Increase in Reaction Rate Consequent on the Use of a Polymer-supported Reagent. Evidence for Interaction between a High Proportion of the Groups of a Polymer-supported Reagent

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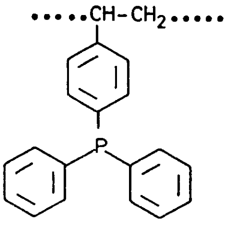
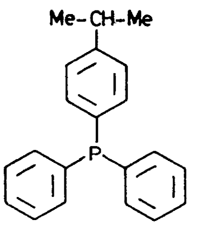
Summary The conversion of alcohols into alkyl chlorides and of acids into acid chlorides by aryl phosphines and carbon tetrachloride proceeds more rapidly when the phosphine is polymer-supported; in these reactions, the main pathway appears to involve two phosphorus-containing residues on the polymer reacting together.

THERE has recently been considerable interest in polymer-supported (P.S.) reagents mainly because of the simplicity of the work-up procedure.[1] Such a reagent is the cross-linked phosphine polymer (I). This reacts smoothly with



(I)



(II)

alcohols[2,3] or acids[2] in CCl_4 at 78 °C to give alkyl chlorides or acid chlorides, respectively, in high yield. We report that these P.S. reactions proceed more rapidly than those using Ph_3P itself and that the main reaction pathway in the P.S. reactions involves two phosphorus-containing residues reacting together. There has been considerable discussion about the extent to which residues on cross-linked polymers may interact.[4] Our results indicate that with the present highly substituted 1% cross-linked polymer, at least 60% of the groups can interact with others.

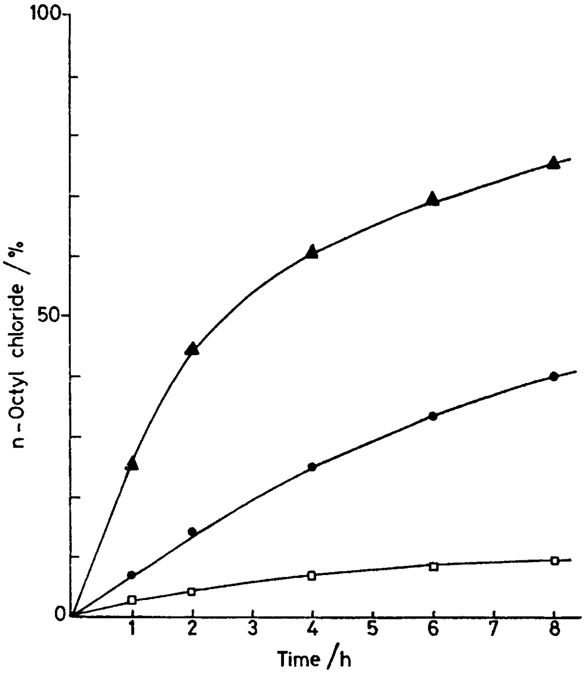


FIGURE. Reactions of n-octanol (1·0 mmol) with phosphines (2·0 mmol) in CCl_4 (10 ml) at 60 °C. ▲, reaction using the polymer (I); ●, reaction using the phosphine (II); □, reaction using Ph_3P. The yield of n-octyl chloride was determined by g.l.c. analysis. The amounts of the chloride and alcohol detected accounted for >90% of the starting material.

The rates of the P.S. reactions were compared with those for analogous reactions using the same number of mmole of Ph_3P or the phosphine (II)† in the same volume of CCl_4 at 60 °C, the reaction temperature being chosen to give readily measured rates. The results obtained using n-octanol as the substrate are shown in the Figure. After 2 h, the yield of n-octyl chloride in the P.S. reaction was 13 times that in the reaction using Ph_3P and 3·5 times that in the reaction using the phosphine (II). Similar results were obtained when 2-n-butoxyethanol, benzyl alcohol, octanoic acid, or benzoic acid were the substrates. Clearly, to some extent, the P.S. reactions are faster because the polymeric phosphine residues are alkyl substituted. The rate of the overall reaction is probably determined mainly by the rate of reaction between the phosphine and CCl_4, because when the polymeric phosphine (I) and Ph_3P were separately treated for 3 h with CCl_4 at 78 °C before addition of the n-octanol, octyl chloride was formed more rapidly (57 and 63% yields respectively after 2 h at 60 °C) than in the previous reactions.

