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IODIDE ION PROMOTION OF BENZYL CHLORIDE-BORATE ESTER CARBONYLATION REACTIONS

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Summary: Esters are isolated in fine yields from the rhodium(I) catalyzed reaction of benzyl chlorides with borate esters and carbon monoxide, in the presence of potassium iodide.

Recently, we have described the use of borate esters to convert benzylic bromides to all types of carboxylic esters by carbon monoxide and a rhodium(I) catalyst.[1] It was disappointing to learn that the corresponding chlorides failed to react in the same manner. It is known from research done in several areas of catalysis that iodide ion can function as an effective promoter,[2] examples including the Monsanto acetic acid process,[3] and the homologation of acids,[4] esters, and ethers[5]. Therefore, it was anticipated that the rhodium catalyzed carbonylation of benzyl chlorides could be achieved by use of borate esters and potassium iodide. We now wish to report that the presence of iodide ion does indeed result in a simple and clean conversion of benzyl chlorides to esters.

Treatment of a series of benzylic chlorides with a borate ester, $B(OR')_3$, $[R'=C_2H_5, i\text{-}C_3H_7, n\text{-}C_4H_9, i\text{-}C_4H_9, t\text{-}C_4H_9]$, carbon monoxide, potassium iodide, and a catalytic amount of the dimer of chloro(1,5-hexadiene)rhodium $[1,5\text{-}HDRhCl]_2$ afforded the corresponding esters. These reaction conditions are identical to those previously described for the bromides[1], except for the change in substrate and the addition of small amounts of potassium iodide (mmol ratio of halide:Rh:KI was 2-3/0.2/0.1). The product yields, which are listed in Table 1, clearly demonstrate the promotional effect of iodide ion since no reaction occurs in the absence of the latter.

What role does iodide ion play in these reactions? One possiblity is that it converts the benzylic chloride to the more reactive benzyl iodide. Although such a process is known to readily occur in polar solvents such as acetone[6], we found that no reaction takes place on treatment of 1-chloromethylnaphthalene with an equivalent amount of potassium iodide with or without borate ester [heptane was used as the solvent in the absence of $B(OC_2H_5)_3$]. An alternative explanation involves the rhodium catalyst. Prior to the formation of any boron-rhodium intermediate[1], the rhodium(I) catalyst would be converted by carbon monoxide to rhodium-carbonyl chloride dimer (one can, in fact, use the latter as the catalyst for the reaction of

$$[1,5\text{-HDRhCl}]_2 + CO \rightarrow [Rh(CO)_2Cl]_2 \xrightarrow{KI} [Rh(CO)_2I]_2$$

benzyl bromides). Iodide ion can then displace chloride to give $[Rh(CO)_2I]_2$ which may be a more active catalyst. This hypothesis was confirmed by $[Rh(CO)_2I]_2$[7] catalyzed reaction of 1-chloromethylnapthalene with $B(OCH(CH_3)_2)_3$ and carbon monoxide (no KI) to form the anticipated ester in 98% yield, compared to 68% yield resulting from the use of $[1,5\ HDRhCl]_2$/KI. These results suggest that the key catalytic species in the benzyl chloride reactions is a rhodium carbonyl iodide complex.

Table 1

Iodide Ion Promotion of the Reaction of Benzylic Chlorides with CO and $B(OR)_3$

$ArCH_2Cl$ Ar=	$B(OR')_3$ R'=	Product[a]	Yield,%[b]
Ph	C_2H_5	$PhCH_2COOC_2H_5$	71
	$n-C_4H_9$	$PhCH_2COOC_4H_9-n$	100
	$i-C_4H_9$	$PhCH_2COOC_4H_9-i$	44
	$C(CH_3)_3$	$PhCH_2COOC(CH_3)_3$	56
$p-CH_3C_6H_4$	C_2H_5	$p-CH_3C_6H_4CH_2COOC_2H_5$	56
	$CH(CH_3)_2$	$p-CH_3C_6H_4CH_2COOCH(CH_3)_2$	70
	$n-C_4H_9$	$p-CH_3C_6H_4CH_2COOC_4H_9$	72
$o-CH_3OC_6H_4$	C_2H_5	$o-CH_3OC_6H_4CH_2COOC_2H_5$	100
	$C(CH_3)_3$	$o-CH_3OC_6H_4CH_2COOC(CH_3)_3$	55
$1-C_{10}H_7$	C_2H_5	$1-C_{10}H_7CH_2COOC_2H_5$	54
	$CH(CH_3)_2$	$1-C_{10}H_7CH_2COOCH(CH_3)_2$	68
$m-CH_3C_6H_4$	C_2H_5	$m-CH_3C_6H_4CH_2COOC_2H_5$	87
	$CH(CH_3)_2$	$m-CH_3C_6H_4CH_2COOCH(CH_3)_2$	82
$p-FC_6H_4$	C_2H_5	$p-FC_6H_4CH_2COOC_2H_5$	93

[a] Products were fully characterized by comparison with authentic materials.

[b] Isolated yields.

In conclusion, potassium iodide is a valuable promoter of the reaction of benzyl chlorides with borate esters and carbon monoxide. From a commercial viewpoint, this is a more economical process than that involving benzyl bromides as substrates.

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