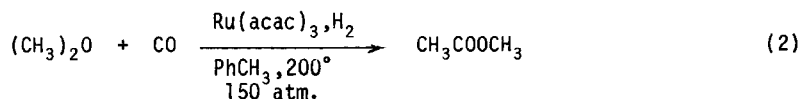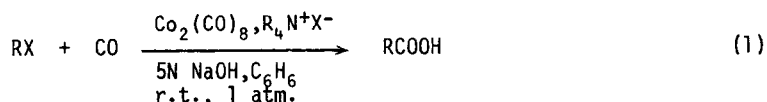# RHODIUM(I) CATALYZED CARBONYLATION REACTIONS OF HALIDES AND ETHERS

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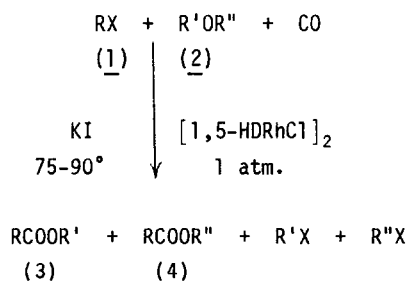Ottawa, Ontario, Canada K1N 9B4

Summary: Benzylic bromides and methyl iodide react with ethers, carbon monoxide, potassium iodide, and the dimer of chloro(1,5-hexadiene)rhodium(I) to give esters in good yields.

There has been considerable interest in the metal complex catalyzed carbonylation of halides and of ethers[2,3]. For example, cobalt carbonyl is an effective catalyst for the phase transfer catalyzed carbonylation of halides to acids at room temperature and atmospheric pressure (eq. 1)[4], and ruthenium acetylacetonate can, under stringent conditions, induce the conversion of methyl ether to methyl acetate, ethyl acetate, and other products (eq. 2)[5]. As

$$RX + CO \xrightarrow[\substack{5N\ NaOH,C_6H_6 \\ r.t.,\ 1\ atm.}]{Co_2(CO)_8,R_4N^+X^-} RCOOH \qquad (1)$$

$$(CH_3)_2O + CO \xrightarrow[\substack{PhCH_3,200° \\ 150\ atm.}]{Ru(acac)_3,H_2} CH_3COOCH_3 \qquad (2)$$

a result of recent work done on the rhodium(I) catalyzed[6] carbonylation reaction of halides with borate esters involving alkoxy transfer, it seemed worthwhile to examine the carbonylation of halides and ethers[7]. We now describe the interesting results of this study.

When carbon monoxide was bubbled through a solution of benzyl bromide [1,R=PhCH$_2$,X=Br]

$$RX + R'OR'' + CO$$
$$(\underline{1}) \quad | \quad (\underline{2})$$
$$KI \quad \Big| \quad [1,5\text{-HDRhCl}]_2$$
$$75\text{-}90° \quad \downarrow \quad 1\ atm.$$

$$RCOOR' + RCOOR'' + R'X + R''X$$
$$(\underline{3}) \qquad (\underline{4})$$

and di-n-butyl ether [2,R'=R"=n-C₄H₉], containing a catalytic quantity of the dimer of chloro [1,5-hexadiene]rhodium(I) [1,5-HDRhCl]₂, at 75°C and 1 atmosphere, n-butyl phenylacetate [3,R=PhCH₂,R'=n-C₄H₉] was isolated in 50% yield. This reaction is promoted by iodide ion, since repetition of the experiment with a small amount of added potassium iodide afforded the ester in 81% yield. The reaction was conducted in the ether or by using equimolar amounts of ether and halide in n-heptane. The best ratio of 1/Rh/KI was 10/1/0.6. No reaction occurred in the absence of the metal complex.

A variety of other benzylic bromides reacted with symmetrical ethers and carbon monoxide to form esters in good yields. The yields of the products are listed in Table 1. The reaction is insensitive to inductive effects since di-n-butyl ether reacts with benzylic bromides, bearing methoxy or fluorine substituents in the para position, to give esters in similar yields. When t-butyl methyl ether was used as the reactant with benzyl bromide, methyl phenylacetate was the only ester formed [i.e., no PhCH₂COOC(CH₃)₃ was detected]. The reaction was less selective using an unsymmetrical ether where both alkyl groups are primary. Specifically, treatment of n-butyl ethyl ether with benzyl bromide, carbon monoxide, and [1,5-HDRhCl]₂, afforded n-butyl phenylacetate and ethyl phenylacetate in a 2:1 ratio.

