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SYNTHESIS OF ESTERS BY RHODIUM(I) CATALYZED BORATE ESTER-BENZYLIC BROMIDE CARBONYLATION REACTIONS

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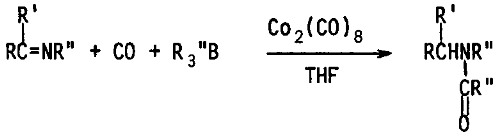
Summary: Benzylic halides react with trialkylborates and carbon monoxide, in the presence of 1,5-hexadienerhodium chloride dimer, to give esters in excellent yields. The reaction is applicable to the synthesis of primary, secondary and even tertiary esters.

Metal catalyzed reactions of organoboranes have attracted considerable attention in recent years. For example, palladium (0) or (II) complexes induce coupling of alkenylboranes with different halides under basic conditions (eg. 1).[1-6] Carbonylation reactions of trialkyl

$$[C_2H_5OCH{=}CH]_3B + RX \xrightarrow[\text{NaOH,THF}]{\text{Pd(0,II)}} C_2H_5OCH{=}CHR \qquad \text{(eq. 1)}$$

or triarylboranes with Schiff bases occur in reasonable yields using cobalt carbonyl as the noted catalytic species (eq. 2)[7].



$$RC(R'){=}NR'' + CO + R_3''B \xrightarrow[\text{THF}]{Co_2(CO)_8} RCH(R')N(R'')C(=O)R'' \qquad \text{(eq. 2)}$$

Borates are much cheaper than boranes, and reactions involving such substrates may have industrial potential. There have been no reports, to our knowledge, on metal induced reactions of borate esters. We now wish to report that the carbonylation of halides with borates is catalyzed by rhodium(I) complexes to give esters in excellent yields.

When carbon monoxide was bubbled through a mixture of a benzylic bromide (1), trialkylborate (2) and 1,5-hexadienerhodium chloride [1,5-HDRhCl] dimer as the catalyst, at 75° and 1 atm., the ester (3) was isolated in high yields. The reaction could be effected using the borate as the solvent, or in heptane. In the latter case, a 3/1/0.15-0.30 mole ratio of 1/2/$[1,5\text{-HDRhCl}]_2$ was used. No reaction occurs in the absence of the metal catalyst. One can also use chlorodicarbonyl-rhodium (I) dimer as the catalyst. The reaction also occurs at room temperature, over a 3-day period.

** U.K. Patent Appl. 83 19291 (16 July, 1983).

$$\underset{(1)}{3ArCH_2Br} + \underset{(2)}{B(OR')_3} + 3CO \xrightarrow[75^\circ,\ 1\ atm.]{[1,5\text{-}HDRhCl]_2} \underset{(3)}{3ArCH_2COOR'} + BBr_3$$

The yields of esters are indicated in Table 1. The reaction proceeds smoothly for various benzylic halides, is applicable to different borates, including tert-butyl borate, thereby providing an entry to tertiary as well as primary and secondary esters. It is also noteworthy that no t-butyl ester was detected when t-butanol was used in place of tert-butyl borate (using 1, Ar=p-$CH_3C_6H_4$ as the substrate).

The pathway outlined in Scheme 1 should be considered as a working hypothesis for the halide-borate reaction. Exposure of the borate ester (2) to the rhodium catalyst and carbon monoxide may give 4[9]. Migration of an alkoxy group from boron to a carbonyl carbon would afford 5. Addition of the benzylic bromide can then give 6 from which the ester is obtained on reductive elimination, together with 7[10]. Repetition of this sequence of steps [alkoxy migration, addition of 1 and reductive elimination] would generate more ester and give 8 and eventually 9. The latter can recycle to 4 and liberate a third equivalent of ester (3) as well as boron tribromide (detected by bubbling the evolved gases through a solution of silver nitrate).

