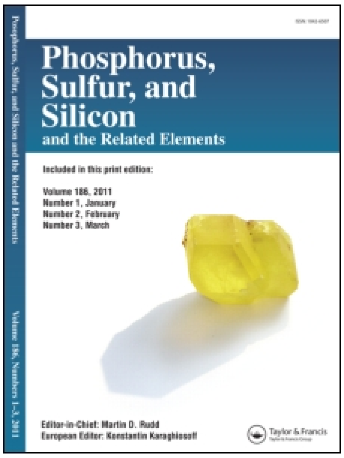

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# Chemical Modification of Polyvinylbenzyltriphenylphosphonium Salts and their Applications as Reagents in Organic Synthesis

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# CHEMICAL MODIFICATION OF POLY-VINYLBENZYLTRIPHENYLPHOSPHONIUM SALTS AND THEIR APPLICATIONS AS REAGENTS IN ORGANIC SYNTHESIS

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Abstract Insoluble polymer-bound reagents derived from poly(vinylbenzyltriphenylphosphonium salts) have been prepared and used as reagents in organic synthesis. The polymer-supported borohydride was used as reducing agent towards carbonyl compounds. The reaction of polymer-supported thiocyanate and nitrile anions with alkyl halides in hydrocarbon solvents gave good yields of the corresponding alkyl thiocyanates and nitroalkanes, respectively. In addition, polymer-bound carboxylate, phenoxide, and sulfinate anions were used for the synthesis of esters, ethers, and sulfones by reaction with alkyl halides in non-polar solvents.

## INTRODUCTION

Solid phase synthesis has recently emerged as an attractive new technique for providing the possibility of automation in multistep synthesis. This technique offers a great promise for solving the problem accompanied with the conventional chemical reaction procedures in a commercial industrial scale. The advantages of the utilization of functionalized polymers in this technique have been described in a number of reviews[1-4].

Functionalized polymers containing phosphine moieties have been widely used as mild and efficient reagents in numerous syntheses[2]. However, polymeric phosphonium salts which have only been used as phase transfer catalysts have not been used as stoichiometric reagents in spite of their prior chemical and thermal stabilities than the corresponding ammonium salts.

In connection with our interest in functionalized polymers we now describe the synthesis and application of polymeric phosphonium salt-bound different anions to increase the reactivity of the bound species in the organic synthesis.

## EXPERIMENTAL

### Preparation of Poly(vinylbenzyltriphenylphosphonium Chloride), I

It was prepared from poly(chloromethylstyrene) and triphenylphosphine employing a published procedure[5]. Phosphorus analysis: P, 6.44%.

### General Procedure for the Preparation of the Polymeric Reagents

To 50 mmol of the swelled polymeric salt I in 100 ml 50% aqueous methanol 100 mmol of the sodium salt of the anion in aqueous methanol were added at room temperature. After stirring the reaction mixture overnight the resin was filtered, washed with water and methanol, and then dried in vacuum. The amounts of the anions bound to the polymeric reagents are listed in Table 1.

### General Procedure for Reaction with Polymeric Reducing Reagents

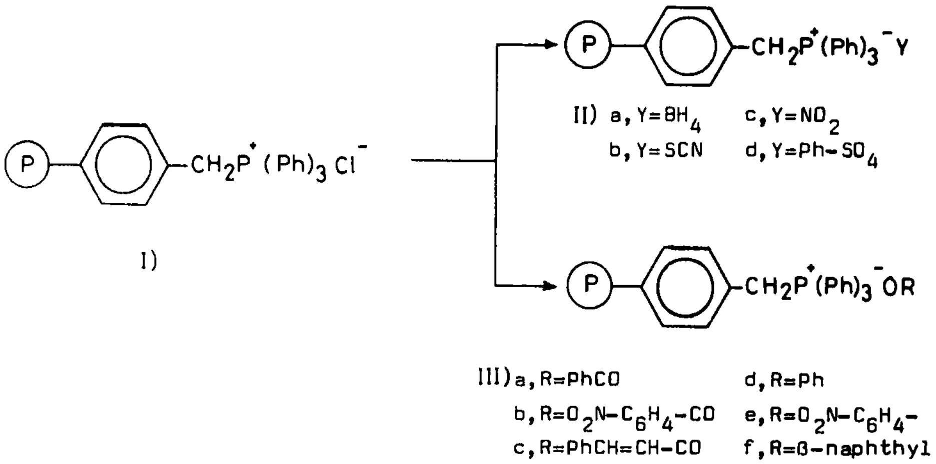
A mixture of 10 mmol of reagent IIa and 8 mmol of the carbonyl compound was refluxed in 30 ml benzene. The polymeric by-product was separated from the product by filtration after addition of methanolic dilute HCl. The reaction conditions and yields of products are listed in Table 2.

