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Preliminary communication

PHASE-TRANSFER CATALYSIS IN COBALT-CATALYZED CARBONYLATION OF BENZYL HALIDES

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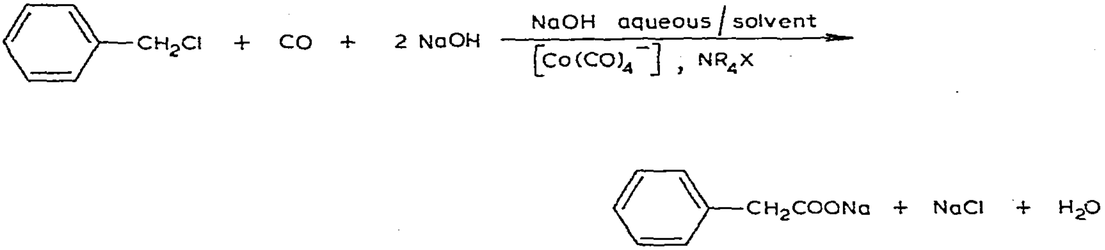
Summary

Carbonylation of benzyl chloride of bromide (to give $PhCH_3COONa$) can be carried out by stirring aqueous sodium hydroxide with an organic solvent such as diphenyl ether or benzene and an ammonium salt such as $PhCH_2NMe_3Cl$.

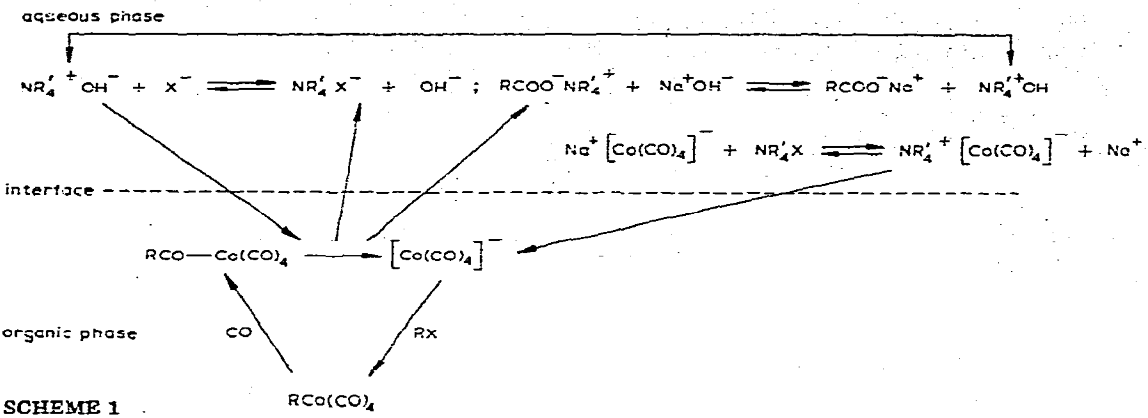
The application of phase transfer processes to organometallic chemistry and homogeneous catalysis has recently been shown to be of great value [1]. We report briefly below on the use of this technique in the cobalt-catalyzed carbonylation of benzylic halides [2].

The carbonylation reaction is carried out by stirring an aqueous solution of sodium hydroxide, an organic solvent (e.g. diphenyl ether, benzene etc.), $Na[Co(CO)_4]$, and an ammonium salt such as $C_6H_5CH_2N(CH_3)_3Cl$.



Benzyl chloride (or bromide) is slowly added to the reaction mixture under carbon monoxide to give the sodium salt of phenylacetic acid. For example benzyl chloride (16.5 g) was added during 1 h to a stirred mixture of aqueous NaOH (40%; 50 ml), $[C_6H_5CH_2N(CH_3)_3]Cl$ (1.0 g), diphenyl ether (50 ml), and $Na[Co(CO)_4]$ (0.5 g) under one atmosphere pressure of CO at 55°C. The mixture was kept at 55°C for 2 more hours. Phenylacetic acid was obtained in 85% yield. No carbonylation occurs in the absence of the ammonium salt.

$Co_2(CO)_8$ can be used as catalyst with similar results, because it is converted into the anionic cobalt complex in phase transfer conditions [1c].



SCHEME 1

Scheme 1 shows the reactions probably involved in this carbonylation. The main functions of the ammonium cation are: (1) to facilitate the transfer of the cobalt carbonyl anion into the organic phase, (2) to induce the conversion of $Co_2(CO)_8$ to $Co(CO)_4^-$, and (3) to assist the removal of the organic acid from the organic phase to the aqueous phase.

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