The Double Carbonylation of Diiodomethane Catalysed by Rhodium Complexes

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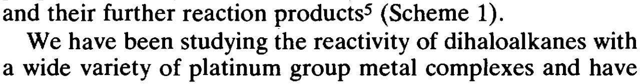
In alcohols, ROH, in the presence of $[\mathrm{Rh_2(OAc)_4}]$, and optionally also in the presence of a tertiary phosphorus ligand $\mathrm{PR'_3}$, $\mathrm{CH_2I_2}$ reacts with CO to give $\mathrm{CH_2(CO_2R)_2}$, $\mathrm{CH_2(OR)_2}$ and RI.

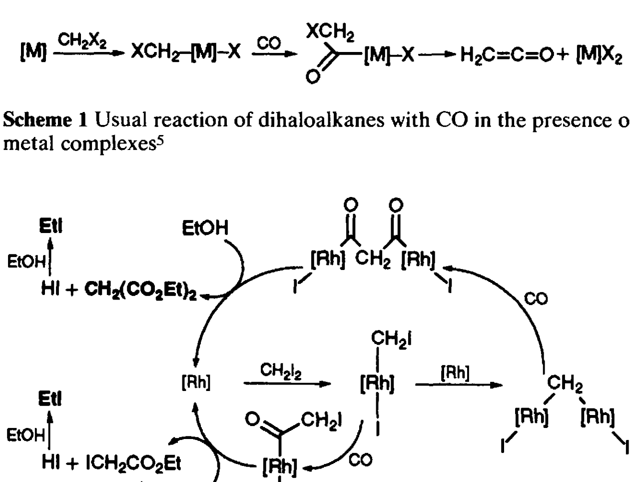
Although the double carbonylation of aryl halides to give 1,2-dicarbonyl compounds is relatively well known[1] and the catalytic formation of diesters from 1,4-dichlorobenzene has been reported,[2,3] the double carbonylation of geminal dihalides to give 1,3-dicarbonyl species is not well established. There has been one isolated report[4] of the double carbonylation of $\mathrm{CH_2Cl_2}$ by a palladium based catalyst though the yields were low even in the presence of added bases and few details of this system have appeared. Attempts to promote reactions of this kind generally lead to the elimination of halide from the proposed haloacyl intermediate with the formation of ketenes and their further reaction products[5] (Scheme 1).

We have been studying the reactivity of dihaloalkanes with a wide variety of platinum group metal complexes and have found that, under some conditions, diesters of malonic acid can be formed from $\mathrm{CH_2I_2}$ and CO, a rare example of the selective formation of a $\mathrm{C_3}$ product from $\mathrm{C_1}$ building blocks.

In the presence of $[\mathrm{Rh_2(OAc)_4}]$, $\mathrm{CH_2I_2}$ reacts with CO in ethanol to give diethyl malonate, diethoxymethane, ethyl iodide and a trace of ethyl propanoate (See Table 1). The overall conversion of diiodomethane is low (30%), the selectivity to the malonate ester is also modest (30%) and there is a considerable amount of reacted $\mathrm{CH_2I_2}$ unaccounted for. Lower conversions to diethyl malonate are observed when the reaction is carried out in the presence of a tertiary phosphorus ligand $\mathrm{PR'_3}$ ($\mathrm{PR'_3 = PMe_3, PEt_3, P(OEt)_3, PPr^i_3}$) but, at least for $\mathrm{PEt_3}$, the selectivity for diethyl malonate is higher and there is considerably less $\mathrm{CH_2I_2}$ unaccounted for. The yield of diethyl malonate in the $\mathrm{PEt_3}$ promoted system can be improved by the addition of NaOAc as a base although the selectivity is somewhat reduced. When NaOAc is added to a system in the absence of a phosphine no diethyl malonate is produced. $\mathrm{K_2CO_3}$ inhibits the formation of malonate esters even in the presence of $\mathrm{PEt_3}$, but $\mathrm{CH_2(OEt)_2}$ is still produced.



Scheme 1 Usual reaction of dihaloalkanes with CO in the presence of metal complexes[5]



Scheme 2 Proposed mechanisms for formation of diethyl malonate from $\mathrm{CH_2I_2}$, CO and ethanol in the presence of rhodium complexes, [Rh]

Replacing ethanol with methanol or propan-2-ol produces dimethyl or diisopropyl malonate respectively but, where no alcohol or a tertiary alcohol is used as the solvent no carbonylation reaction occurs. In the presence of $\mathrm{PEt_3}$ the use of a 1 : 1 mixture of ethanol and DMF gave an increased yield of the malonate ester over that obtained from the reaction carried out in ethanol alone.

