Elaboration of α-Substituted Benzyl Ethers and Sulphides by Suppression of the Wittig and Related Rearrangements

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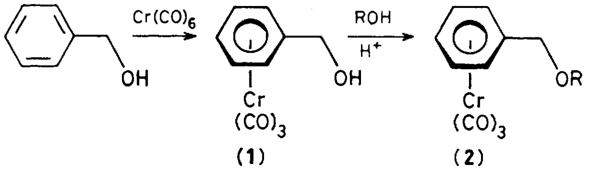
Co-ordination of benzyl alkyl ethers and sulphides to chromium tricarbonyl allows α-substitution *via* the corresponding α-carbanions to be achieved by suppression of the Wittig and related rearrangements.

The synthetic potential of α-carbanions derived from benzyl alkyl ethers has not been realised because they undergo the Wittig rearrangement to the corresponding alkoxides, equation (1).[1] We were interested to see whether stabilisation



(2)

a; R = Me
b; R = Et
c; R = Bu^s
d; R = CH_2=$CHCH_2$
e; R = CH_2=CHCHMe
f; R = $PhCH_2$

of the initial α-carbanion would suppress the Wittig rearrangement and allow clean alkylation reactions to occur.

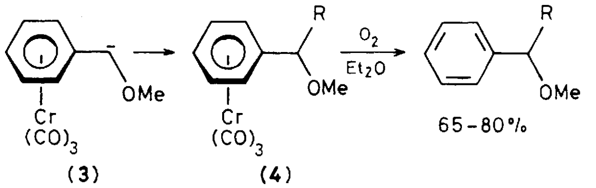
$$PhCH_2OR \rightarrow [Ph\overset{-}{C}HOR] \rightarrow PhCH(R)O^- \qquad (1)$$

Treatment of arenes co-ordinated to chromium tricarbonyl can lead to either ring or benzylic metallation.[2] Furthermore regioselective *ortho*-metallation has been observed for alkoxyarenes. We report here that benzyl alkyl ethers co-ordinated to chromium tricarbonyl undergo regioselective α-deprotonation and that the carbanions thus formed do not undergo the Wittig rearrangement.

Thermolysis of chromium hexacarbonyl in the presence of benzyl alcohol generates $(C_6H_5CH_2OH)Cr(CO)_3$ (**1**) which on treatment with alcohols in the presence of acid (HBF_4 or H_2SO_4) yields the $(C_6H_5CH_2OR)Cr(CO)_3$ complexes (**2**), equation (2).[3]

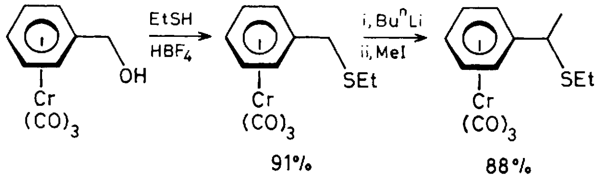
Treatment of the benzyl methyl ether complex (**2a**) with Bu^{n}Li (−40 °C, 1 h) in tetrahydrofuran generates the α-carbanion (**3**) which on quenching with methanol regenerates (**2a**). Similar treatment of benzyl methyl ether itself results in the Wittig rearrangement to produce 1-phenylethanol. The α-carbanions from complexes (**2b**)—(**2f**) are similarly stable towards rearrangement.

The α-carbanion (**3**) may be readily trapped by a variety of alkylating agents (MeI, EtBr, Pr^{i}Br, $PhCH_2Br$, $PhCO_2Me$, MeCHO) to give the α-substituted benzyl ethers (**4**), equation (3). No ring alkylation products were detected in any of these reactions. Decomplexation of the α-substituted benzyl ethers is achieved on exposure of ether solutions to air and sunlight. The α-carbanions from complexes (**2b**)—(**2e**) similarly undergo α-methylation on treatment with methyl iodide.



(3)

R = Me, Pr^i, $PhCH_2$, PhCO, or MeCH(OH) (2:1 mixture of diastereoisomers).



(4)

α-Carbanions generated from benzyl alkyl sulphides are prone to even more rearrangements and decomposition than their oxygen analogues.[4] Complexation of such sulphides to chromium tricarbonyl again stabilises the derived α-carbanions and allows α-alkylation to proceed, equation (4).

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