

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

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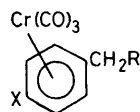
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Effects of a *meta*- or *para*-electron withdrawing substituent on benzylic functionalization of arene–chromium–tricarbonyl complexes have been studied; tricarbonyl(η^6 -(*t*-butyl 3,4-dimethylbenzoate))chromium promoted the attachment of the CRHOH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

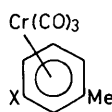
Several reports have appeared in the literature on substituent effects in electrophilic^{1,2} and nucleophilic addition^{3–5} to the aromatic ring of arene–chromium–tricarbonyl complexes. The dominance of conformational effects in directing the attack of both electrophilic and nucleophilic reagents has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

In tricarbonyl(methoxybenzene)chromium the Cr(CO)₃ unit adopts an eclipsed conformation^{8,9} for electronic reasons.

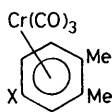


(1) R = H

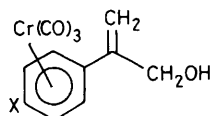
(2) R = Me



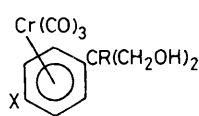
(3)



(4)

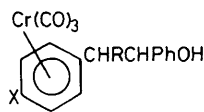


(5)



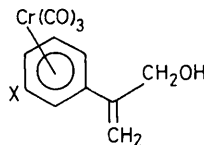
(6) R = CH₂OH

(7) R = Me

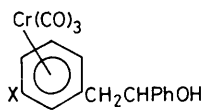


(8) R = H

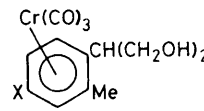
(9) R = Me



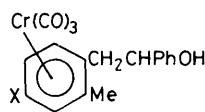
(10)



(11)



(12)



(13)

X = Bu^tO₂C

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 –CH₂OH groups occurs exclusively at the 3-alkyl α -carbon while the 4-alkyl group remains unchanged.

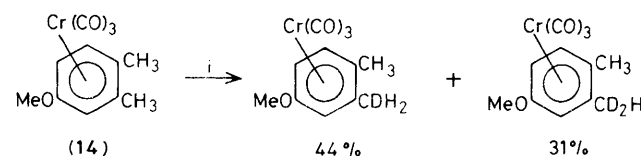
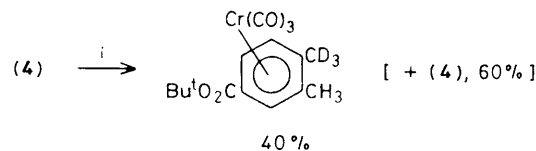
Owing to the importance of regioselectivity in aromatic synthesis, the behaviour of tricarbonyl(alkylbenzene)chromium complexes bearing an electron-withdrawing substituent was examined. We now report the reaction of tricarbonyl(*t*-butyl alkylbenzoate)chromium complexes with aldehydes in the presence 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 Me₂SO, 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, Me₂SO; then (CD₃)₂CO, then H₂O–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 (CD₃)₂CO. Deuterium incorporation occurs exclusively *para* to the CO₂Bu^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.

Received, 15th November 1983; Com. 1494

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