These reactions are genuinely catalytic since up to *ca.* 60 catalyst turnovers can be observed under various conditions. However conditions for the high conversion of $\mathrm{CH_2I_2}$ to $\mathrm{CH_2(CO_2Et)_2}$ have not been elucidated. We are currently attempting to identify the causes of inhibition of the reaction, but model studies[6] involving reactions of the complex, $[\mathrm{RhClI(CH_2I)(CO)(PEt_3)_2}]$ with high pressures of CO in $\mathrm{CH_2Cl_2}$ suggest that $[\mathrm{RhClI_2(CO)(PEt_3)_2}]$ is readily formed, although we have not yet studied this reaction in alcoholic solvents. We have also shown that $[\mathrm{Et_3PCH_2I}]\mathrm{I}$, which is formed on heating $\mathrm{CH_2I_2}$ with $\mathrm{PEt_3}$, reacts with $[\mathrm{RhI(CO)(PEt_3)_2}]$ to give $[\mathrm{RhI_3(CO)(PEt_3)_2}]$. Formation of such a rhodium(III) complex during the catalytic reaction would stop the activation of $\mathrm{CH_2I_2}$ and terminate the reaction. Inhibition by one of the reaction products HI or EtI may also occur.

Although the exact nature of the catalytic cycle for diethyl malonate formation is not known, it is possible to rationalise the formation of the various products on the basis of Scheme 2. Thus, oxidative addition of $\mathrm{CH_2I_2}$ to a rhodium(I) centre leads to the corresponding rhodium(III) species which either inserts CO into the Rh–C bond or oxidatively adds to another

Table 1 Products from the carbonylation of $\mathrm{CH_2I_2}$ in ethanol[a]

$\mathrm{PR_3}$	Additive[b]	Conversion (%)	$\mathrm{CH_2(CO_2Et)_2}$ (%)[c]	$\mathrm{CH_2(OEt)_2}$ (%)[c]	EtI (%)[d]	$\mathrm{EtCO_2Et}$ (%)[d]
—	—	32.7	9.5	2.7	40	0.9
—	NaOAc	—	—	—	—	—
$\mathrm{PEt_3}$	—	8.1	5.9	1.3	14	Trace
$\mathrm{PEt_3}$	NaOAc	15.4	9.0	2.4	38	0.2
$\mathrm{PEt_3}$	$\mathrm{K_2CO_3}$	89.4	—	0.8	16	—
$\mathrm{PEt_3}$[e]	—	46.0	6.6	Trace	9	Trace
$\mathrm{P(OEt)_3}$	—	44.4	6.2	1.9	19	—
$\mathrm{P^iPr_3}$	—	49.2	2.2	0.6	10	—
$\mathrm{Me_2PCH_2CH_2PMe_2}$[f]	—	29.9	2.6	0.6	9	—
$\mathrm{PEt_3}$[g]	—	100	—	—	—	—

[a] $[\mathrm{Rh_2(OAc)_4}] = 4 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{PR_3}] = 0.012$ mol dm^{-3}, $\mathrm{CH_2I_2}$ (1 cm^3) in EtOH (4 cm^3), $p_{\mathrm{CO}} = 40$ atoms, 120 °C, 4 h. [b] 0.024 mol added as a solid. [c] Based on initial $[\mathrm{CH_2I_2}]$. [d] Based on $\mathrm{CH_2I_2}$ consumed. It is assumed that each molecule of $\mathrm{CH_2I_2}$ consumed should produce 2 mol of EtI or $\mathrm{EtCO_2Et}$. [e] EtOH–DMF, 1:1. [f] 8×10^{-3} mol dm^{-3}. [g] $\mathrm{ICH_2CO_2Et}$ (1 cm^3) as substrate, main product is $\mathrm{EtOCH_2CO_2Et}$.

Rh^I centre. The mononuclear pathway leads initially to ethyl iodoacetate (ICH_2CO_2Et) either by reductive elimination of ICH_2CO_2I followed by reaction with the solvent or by direct attack of ethoxide onto the coordinated iodoacetyl ligand. A similar sequence of reactions would convert ICH_2CO_2Et through to diethyl malonate. The alternative binuclear pathway on the other hand would lead directly to diethyl malonate. Preliminary studies using ICH_2CO_2Et as a substrate do not yield diethyl malonate, suggesting that the mononuclear pathway is unlikely. If the dinuclear pathway operates, oxidative addition to the second rhodium centre must be considerably more facile than to the first because of the relative concentrations of CH_2I_2 and the rhodium complex. Our model studies on oxidative addition of dihalomethanes to $[RhCl(CO)(PEt_3)_2]$ show that the more electron poor carbon atoms add less readily. Thus, when ICH_2– is attached to Rh, it should add more readily to another rhodium centre than when it is attached to I. Detailed kinetic and model studies will, however, be required to prove that the dinuclear pathway does in fact operate.

Diethoxymethane is produced in low yield if the rhodium catalyst is omitted, and is the major product in the presence of base. Catalysed and non-catalysed reactions probably contribute to its formation, but it is premature to speculate on the mechanism of its formation. EtI is formed by the reaction of the solvent ethanol with HI produced during the formation of the other reaction products.

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