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Preliminary communication

THE BEHAVIOUR OF ALKYLCOBALT CARBONYLS UNDER "OXO" CONDITIONS

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Summary

Both normal and secondary alkylcobalt carbonyls are shown not to undergo isomerization under catalytic "oxo" conditions, and the relevance of this observation for the mechanism of the "oxo" reaction is discussed.

Alkylcobalt carbonyls, first synthesised by Hieber et al. [1], were later studied by Heck et al. [2], who suggested that they were intermediates in the hydroformylation of olefins.

While n-alkylcobalt carbonyls were obtained with some ease, and their reactions investigated, secondary alkylcobalt carbonyls were not isolated [3]. These complexes were found to isomerize when their solutions were allowed to stand at room temperature [3] or were heated [4]. Evidence for the formation of both normal and secondary alkylcobalt carbonyls was obtained by Heck in studies of the carboxyalkylation reaction of alkyl halides [5] under mild conditions.

We have now obtained evidence for the formation of normal and secondary alkylcobalt carbonyls on treatment of the appropriate alkyl halide with sodium tetracarbonylcobaltate under the conditions of the catalytic "oxo" reaction, and made observations on their stability. The substrates used were 1-iodopropane and 2-iodopropane.

Sodium tetracarbonylcobaltate (20 mmol) in diethyl ether (40 ml) was placed in a rocking autoclave under carbon monoxide (80 atm) and heated to 80 °C. A solution of iodopropane (18 mmol) in diethyl ether (10 ml) was then introduced together with hydrogen sufficient to raise the total pressure to 150 atm. After 5 h GLC analysis showed that the liquid did not contain any of the original alkyl halide and only one aldehyde, which was n-butanal when 1-iodopropane was used and 2-methylpropanal when 2-iodopropane was used.

The aldehyde is evidently formed through the following sequence of reactions:

$$\begin{aligned} &\mathrm{RI + NaCo(CO)_4} &&\longrightarrow \mathrm{RCo(CO)_4 + NaI} \\ &\mathrm{RCo(CO)_4 + CO} &&\longrightarrow \mathrm{RCOCo(CO)_4} \\ &\mathrm{RCOCo(CO)_4 + H_2} &&\longrightarrow \mathrm{HCo(CO)_4 + RCHO} \end{aligned}$$

The results show that under "oxo" conditions neither normal nor secondary alkylcobalt carbonyls, like the corresponding acylcobalt carbonyls [6], isomerize to any detectable extent. This supports the suggestion [6] that, contrary to previous proposals [2,7,8], the step responsible for the formation of isomeric aldehydes by hydroformylation of olefins under typical "oxo" conditions precedes the formation of the alkylcobalt carbonyl intermediates.

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