


(12)



(13)

X = Bu^tO_2C

Thus the reaction with a nucleophile will occur at the *meta*-carbon which is eclipsed by metal–carbonyl bonds.[3,6]

It has recently been established that the *meta*-directing effect of an electron donor group also occurs at benzylic sites.[10] For example, with tricarbonyl(1-methoxy-3,4-dialkylbenzene)chromium the attachment of $-CH_2OH$ groups occurs exclusively at the 3-alkyl α-carbon while the 4-alkyl group remains unchanged.

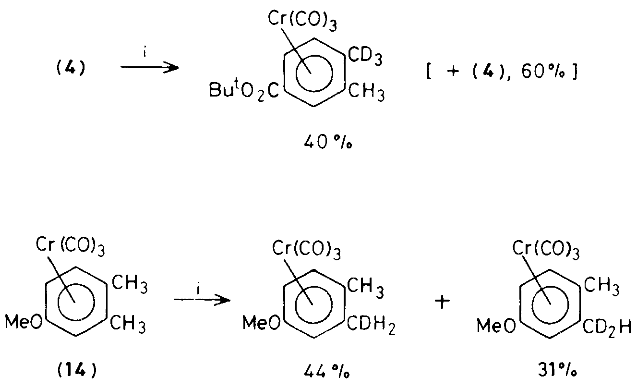
Owing to the importance of regioselectivity in aromatic synthesis, the behaviour of tricarbonyl(alkylbenzene)chromium complexes bearing an electron-withdrawing substituent was examined. We now report the reaction of tricarbonyl(t-butyl alkylbenzoate)chromium complexes with aldehydes in the presence of Bu^tOK.[11,12] The results are summarized in Table 1.

With HCHO double or even triple attack of the aldehyde occurs, leading to the diol complexes (**7**) and (**12**), the alkenol complexes (**5**) and (**10**), or the triol complex (**6**) depending on the nature and position of the substituents in the starting complex. Under the same conditions PhCHO gives the monohydroxy complexes (**8**), (**9**), (**11**), and (**13**). In contrast to

Table 1. Reactions of the aromatic ester complexes (**1**)—(**4**).[a]

Starting complex	R in RCHO	Products, % yield[b]
(**1**)	H	(**5**), 15; (**6**), 25
(**2**)	H	(**7**), 50
(**1**)	Ph	(**8**), 50
(**2**)	Ph	(**9**), 45
(**3**)	H	(**10**), 20
(**3**)	Ph	(**11**), 40
(**4**)	H	(**12**), 40[c]
(**4**)	Ph	(**13**), 52[c]

[a] *Conditions*: Bu^tOK in Me_2SO, then RCHO [in excess for reactions of (**4**)]. [b] Yields take into account the starting material recovered (10—15%). [c] Only isomer observed.



Scheme 1. *Reagents*: Bu^tOK, Me_2SO; then $(CD_3)_2CO$, then H_2O-H^+.

the striking difference observed with the corresponding *meta*- and *para*-methoxytoluene–tricarbonylchromium complexes,[10] there is only a small directing effect in this reaction. Nevertheless the *para*-compounds (**1**) and (**2**) appear to be more reactive than the *meta*-compound (**3**).

However, when two potential sites of attack (namely the *meta*- and *para*-position with respect to the t-butoxycarbonyl group) are present, *e.g.* (**4**), only products bearing methyl hydroxy-groups (**12**) or a benzyl hydroxy-group (**13**) on the *para*-carbon atom were produced, depending on which aldehyde was used.

Additional supporting evidence for this selective metallation was provided by isotopic labelling experiments with compound (**4**) in $(CD_3)_2CO$. Deuterium incorporation occurs exclusively *para* to the CO_2Bu^t group (Scheme 1), in contrast to the results for the methoxy compound (**14**) where deuterium is incorporated at the *meta* position with respect to the OMe group.

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