Rhodium and Palladium Catalyzed Carbonylation Reactions with Titanium and Zirconium Alkoxides

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Received September 21, 1984

Benzylic bromides react with titanium or zirconium alkoxides and carbon monoxide, in the presence of catalytic quantities of the dimer of chloro(1,5-hexadiene)rhodium, to give esters in good to excellent yields. Ethers and ketones are byproducts of several of these reactions. Esters are also formed in fine yields from aryl, vinyl, and alkyl bromides by using monometallic [$Pd(PPh_3)_4$–$Ti(OR)_4$ as reagent] or bimetallic [$Pd(PPh_3)_4$/$[1,5\text{-}HDRhCl]_2$–$Zr(OR)_4$ as reagent] catalysis.

The use of main group metal alkoxides, carbon monoxide, and a rhodium(I) catalyst [e.g., the dimer of chloro(1,5-hexadiene)rhodium] to convert benzylic bromides to esters has been the subject of several recent publications.[1-3] Specifically, borate esters (**1**, M = B)[1,2] and aluminum alkoxides (**1**, M = Al)[3] are useful for these purposes. A question which arises is what is the scope of the reaction as far as the metal alkoxide is concerned. Is the process limited to Group 3 metals, or can other metal alkoxides function as alkoxy transfer agents? Alkoxides of the early transition metals, titanium and zirconium, are relatively inexpensive materials and have quite a rich chemistry.[4]

$$3ArCH_2Br + 3CO + \underset{\mathbf{1}}{M(OR)_3} \xrightarrow{[1,5HDRhCl]_2} 3ArCH_2COOR + MBr_3$$

We now describe the use of a rhodium(I) catalyst for the reaction of benzylic halides with titanium or zirconium alkoxides and carbon monoxide to give esters and, in some instances, significant quantities of ethers. In addition, tetrakis(triphenylphosphine)palladium(0), while not useful as a catalyst when benzyl bromide is the substrate, is effective for the carbonylation of aryl, vinyl, and alkyl bromides with titanium alkoxides.

Treatment of a benzylic bromide (**2**, X = Br) with titanium or zirconium alkoxides (**3**, M = Ti, Zr), carbon monoxide, and a catalytic amount of the dimer of chloro(1,5-hexadiene)rhodium, neat [i.e., in $M(OR)_4$] or in n-heptane at 75-100 °C and 1 atm, affords esters **4** in reasonable yields. Chloro(dicarbonyl)rhodium(I) dimer is also a useful catalyst for this transformation. Some representative examples are given in Table I. Of more value are the results obtained with benzylic chlorides which do not react with borate esters or aluminum alkoxides. Zirconium ethoxide or titanium n-butoxide are capable of cleanly producing esters from chlorides, the only other organic material found being unreacted halide. Interestingly, titanium ethoxide affords esters in low yields with ketones as the accompanying products. Similarly, zirconium n-butoxide can, in certain instances, give esters in good yields but ethers are also formed as well. Mixtures of esters and ethers result when zirconium n-propoxide is employed as the alkoxide. These results contrast with those of borate esters and aluminum alkoxides where only esters are formed as products. It is not apparent why the various alkoxides show the noted reactivity—an explanation cannot be made on the basis of a steric or an inductive effect.

$$\underset{\mathbf{2}}{4ArCH_2X} + 4CO + \underset{\mathbf{3}}{M(OR)_4} \xrightarrow[\substack{75\text{–}100\ °C \\ 1\ atm,\ n\text{-}C_7H_{16}}]{[1,5HDRhCl]_2} \underset{\mathbf{4}}{4ArCH_2COOR} + MX_4$$

