Stoicheiometric Reduction of Activated Olefins by Co-ordinated and Free Tertiary Alkyl Phosphines†

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Summary Activated olefins, $HR^1C{=}CR^1H$ ($R^1 = CO_2Me$ or COPh), are reduced rapidly and stoicheiometrically by some alkyl phosphines, PR^2_3, (R^2 = Et, Pr^n, or Bu^n), both free and initially bound to cobalt, in anhydrous methanol; the reaction proceeds by the formation of an ylide.

PHOSPHINES are commonly used to stabilise transition metals in their lower oxidation states.[1] These co-ordinated phosphines have generally been regarded as relatively inert towards the olefins frequently used as model substrates for catalytic hydrogenation. However, we have found that some phosphines will themselves stoicheiometrically reduce activated olefins, even though the phosphines were originally bound to a metal centre.

Triphenylphosphine adds to activated olefins (**1**) to give,[2] at equilibrium, a low concentration of the phosphonium

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† No reprints available.

ylide (**2**), which in all reported cases is stable to refluxing alcohols. We have found that some trialkylphosphines react at 35 °C with certain doubly activated olefins (**3**) in anhydrous methanol to form ylides which subsequently decompose to give the corresponding alkane derivative. This reaction is not limited to free phosphine but will also induce the decomposition of an otherwise stable metal–phosphine complex (see Table). In a study of the hydrogenation of dimethyl fumarate catalysed by $[\mathrm{CoH_2(bip)(PBu^n_3)_2}]^+$ (bip = 2,2′-bipyridine), we observed that the hydrogenation was almost entirely due to $\mathrm{PBu^n_3}$ 2 moles of which were liberated per mole of the catalyst. The results of subsequent experiments are summarised in the Table.

Table. Reaction of phosphines with dimethyl fumarate at 35 °C in dry methanol.

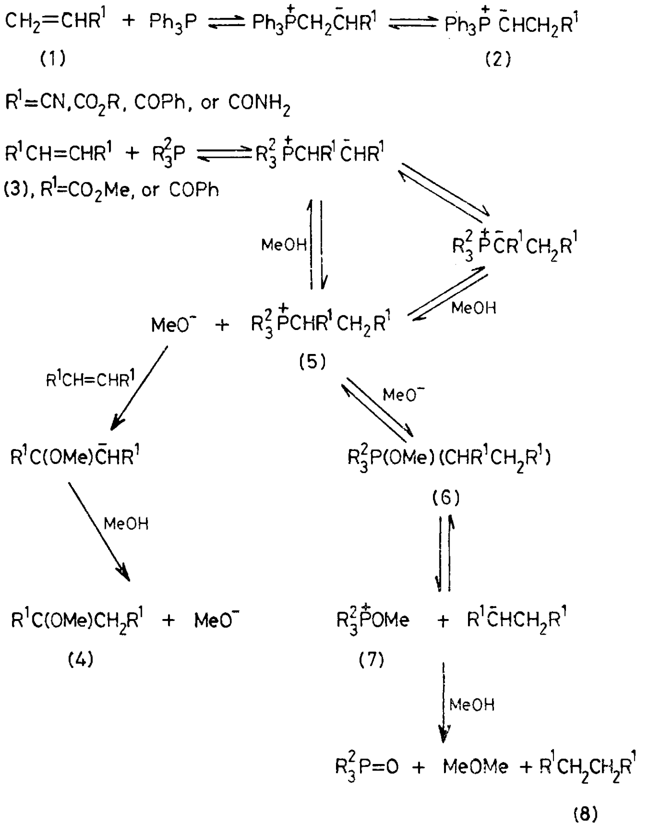
Phosphine	Ylide formed[a]	(**8**) formed	$t_{\frac{1}{2}}$/s[b]
$\mathrm{PEt_3}$	Yes	Yes	1530
$\mathrm{PPr^n_3}$	Yes	Yes	1640
$\mathrm{PPr^i_3}$	No	No	—
$\mathrm{PBu^n_3}$ (free)	Yes	Yes	1670
$\mathrm{PBu^n_3}$ {added as 0·05 M $[\mathrm{CoH_2(bip)(PBu^n_3)_2}]^+$}	Yes	Yes	12,000
$\mathrm{PBu^t_3}$	No	No	—
P(cyclohexyl)$_3$ ..	No	No	—
$\mathrm{PH_2Ph}$	No	No	—
$\mathrm{PPh_3}$	No	No	—
$\mathrm{P(CH_2CH_2CN)_3}$ ..	No	No	—

[a] Detected by a measurable decrease in the concentration of dimethyl fumarate found by g.l.c., *i.e.* 5% or more, without corresponding product formation. [b] [Dimethyl fumarate] = [phosphine] = 0·1 M. $t_{\frac{1}{2}}$ = Time for the formation of 0·05 M (**8**).

Comparison of the results for $\mathrm{PPr^n_3}$ and $\mathrm{PPr^i_3}$ indicates the relative importance of electronic and steric effects in the reaction. Increasing electron-donation in the phosphine largely balances steric hindrance to ylide formation for the n-alkyl groups although it is insufficient for the more sterically hindered cases of $\mathrm{PPr^i_3}$ and $\mathrm{PBu^t_3}$.

Provided there was no trace of water, excess of fumerate was catalytically removed as the ether (**4**) at the same time as it was also being stoicheiometrically reduced to the succinate (**8**) by the phosphine. In the presence of 0·03 M water, the formation of (**4**) showed an induction period corresponding to the removal of the water by the aqueous hydrolysis[3] of the phosphonium salt (**5**).

The overall mechanism operating is summarised in the Scheme. The mild conditions necessary for the decomposition of the methoxide (**5**) are presumably due to stabilisation of the anionic leaving group.[4] The addition of methoxide ion to a reacting mixture did not affect the rate of formation of dimethyl succinate (**8**), indicating that the rate determining step is the formation of the methoxyphosphonium salt (**7**) from the quinquevalent intermediate (**6**). This is further supported by the similarity in the rates of formation of (**8**) shown in the Table for free phosphines and is in complete contrast with the mechanism proposed for alkaline hydrolysis.[5]



Scheme

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