Dalton Communications

Carbonylation of Organic Halides catalysed by Rhodium Triethylphosphine Complexes

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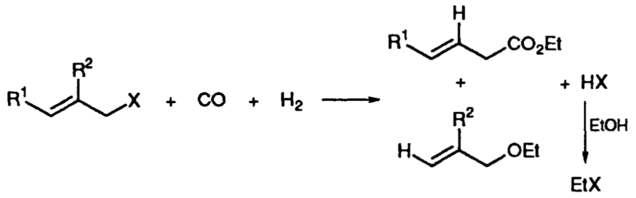
Allyl and benzyl halides but not phenyl or propyl halides have been carbonylated in ethanol in the presence of rhodium triethylphosphine complexes to their respective butenoic or benzylic esters; no added base was required.

The carbonylation of organic iodides to esters is possible using a variety of different catalysts, but is much less common for the more readily available organic chlorides.[1] There are a few isolated reports of carbonylation of *e.g.* 3-chloropropene or benzyl chloride[2] in the presence of homogeneous Ni-,[3] Pd-[4] or Co-based[5] catalysts but yields are often low, a base is required and isomerisation to bring the double bond into conjugation with the carbonyl group is sometimes a side reaction. Rhodium-based catalysts tend to have very low activity because of the ready formation of inactive $[\{RhCl(CO)_2\}_2]$.[6] There have also been recent reports of the carbonylation of a range of organic chlorides using $[Pd\{Pr^i_2P(CH_2)_3PPr^i_2\}_2]$ as catalyst[6] as well as of the carbonylation of aryl chlorides using palladium complexes with bulky phosphines[7] or under phase-transfer conditions.[8] Once again, a base is required.

We have recently been investigating the hydrocarbonylation of alkenes using rhodium triethylphosphine catalysts and have shown that *e.g.* heptanol and 2-methylhexanol can be produced directly from hexene under mild conditions without the intermediacy of aldehydes[9–11] and that prop-2-en-1-ol produces butane-1,4-diol and 2-methylpropanol.[12] In an attempt to extend this type of reaction to other substrates, we studied 3-chloropropene in the expectation that 3-chlorobutanol and its branched analogue might be formed.

If 3-chloropropene is heated with $[Rh_2(O_2CMe)_4]$ and PEt_3 in ethanol under CO/H_2 or CO, the double bond is unaffected but conversion to ethyl but-3-enoate and ethyl prop-2-enyl ether† occurs even in the absence of added base (Table 1 and Scheme 1). The other major product is HCl, although EtCl is formed from reaction of HCl with ethanol. Analogous reactions occur for 3-bromo- and 3-iodo-propene, although in the latter small amounts of ethyl propanoate are also produced. Propene is identified as a product in all of these reactions, although its volatility makes quantification difficult. We assume it is formed by protonation of a σ-allyl rhodium complex and that it accounts for the lack of mass balance in the figures of Table 1.

The results presented in Table 1 suggest that the overall reactivity of the propenyl halides is in the order RI > RBr > RCl, but that selectivity towards the ester product is largely determined by the rate of the etherification reaction, which also occurs in the absence of catalyst. If this is high (RI), the reaction shows low selectivity towards the ester whilst if it is low (RCl), the selectivity towards the ester is high. The overall yield of ester, although not selectivity towards it, is highest for RBr because the overall reactivity of propenyl bromide is high but the rate of etherification is moderate. By carrying out reactions to higher overall conversions, chlorides offer the highest yield and selectivity to ester formation.



Scheme 1 Carbonylation of allyl halides catalysed by $[Rh_2(O_2CMe)_4]$–PEt_3 in ethanol; R^1 and R^2 are Me or H, X is Cl, Br or I

We have also investigated reactions with other alkyl halides and find that, whereas benzyl chloride gives low conversions to $PhCH_2CO_2Et$, chlorobenzene, 1-chloropropane and iodoethane are all unreactive towards carbonylation. This reactivity pattern can be rationalised in two different ways. Either η^3-allyl formation, which is possible for propenyl or benzyl, but not for alkyl or aryl groups, is important, or the reaction may involve the intermediacy of free radicals, which are stabilised for propenyl or benzyl. In order to try to distinguish between these possibilities, we have studied reactions of Bu^tBr which cannot form an η^3-allyl intermediate but would give stabilised free Bu^t radicals. In this case, carbonylation does not occur suggesting that the free radical explanation is probably not correct. Partial support for the intermediacy of η^3-allyl intermediates is provided by the products obtained from halogenobut-2-enes and 3-chlorobutene. In all cases, the only esters produced are ethyl pent-3-enoate (6:1 *E*:*Z*) showing that the reactions involve a step in which the two ends of the allyl group become equivalent, but we cannot be certain whether this is because the oxidative addition involves free allyl radicals or because an η^3-allyl intermediate is formed. The conversions in these reactions are higher than in the other cases because the autoclaves were heated with heating bands. We have shown[13] that this method of heating allows the reaction temperature to be reached in 10 min, whereas a cold autoclave placed into a preheated oven (the method used for the other reactions) takes *ca.* 2 h to reach the required reaction temperature. Investigations for nickel- and palladium-catalysed systems have indicated that η^3-allyl intermediates may be important in those