Concentration, solvent, temperature, and pressure effects were examined using the rhodium(I)-catalyzed carbonylation reaction of α-chloro-o-xylene and zirconium n-propoxide. When the reaction was effected in neat zirconium alkoxide at 100 °C, nearly equal amounts of ether and ester were produced, while the ether was the major product at a reaction temperature of 135 °C [64/36 ether/ester]. No reaction occurred when the dipolar aprotic solvent, sulfolane, was employed as the reaction medium. As noted above, one can use a nonpolar solvent such as n-heptane and, at a reaction temperature of 100 °C and a chloride/zirconium ratio of 1:1, the ether and ester were formed in a combined yield of 95%, 53% of which is the ester. Increasing the chloride/zirconium ratio to 2:1 increased the proportion of ester to 63% (95% total yield), while the ester was obtained as the sole product by using a 4:1 ratio of chloride/zirconium alkoxide. However, the yield was only 40% in the latter case, the remainder being recovered starting material. A similar observation was made in the reaction of 1-(chloromethyl)naphthalene with $Zr(On\text{-}C_3H_7)_4$ (4:1 ratio of chloride/Zr) and CO which afforded the ester in 15% yield (remainder was starting material) in contrast to standard conditions which gave ether/ester in a ratio of 61:39 [total yield was quantitative]. Therefore, the process can be made selective for the ester at high chloride/zirconium alkoxide ratios, but at the expense of yield (and reaction rate). When equimolar quantities of α-chloro-o-xylene and $Zr(On\text{-}C_3H_7)_4$ were reacted with CO at 100 °C and 300 psi in n-heptane, the proportion of ester was only slightly greater than that found in the identical reaction effected at atmospheric pressure (i.e., 56% vs. 53%).

Non-benzylic chlorides failed to react with any of the alkoxides and carbon monoxide in the presence of a rhodium(I) catalyst. Previous work[2,3] has shown that in the case of a bimetallic catalyst system consisting of $[1,5\text{-}HDRhCl]_2$ and tetrakis(triphenylphosphine)palladium(0), aryl, vinyl, and alkyl bromides can be carbonylated to esters with **1**, M = B, Al. Indeed, we observed that such classes of bromides (but not chlorides) react with titanium n-butoxide or zirconium n-propoxide and carbon monoxide, in the presence of the rhodium and palladium catalysts, to

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Table I. Products Obtained from the Rhodium(I)-Catalyzed Carbonylation Reaction of Benzylic Halides with $M(OR)_4$ [M = Ti, Zr]

$ArCH_2X$ Ar =, X =	$M(OR)_4$ M =, R =	product[a]	yield, %[b]
Ph, Br	Ti, $(CH_3)_2CH$	$PhCH_2COOCH(CH_3)_2$	98
	Ti, n-C_3H_7	$PhCH_2COOCH_2CH_2CH_3$	67
		$(PhCH_2)_2CO$	27
	Zr, C_2H_5	$PhCH_2COOC_2H_5$	64
2-$C_{10}H_7$, Br	Ti, $CH(CH_3)_2$	2-$C_{10}H_7CH_2COOCH(CH_3)_2$	72
	Ti, n-C_4H_9	2-$C_{10}H_7CH_2COO$-n-C_4H_9	50
Ph, Cl	Ti, C_2H_5	$PhCH_2COOC_2H_5$	31
		$(PhCH_2)_2CO$	14
	Ti, n-C_4H_9	$PhCH_2COO$-n-C_4H_9	100
	Zr, C_2H_5	$PhCH_2COOC_2H_5$	76
	Zr, n-C_3H_7	$PhCH_2COO$-n-C_3H_7	90
		$PhCH_2O$-n-C_3H_7	10
	Zr, $CH(CH_3)_2$	$PhCH_2COOCH(CH_3)_2$	83
	Zr, n-C_4H_9	$PhCH_2COO$-n-C_4H_9	80
		$PhCH_2O$-n-C_4H_9	20
o-$CH_3C_6H_4$, Cl	Ti, n-C_4H_9	o-$CH_3C_6H_4CH_2COO$-n-C_4H_9	87
	Zr, C_2H_5	o-$CH_3C_6H_4CH_2COOC_2H_5$	89
	Zr, n-C_3H_7	o-$CH_3C_6H_4CH_2COO$-n-C_3H_7	49
		o-$CH_3C_6H_4CH_2O$-n-C_3H_7	50
	Zr, n-C_4H_9	o-$CH_3C_6H_4CH_2COO$-n-C_4H_9	69
		o-$CH_3C_6H_4CH_2O$-n-C_4H_9	31
p-$CH_3C_6H_4$, Cl	Ti, C_2H_5	p-$CH_3C_6H_4CH_2COOC_2H_5$	18
		$(p$-$CH_3C_6H_4CH_2)_2CO$	23
	Ti, n-C_4H_9	p-$CH_3C_6H_4CH_2COO$-n-C_4H_9	89
	Zr, C_2H_5	p-$CH_3C_6H_4CH_2COOC_2H_5$	83
m-$CH_3OC_6H_4$, Cl	Ti, n-C_4H_9	m-$CH_3OC_6H_4CH_2COO$-n-C_4H_9	58
	Zr, n-C_3H_7	m-$CH_3OC_6H_4CH_2COO$-n-C_3H_7	50
		m-$CH_3OC_6H_4CH_2O$-n-C_3H_7	50
1-$C_{10}H_7$, Cl	Ti, n-C_4H_9	1-$C_{10}H_7CH_2COO$-n-C_4H_9	79
	Zr, C_2H_5	1-$C_{10}H_7CH_2COOC_2H_5$	47
	Zr, n-C_3H_7	1-$C_{10}H_7COO$-n-C_3H_7	39
		1-$C_{10}H_7CH_2O$-n-C_3H_7	61
	Zr, n-C_4H_9	1-$C_{10}H_7CH_2COO$-n-C_4H_9	21
		1-$C_{10}H_7CH_2O$-n-C_4H_9	42
		1-$C_{10}H_7CH_3$	37

