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Use of Carbonylchromium Groups for Selective Activation of Arene Substituents

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Summary The $Cr(CO)_2L$ unit [L = CO, CS, PPh_3, $P(OPh)_3$] may be used to increase reactivity, enhance selectivity, or protect the substituents of complexed arene rings with respect to alkylation.

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. We report here the use of chromiumcarbonyl intermediates in the activation towards alkylation of arene substituents. (See Scheme for the general reaction with carbonyl compounds.)

$$[Cr(CO)_2L(PhCOCHR^1R^2)] \xrightarrow[Base]{R^3X} [Cr(CO)_2L(PhCOCR^1R^2R^3)]$$

$$\downarrow h\nu,\ O_2$$

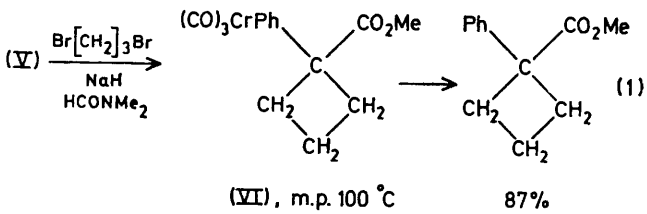
$$PhCOCR^1R^2R^3$$

Scheme

Complexation of the $Cr(CO)_3$ group to an arene ring is easily accomplished,[1] while quantitative oxidative decomplexation may be easily performed using a variety of methods.[2-4] Though the strong electron-withdrawing character of the $Cr(CO)_3$ group has previously been recognized,[1] this property has not been used in synthesis, with the exception of recent work concerning nucleophilic attack on complexed arenes.[2]

$[Cr(CO)_3(PhCOMe)]$ (I), m.p. 89—90 °C, was rapidly converted into $[Cr(CO)_3(PhCOPr^i)]$ (II), m.p. 41 °C, in $HCONMe_2$ with MeI and NaH (25 °C, 15 min, 90% yield). Under similar conditions, free PhCOMe gives PhCOEt and $PhCOPr^i$ and starting material. Complex (II) may also be obtained from $[Cr(CO)_3(PhCOEt)]$ (III), m.p. 96 °C. The complexes (I), (II), or (III), in Me_2SO with Bu^tOK as base, all give $[Cr(CO)_3(PhCOBu^t)]$ (IV), m.p. 59 °C (78% yield). These reactions are free from byproducts, as is the decomplexation of the ketones by exposure of ether solutions of the complexes to sunlight in air.[4] Thus, preparatively, isolation of the complexes is unnecessary.

While free $PhCH_2CO_2Me$ is inert to MeI and NaH at 25 °C in $HCONMe_2$, the complex $[Cr(CO)_3(PhCH_2CO_2Me)]$ (V), m.p. 74 °C, rapidly gives $[Cr(CO)_3(PhCMe_2CO_2Me)]$, m.p. 55 °C (97%), under these conditions. Small alicyclic compounds may also be formed by double attack at the α-position of (V) (reaction 1).



(1)

(VI), m.p. 100 °C 87%

In the preceding examples, the presence of electron-withdrawing ketone and ester groups also favours the reaction, and participation of the $Cr(CO)_3$ group may not

be involved. Under similar conditions, however, $PhPr^i$ can be obtained (71%), together with $PhBu^t$ (8%), from the complex $[Cr(CO)_3(PhEt)]$ (VII), m.p. 48 °C, using MeI and Bu^tOK in Me_2SO.

The activating power of the carbonylchromium group may also be changed by photochemical replacement of one of the CO groups by, *e.g.*, CS, PPh_3, or $P(OPh)_3$, by literature methods.[5] Polarographic and pK_a data indicate the following order of activating ability of the $Cr(CO)_2L$ units: $Cr(CO)_2CS > Cr(CO)_3 > Cr(CO)_2P(OPh)_3 > Cr(CO)_2PPh_3$.

Like $PhCH_2CO_2Me$ itself, the complex $[Cr(CO)_2(PPh_3)(PhCH_2CO_2Me)]$ is inert to alkyl substitution (MeI, NaH, 25 °C, $HCONMe_2$) but the complex $[Cr(CO)_2\{P(OPh_3)_3\}(PhCH_2CO_2Me)]$, m.p. 120 °C, under similar conditions gives the monoalkylated complex $[Cr(CO)_2\{P(OPh)_3\}(PhCHMeCO_2Me)]$, m.p. 120 °C, together with small quantities of the dialkylated derivative, m.p. 114 °C. As mentioned previously, complex (VII) reacts to give mainly the monomethylated derivative whereas $[Cr(CO)_2(CS)(PhEt)]$, m.p. 56 °C, gives the fully methylated derivative $[Cr(CO)_2(CS)(PhCMe_3)]$ in <1 h. Decomplexation may be performed as described for the $Cr(CO)_3$ complexes, except that purification by t.l.c. is necessary.

Finally, alkylation of $[Cr(CO)_3(PhCH_2CH_2CO_2Me)]$ is of particular interest since reactive sites are available either α- or β- to the arene ring. Methylation (25 °C, $HCONMe_2$ NaH–MeI, 9 h) is found to be regiospecific at the β-carbon, giving 10% of the disubstituted derivative $[Cr(CO)_3(PhCH_2CMe_2CO_2Me)]$ and 65% of the monosubstituted complex $[Cr(CO)_3(PhCH_2CHMeCO_2Me)]$, m.p. 78 °C. If the stronger electron-withdrawing $Cr(CO)_2CS$ group is used the reaction is still regiospecific, but only the dimethylated derivative is obtained. The reasons for this β-activation are still obscure, but may involve carbanion stabilization either by the metal or the arene ring.

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

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[1] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.
[2] M. F. Semmelhack, H. T. Hall, M. Yoshifugi, and G. Clark, *J. Amer. Chem. Soc.*, 1975, **97**, 1247.
[3] W. S. Trahanovsky and R. J. Card, *J. Amer. Chem. Soc.*, 1972, **94**, 2897.
[4] G. Jaouen and R. Dabard, *Tetrahedron Letters*, 1971, 1015.
[5] G. Jaouen and R. Dabard, *J. Organometallic Chem.*, 1974, **72**. 377.