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† Ethers can also be side products in related cobalt catalysed reactions with the ether : ester ratio being base dependent.[5]

Table 1 Products obtained from carbonylation of organic halides in the presence of rhodium catalysts[a]

		Products (%)			
Substrate (RX)	Conversion (%)	RCO_2Et	ROEt	EtX	$EtCO_2Et$
CH_2=$CHCH_2Cl$	64	33	7	*b*	
CH_2=$CHCH_2Cl$[c]	Trace	0	Trace		
CH_2=$CHCH_2Br$	91	55	27	*b*	
CH_2=$CHCH_2I$	88	16	57	91	Trace
MeCH=$CHCH_2Cl$[d]	100	47,[e] 8[f]	17[g]	*b*	
MeCH=$CHCH_2Br$[h]	100	31,[e] 5[f]	22[g]	*b*	
CH_2=CHCH(Me)Cl[i]	100	61,[e] 9[f]	16[g]	*b*	
$PhCH_2Cl$	43	1	19	*b*	
PrCl	0	—	—		
EtI	11	0	16	*b*	
Bu^tBr[j]	15	0	13	*b*	

[a] $[Rh_2(O_2CMe)_4]\cdot 2MeOH$ (2×10^{-5} mol), PEt_3 (4×10^{-4} mol), RX (1 cm^3), EtOH (4 cm^3), CO (40 atm), 120 °C, 4 h. Propene is detected as a product from allyl halides and is assumed to account for the mass imbalance. [b] Not quantified. [c] Omitting PEt_3. [d] Catalyst was preformed $[Rh(O_2CMe)(CO)(PEt_3)_2]$. Other products are CH_2=CHCH(Me)OH (24%) and isomers of C_8H_{14} (10%) which are formed together with the ethers in the absence of catalyst. Heating bands were employed. [e] *E*-MeCH=$CHCH_2CO_2Et$. [f] *Z*-MeCH=$CHCH_2CO_2Et$. [g] CH_2=CHCH(Me)OEt. [h] Catalyst was preformed $[Rh(O_2CMe)(CO)(PEt_3)_2]$. Other products are CH_2=CHCH(Me)OH (19%) and isomers of C_8H_{14} (19%) which are formed together with the ethers in the absence of catalyst. Heating bands were employed. [i] Catalyst was preformed $[Rh(O_2CMe)(CO)(PEt_3)_2]$. Other products are CH_2=CHCH(Me)OH (9%) and isomers of C_8H_{14} (14%) which are formed together with the ethers in the absence of catalyst. Heating bands were employed. [j] Trace of 2-methylpropene observed.

cases.[5] Interestingly, the only ether formed during the carbonylation of CH_2=CHCH(Me)Cl or MeCH=$CHCH_2X$ (X = Cl or Br) is CH_2=CHCH(Me)OEt perhaps suggesting that a different pathway operates for the formation of the ether than is involved in the ester formation.

Finally, reactions carried out in the absence of PEt_3 do not produce ester products suggesting that the important intermediates contain PEt_3. Interestingly, in the dicarbonylation of CH_2I_2 to malonate esters using similar catalytic systems, PEt_3 is not essential for the reaction.[14]

The main advantage of the system described here over others that have been reported in the literature is that no base is required so that salts are not produced as wasteful side products which must be separated and disposed of. It is possible to produce similar products from the carbonylation of allyl carbonates using palladium catalysts,[15] but the advantage is lost in this case because a base (pyridine) is used in the synthesis of the allyl carbonates from allyl alcohols and ethyl chloroformate.[15]

Acknowledgements

We thank Drs. M. Green and S. Taylor for many helpful discussions and BP Chemicals and the SERC for two studentships (to M. C. S. and M. J. P.).

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Received 21*st June* 1994; *Communication* 4/03775H