[a] Products were identified by comparison of physical properties [boiling point, IR, nm (^1H, ^{13}C, ms] with those for authentic materials. [b] Isolated yields.

Table II. Products Obtained from the Metal-Catalyzed Carbonylation Reaction of Non-Benzylic Bromides with $M(OR)_4$ [M = Ti, Zr]

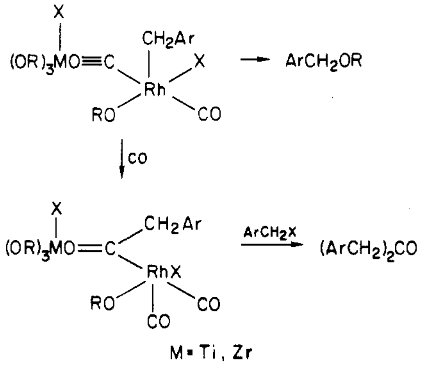
bromide	$M(OR)_4$ M =, R =	catalyst(s)	product[a]	yield, %[b]
m-$CH_3C_6H_4Br$	Ti, $CH(CH_3)_2$	$Pd(PPh_3)_4$	m-$CH_3C_6H_4COOCH(CH_3)_2$	92
	Ti, n-C_4H_9	$Pd(PPh_3)_4$	m-$CH_3C_6H_4COO$-n-C_4H_9	98
1-$C_{10}H_7Br$	Ti, n-C_4H_9	$Pd(PPh_3)_4$	1-$C_{10}H_7COO$-n-C_4H_9	98
	Zr, n-C_3H_7	$Pd(PPh_3)_4$, $[1,5\text{-}HDRhCl]_2$	1-$C_{10}H_7COO$-n-C_3H_7	80
$PhCH{=}CHBr$	Ti, n-C_4H_9	$Pd(PPh_3)_4$	$PhCH{=}CHOO$-n-C_4H_9	85
	Zr, n-C_3H_7	$Pd(PPh_3)_4$, $[1,5\text{-}HDRHCl]_2$	$PhCH{=}CHCOO$-n-C_3H_7	72
n-$C_8H_{17}Br$	Ti, n-C_4H_9	$Pd(PPh_3)_4$	n-$C_8H_{17}COO$-n-C_4H_9	63

[a] Products were identified by comparison of physical properties [boiling points, IR, NMR (^1H, ^{13}C), MS] with those for authentic materials. [b] Isolated yields.

form esters in reasonable yields (Table II). However, in contrast to borate esters and aluminum alkoxides, rhodium is not required in the titanium reaction, i.e., palladium alone will suffice [both metal catalysts are required when zirconium alkoxides are used]. Surprisingly, tetrakis(triphenylphosphine)palladium(0) will *not* catalyze the conversion of benzyl bromide to n-butylphenyl acetate by titanium n-butoxide and carbon monoxide (28% benzyl n-butyl ether was isolated, the remainder being recovered starting material).