The by-product in all of these reactions is an alkyl halide. Alkyl halides do not usually react with ethers and carbon monoxide under the conditions described above. This is fortunate since if reaction had occurred with alkyl halides, then the benzylic halide-ether carbonylation reaction would be complex and not a viable process.

One alkyl halide which does react with ethers and carbon monoxide is methyl iodide. Higher temperatures and some pressure are required in order to form the ester. Treatment of methyl iodide with diethyl ether, CO, KI, and the rhodium(I) catalyst at 60°C and 6.7 atm., gave ethyl acetate in only 2% yield. Increasing the presence to 44 atm. afforded the ester in 13% yield. Reasonable quantities of ethyl acetate were obtained at higher temperatures. At 150° and 20 atm., ethyl acetate was formed in 42% yield with ethyl propionate being isolated in nearly 60% yield. The latter product likely arises by the known carbonylation of diethyl ether[5]. Nevertheless, satisfactory amounts of ethyl acetate can be produced from methyl iodide and diethyl ether. This method is significantly superior, in reaction conditions and product yields, to that claimed in a patent by Matsui and co-workers,[8] whereby ethyl acetate and ethyl propionate were formed in 15.8% and 16.3% yields, respectively, by reaction of ethyl ether with methyl iodide, carbon monoxide and tris(triphenylphosphine)rhodium(I) chloride as the catalyst at high pressure [146 atm., 170° - no KI].

The following general procedure was used: to 0.09 g [0.20 mmol] of chloro(1,5-hexadiene) rhodium(I) dimer[9] and 0.020 g.[0.12 mmol] of KI in the ether (2 ml.) was added the halide [2.0 mmol] (alternatively, a stoichiometric amount of ether was used in 3-5 ml. of n-heptane). Carbon monoxide was bubbled through the stirred solution overnight at 75-90°C. After cooling to room temperature, 2 ml. of dilute base [0.5-1N NaOH] was added, the mixture was filtered

through Celite, and the Celite was washed successively with ether and distilled water. The filtrate and washings were combined, the organic phase was separated, dried ($MgSO_4$), and distilled to give pure ether.

Table 1

Products Obtained from Rhodium(I) Catalyzed Reactions of Halides with Ethers and Carbon Monoxide

Halide	Ether	KI	Product[a]	Yield,%[b]
$PhCH_2Br$	$(n-C_4H_9)_2O$	Yes	$PhCH_2COOn-C_4H_9$	81
		No	$PhCH_2COOn-C_4H_9$	50
	$(C_2H_5CH)_2O$ $\mid$ CH_3	Yes	$PhCH_2COOCHC_2H_5$ $\mid$ CH_3	98
	$(CH_3)_3COCH_3$	Yes	$PhCH_2COOCH_3$	68
	$n-C_4H_9OC_2H_5$	Yes	$PhCH_2COOC_4H_9-n$	64
			$PhCH_2COOC_2H_5$	32
$p-CH_3C_6H_4CH_2Br$	$[(CH_3)_2CH]_2O$	Yes	$p-CH_3C_6H_4CH_2COOCH(CH_3)_2$	78
		No	$p-CH_3C_6H_4CH_2COOCH(CH_3)_2$	37
	$(n-C_4H_9)_2O$	Yes	$p-CH_3C_6H_4CH_2COOC_4H_9-n$	66
$p-FC_6H_4CH_2Br$	$(n-C_4H_9)_2O$	Yes	$p-FC_6H_4CH_2COOC_4H_9-n$	83
$p-CH_3OC_6H_4CH_2Br$	$(n-C_4H_9)_2O$	Yes	$p-CH_3OC_6H_4CH_2COOC_4H_9-n$	81
$2-NpCH_2Br$	$[(CH_3)_2CH]_2O$	Yes	$2-NpCH_2COOCH(CH_3)_2$	85
CH_3I	$(C_2H_5)_2O$	Yes	$CH_3COOC_2H_5$	42[c]

[a]Products were identified by comparison of physical data [b.p., g.c., i.r., n.m.r. (^{1}H,^{13}C), m.s.] with authentic materials. [b]Yields are of isolated products, except for ethyl acetate which is a g.c. yield. [c]See text for details.

In conclusion, chloro(1,5-hexadiene)rhodium(I) dimer is a useful catalyst, together with potassium iodide, for the carbonylation of benzylic bromides or methyl iodide with ethers to form esters. The reaction occurs under mild conditions and is simple in both execution and work-up.

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