SCHEME 1

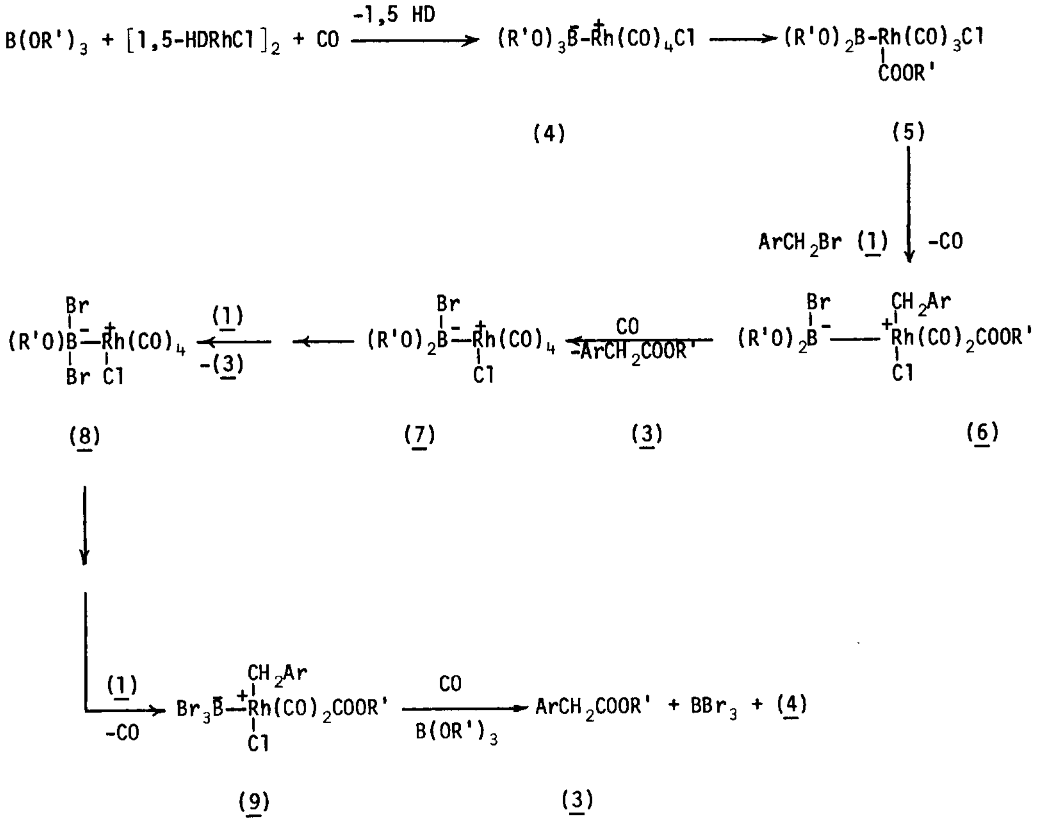


Table 1

Yields of Esters Obtained from Halides, Carbon Monoxide, Borate Ester

Halide	Borate ester	Product[a]	Yield, %[b]
$PhCH_2Br$	$B(OC_2H_5)_3$	$PhCH_2COOC_2H_5$	85
	$B(OC_3H_7)_3$	$PhCH_2COOC_3H_7$	97
	$B(OC_4H_9^n)_3$	$PhCH_2COOC_4H_9^n$	100
$p\text{-}CH_3C_6H_4CH_2Br$	$B(OC_2H_5)_3$	$p\text{-}CH_3C_6H_4CH_2COOC_2H_5$	89
	$B(OC_3H_7)_3$	$p\text{-}CH_3C_6H_4CH_2COOC_3H_7$	100
	$B(OC_4H_9^n)_3$	$p\text{-}CH_3C_6H_4CH_2COOC_4H_9^n$	90
$m\text{-}CH_3C_6H_4CH_2Br$	$B(OC_2H_5)_3$	$m\text{-}CH_3C_6H_4CH_2COOC_2H_5$	100
	$B(OC_3H_7^n)_3$	$m\text{-}CH_3C_6H_4CH_2COOC_3H_7^n$	100
	$B(OC_4H_9^n)_3$	$m\text{-}CH_3C_6H_4CH_2COOC_4H_9^n$	86
	$B(OPr^i)_3$	$m\text{-}CH_3C_6H_4CH_2COOC_3H_7^i$	93
	$B(OBu^t)_3$	$m\text{-}CH_3C_6H_4CH_2COOBu^t$	90
$o\text{-}BrC_6H_4CH_2Br$	$B(OC_2H_5)_3$	$o\text{-}BrC_6H_4CH_2COOC_2H_5$	67
	$B(OC_3H_7^n)_3$	$o\text{-}BrC_6H_4CH_2COOC_3H_7^n$	46
	$B(OC_4H_9^n)_3$	$o\text{-}BrC_6H_4CH_2COOC_4H_9^n$	81
2-Bromomethylnaphthalene	$B(OC_2H_5)_3$	$2\text{-}NpCH_2COOC_2H_5$	82
	$B(OC_3H_7)_3$	$2\text{-}NpCH_2COOC_3H_7$	96
	$B(OC_4H_9^n)_3$	$2\text{-}NpCH_2COOC_4H_9^n$	100
	$B(OBu^t)_3$	$2\text{-}NpCH_2COOBu^t$	68

[a] Products were identified by comparison of physical properties [b.p., ir, nmr, (^1H, ^{13}C), ms] with those for authentic materials. [b] Isolated yields.

The following general procedure was used: a mixture of $[1,5\ HDRhCl]_2$ [0.1-0.2 mmol], borate [2 ml - or 0.65 mmol when heptane was employed as the solvent], and benzylic bromide [2.0 mmol] was heated overnight at 75° under an atmosphere of carbon monoxide. The solution was cooled, ether (10 ml.) and 1M NaOH (5 ml.) were added, and then the mixture was filtered through Celite. The filtrate was extracted three times with ether (total of 250 ml.), the ether extract was dried ($MgSO_4$) and concentrated. Pure ester was obtained by chromatography and/or distillation.

ACKNOWLEDGEMENT

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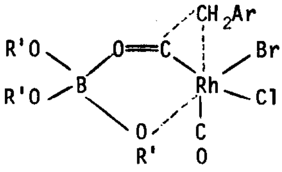
9. Instead of boron-rhodium bond formation, the borate ester may interact with a metal carbonyl oxygen which could then facilitate migration as depicted in (i) [Butts, S.B.; Strauss, S.H.; Holt, E.M.; Stimson, R.E.; Alcock, N.W.; Shriver, D.F. J. Amer. Chem. Soc., 1980, 102, 5093].



(i)

10. Alternatively, addition of $ArCH_2Br$ to 5 may result in cleavage of the boron-rhodium bond giving $BBr(OR')_2$ and $ArCH_2Rh(COOR)(CO)_3Cl$. Reductive elimination of ester from the latter complex, under CO, would give $Rh(CO)_4Cl$ which can form I on interaction with $BBr(OR)_2$.

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