In the interaction between borate esters, $[1,5\text{-}HDRhCl]_2$, and carbon monoxide, it was proposed that an intrmediate complex was formed which may or may not contain a B–Rh bond (structure 4 and i in ref 1). Alkoxy transfer would occur from boron to either rhodium or a carbonyl carbon. **Analogous rhodium intermediates, which may be involved in the titanium and zirconium alkoxide reactions, can account for the formation of esters.** The isolation of ethers (and ketones) can best be rationlized by titanium **or zirconium–rhodium complexes containing a Rh–OR group (Scheme I).**

Scheme I



It should be noted that treatment of chloro(dicarbonyl)rhodium(I) dimer with zirconium n-propoxide results in the rapid appearance of new carbonyl stretching bands in the infrared region. Rhodium carbonyl chloride dimer in *n*-heptane, has IR bands at 2103, 2084, 2075, 2032, and 2000 cm^{-1}. Exposure of the rhodium compound to an equivalent amount of zirconium *n*-propoxide results in the appearance of broad bands at 2068 and 1967 cm^{-1}. When a 10-fold excess of the zirconium alkoxide was used, only the two noted intense bands were observed. Analogous results were obtained with zirconium ethoxide or titanium *n*-butoxide in place of zirconium *n*-propoxide. Attempts to isolate these complexes in analytically pure form failed. Treatment of the generated complex with halide affords ester.

In conclusion, titanium and zirconium alkoxides are valuable reagents for converting halides to esters, using rhodium and/or palladium catalysts. The reaction is very sensitive to the nature of the alkoxy groups.

Experimental Section

General Methods. All reactants (halides, titanium or zirconium alkoxides) were used as received. Chloro(1,5-hexadiene)rhodium(I) dimer was prepared from rhodium chloride according to the procedure of Marko and co-workers.[5] Tetrakis(triphenylphosphine)palladium(0) was synthesized by standard methods.[6] Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer. Varian T-60, EM-360, and FT-80 instruments were used for recording NMR spectra. A VG 5050 Micromass spectrometer was used for mass spectral determinations.

General Procedure for the Carbonylation Reaction of Benzylic Halides with Titanium and Zirconium Alkoxides. A mixture of benzylic halide [2.0 mmol], metal alkoxide [2 mL—or an equimolar amount in *n*-heptane], and rhodium(I) catalyst [0.10–0.15 mmol] was heated overnight under a carbon monoxide atmosphere at 75 °C (bromide) or 100 °C (chloride). After cooling to room temperature, 1 M NaOH was added and the solution was extracted with ether or hexane. The organic extract was dried ($MgSO_4$) and concentrated and the pure ester was obtained by distillation and/or chromatography.

General Procedure for the Carbonylation Reaction of Non-Benzylic Bromides with $M(OR)_4$ [M = Ti, Zr]. Carbon monoxide was bubbled through a solution containing the bromide [2.0 mmol], metal alkoxide [2.0 mL], and tetrakis(triphenylphosphine)palladium [0.13 g, 0.11 mmol, M = Ti] or $Pd(PPh_3)_4$ [0.13 g, 0.11 mmol]/$[1,5\text{-HDRhCl}]_2$ [0.090 g, 0.20 mmol, M = Zr]. The reaction mixture was stirred overnight at 150 °C. Workup was effected in the same manner as that described for benzylic bromide.