Reactions of alcohols with Ph_3P and CCl_4 produce alkyl halides by two pathways [reactions (1) and (2)].[5,6] The latter may be followed by reactions (3) and (4).[6]‡ The relative contributions of these pathways can be estimated by determining the amounts of chloroform produced and the number of moles of phosphine required for each mole of alkyl halide formed.

$$ROH + Ph_3P + CCl_4 \longrightarrow RCl + Ph_3P{=}O + CHCl_3 \qquad (1)$$

$$ROH + 2Ph_3P + CCl_4 \longrightarrow RCl + Ph_3P{=}O + Ph_3P^+CHCl_2\,Cl^- \qquad (2)$$

$$\begin{aligned} ROH + Ph_3P + Ph_3P^+CHCl_2\,Cl^- \longrightarrow{} & RCl + Ph_3P{=}O \\ & + Ph_3P^+CH_2Cl\,Cl^- \qquad (3) \end{aligned}$$

$$\begin{aligned} ROH + Ph_3P + Ph_3P^+CH_2Cl\,Cl^- \longrightarrow{} & RCl + Ph_3P{=}O \\ & + Ph_3P^+Me\,Cl^- \qquad (4) \end{aligned}$$

When n-octanol (1·1 mmol) in CCl_4 was treated with the polymer (I) (1·0 mmol) (1% crosslinked, 90% of the polystyrene rings substituted with diphenylphosphinyl residues),[7] 0·31 mmol of $CHCl_3$ was produced per mmole of n-octyl chloride formed, suggesting that 31% of the halide was formed by the P.S. analogue of reaction (1).§ This, and the fact that 2·0—2·2 phosphine residues were required for each molecule of halide produced, suggests that the principal pathway for the formation of halide was reaction (2) with only minor contributions, if any, from reactions (3) and (4).¶

Reaction (2) involves two phosphorus-containing groups on the polymer reacting together [reaction (5)]. Flory has demonstrated that in reactions of this general type a small

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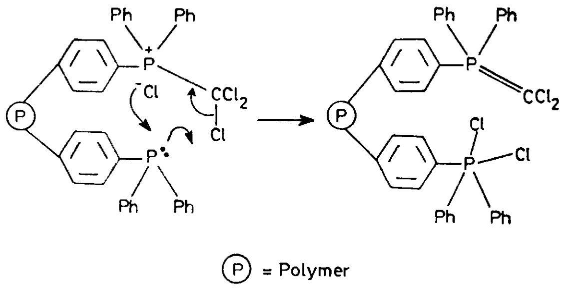
† Satisfactory analytical and spectral data were obtained for this compound.

‡ These reactions also apply to the polymeric systems.

§ This is actually a maximum contribution from reaction (**1**) because reaction of the polymer (I) with CCl_4 in the absence of n-octanol produces small amounts of chloroform. We thank a referee for pointing this out. The chloroform is probably formed as a result of an electrophilic species attacking the benzene rings. If $CHCl_3$ is produced in the same manner and to the same extent when n-octanol is present, the contribution of reaction (1) falls to 18%.

¶ Reaction (2) requires the consumption of 2·0 phosphine residues for each alkyl halide molecule produced; reactions (2) and (3) together require 1·5, reactions (2), (3), and (4) together require 1·3, and reaction (1) requires 1·0. Judging by the efficiency with which alkyl halides react with the phosphine resin to give phosphonium salts, >90% of the phosphine residues are available for reaction.



(5)

percentage of the groups will not be involved for statistical reasons.[8] In the present case, the isolated groups not reacting as in reaction (2) may react *via* reaction (1) or by reactions (3) and (4).

Evidence that reaction (2) is able to make a major contribution to the production of n-octyl chloride was obtained by treating the polymer (I) (2·0 mmol) with CCl_4 in the presence of benzaldehyde (1·0 mmol).[9] This gave ββ-dichlorostyrene [60% of the maximum expected if the overall reaction proceeded entirely *via* reaction (5)] and benzylidene chloride (81%). It is clear that with the present polymer at least 60% of the phosphine groups were able to interact with each other.

It is not clear why the P.S. reactions are faster. Of the possible contributing factors, a major one may be that reaction (5) proceeds more rapidly on the polymer owing to the close proximity of the phosphorus-containing residues, but other factors, for example, that as the reaction proceeds the interior of the polymer becomes a relatively polar environment, may make a contribution.

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