Acknowledgment. We are grateful to British Petroleum and to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. **2** (Ar = Ph, X = Br), 100-39-0; **2** (Ar = 2-$C_{10}H_7$, X = Br), 939-26-4; **2** (Ar = Ph, X = Cl), 100-44-7; **2** (Ar = *o*-$CH_3C_6H_4$, X = Cl), 552-45-4; **2** (Ar = *p*-$CH_3C_6H_4$, X = Cl), 104-82-5; **2** (Ar = *m*-$MeOC_6H_4$, X = Cl), 824-98-6; **2** (Ar = 1-$C_{10}H_7$, X = Cl), 86-52-2; **3** (M = Ti, R = $(CH_3)_2CH$), 546-68-9; **3** (M = Ti, R = *n*-C_3H_7), 3087-37-4; **3** (M = Zn, R = C_2H_5), 18267-08-8; **3** (M = Ti, R = *n*-C_4H_9), 5593-70-4; **3** (M = Zr, R = *n*-C_3H_7), 23519-77-9; **3** (M = Zr, R = $(CH_3)_2CH$), 2171-98-4; **3** (M = Zr, R = *n*-C_4H_9), 1071-76-7; **3** (M = Ti, R = C_2H_5), 3087-36-3; **4** (Ar = Ph, R = $(CH_3)_2CH$), 4861-85-2; **4** (Ar = Ph, R = *n*-C_3H_7), 4606-15-9; **4** (Ar = Ph, R = C_2H_5), 101-97-3; **4** (Ar = 2-$C_{10}H_7$, R = $(CH_3)_2CH$), 91759-48-7; **4** (Ar = 2-$C_{10}H_7$, R = *n*-C_4H_9), 2876-68-8; **4** (Ar = Ph, R = *n*-C_4H_9), 122-43-0; **4** (Ar = *o*-$CH_3C_6H_4$, R = *n*-C_4H_9), 96307-73-2; **4** (Ar = *o*-$CH_3C_6H_4$, R = C_2H_5), 40291-39-2; **4** (Ar = *o*-$CH_3C_6H_4$, R = *n*-C_3H_7), 96307-74-3; **4** (Ar = *p*-$CH_3C_6H_4$, R = C_2H_5), 14062-19-2; **4** (Ar = *p*-$CH_3C_6H_4$, R = *n*-C_4H_9), 93578-99-5; **4** (Ar = *m*-$CH_3OC_6H_4$, R = *n*-C_4H_9), 96307-75-4; **4** (Ar = *m*-$CH_3OC_6H_4$, R = *n*-C_3H_7), 96307-76-5; **4** (Ar = 1-$C_{10}H_7$, R = *n*-C_4H_9), 2876-75-7; **4** (Ar = 1-$C_{10}H_7$, R = C_2H_5), 2122-70-5; **4** (Ar = 1-$C_{10}H_7$, R = *n*-C_3H_7), 551-04-2; **4** (Ar = *m*-$CH_3C_6H_4$, R = $(CH_3)_2CH$), 6297-45-6; **4** (Ar = *m*-$CH_3C_6H_4$, R = *n*-C_4H_9), 6640-77-3; $(PhCH_2)_2CO$, 102-04-5; $PhCH_2O$-*n*-C_3H_7, 937-61-1; $PhCH_2O$-*n*-C_4H_9, 588-67-0; *o*-$CH_3C_6H_4CH_2O$-*n*-C_3H_7, 91967-69-0; (*p*-$CH_3C_6H_4CH_2)_2CO$, 70769-70-9; *m*-$CH_3OC_6H_4CH_2O$-*n*-C_3H_7, 96307-77-6; 1-$C_{10}H_7CH_2O$-*n*-C_3H_7, 92297-67-1; 1-$C_{10}H_7CH_2O$-*n*-C_4H_9, 96307-78-7; 1-$C_{10}H_7CH_3$, 90-12-0; $[1,5\text{-HDRhCl}]_2$, 32965-49-4; CO, 630-08-0; $Pd(PPh_3)_4$, 14221-01-3; 1-$C_{10}H_7C(O)O$-*n*-C_4H_9, 3007-95-2; 1-$C_{10}H_7C(O)O$-*n*-C_3H_7, 3007-96-3; $PhCH{=}CHC(O)O$-*n*-C_4H_9, 538-65-8; $PhCH{=}CHC(O)O$-*n*-C_3H_7, 7778-83-8; *n*-$C_8H_{17}C(O)O$-*n*-C_4H_9, 50623-57-9; *m*-$CH_3C_6H_4Br$, 591-17-3; 1-$C_{10}H_7Br$, 90-11-9; $PhCH{=}CHBr$, 103-64-0; *n*-$C_8H_{17}Br$, 111-83-1.

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Iodine-Induced Cyclization Reaction of *O*,*O*-Dialkyl 4-Pentenylphosphonates

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Received October 17, 1984

The stereoselective synthesis of *cis*-2-alkoxy-2-oxo-6-(iodomethyl)-1,2-oxaphosphorinanes is achieved by the treatment of *O*,*O*-dialkyl 4-pentenylphosphonates with iodine. The intermediates involved in iodine-induced cyclization reactions of δ-unsaturated phosphonates could be observed directly by ^{31}P NMR at 37 °C. The effects of the iodine concentration and solvents on the cyclization reaction were investigated. In chloroform, there were two intermediates, the major one being (4,5-diiodopentyl)phosphonate; the other one could be a cyclic alkyl trialkoxyphosphonium ion. In benzene and cyclohexane, in addition to these two intermediates, there was at least one more intermediate which could be either a tight ion pair or a pentacoordinate phosphorus compound.

2-Alkoxy-2-oxo-1,2-oxaphosphorinanes are useful as nonflammable hydraulic fluids, plasticizers, and fire retardants for plastics.[1-3] There are many methods[3-11] to synthesize these compounds, but these procedures require

0022-3263/85/1950-2136$01.50/0