### General Procedure for Nucleophilic Substitution with Polymeric Bound Nucleophilic Reagents

To a stirred mixture of 10 mmol of the polymeric reagent in 25 ml of the solvent, 8 mmol of the alkyl halide in the same solvent were added at room temperature. After stirring the mixture under the conditions given in Table 2 the polymeric by-product was separated from the product.

## RESULTS AND DISCUSSION

The polymeric reagents IIa-d and IIIa-f were prepared by the chemical modification technique, starting with 2% crosslinked poly(chloromethylstyrene). The obtained resin was then treated with triphenylphosphine in the way previously described[5] to give the polymeric salt I containing 2.08 mmol P/g. Resin I was then treated with a slight excess of sodium borohydride, thiocyanate, nitrite, sodium salts of carboxylic acids, phenols, and benzenesulfinic acid in methanol to give the corresponding reagents IIa-d and IIIa-f, according to Scheme I.



SCHEME 1 Preparation of polymeric reagents.

The degrees of substitution of reagents IIb-d and IIIb,e were deduced from the elemental microanalysis using data for the appropriate newly introduced heteroatom. The exchange capacities for reagents IIIa,c,d,f were determined by titration analysis as previously described[6]. The loading of reagent IIa was determined by refluxing with excess benzaldehyde for long time and the yield of the product was used for calculation of the polymer capacity. The determined average capacities of the polymeric reagents are listed in Table 1.

TABLE I Loadings of polymeric reagents.

| Polymer | IIa | IIb | IIc | IId | IIIb | IIIe | IIIa | IIIc | IIId | IIIf |
|---|---|---|---|---|---|---|---|---|---|---|
| Loading mmol / g | 1.87 | 2.30 | 1.07 | 1.72 | 0.75 | 0.96 | 0.79 | 0.75 | 1.06 | 0.94 |
| Method | + | ++ | ++ | ++ | ++ | ++ | ++ | +++ | +++ | +++ |

+) determined from reaction with benzaldehyde
++) estimated from microanalysis
+++) determined from titration analysis

The reactions were performed by a batch technique by stirring a slight excess of the polymeric reagents with substrates. The products and reaction conditions are indicated in Table 2.

The polymeric reducing reagent containing borohydride anion, IIa, was used in hetero-reduction reaction towards aldehydes and ketones in a non-polar solvent as benzene. The obtained alcohols were freed from the polymeric boron esters by acid hydrolysis. The effectiveness of the polymeric salts as anion activating reagents was studied in numerous nucleophilic substitution reactions. Alkylthiocyanates were obtained in good yields from the thiocyanate polymer IIb and alkyl halides. Similarly, the reaction of polymer-supported nitrite anion, IIc, with alkyl halides gave the nitroalkane as main product; no significant amount of organic nitrites was detected. The reaction of polymeric reagent IId with alkyl halides gave excellent yields of the sulfone derivative.

The synthesis of esters from the polymeric reagents IIIa-c and alkyl halides proceeds in non-polar as well as in polar solvents and generally gave excellent yields. The nature of the solvent does appear not to be critical, showing that the reactions involving the polymeric reagent are independent of the nature of the solvent. Runs with catalytic amounts of the polymeric salt, I, did not give satisfactory results with the esterification reactions.

TABLE II Reaction products of treatment of polymeric reagents with substrates.

| Polym | $Y^-$/or R | Substrate | Product | Solv | Temp | Time | Yield |
|---|---|---|---|---|---|---|---|
| IIa | $BH_4^-$ | PhCOMe | PhCH(OH)Me | Bz | ref. | 3h | 70 |
| | | PhCOPh | PhCH(OH)Ph | Bz | ref. | 3h | 90 |
| | | PhCHO | $PhCH_2OH$ | Bz | ref.<br>r.t | 3h<br>48h | 98<br>100 |
| IIb | $SCN^-$ | $PhCH_2Cl$ | $PhCH_2SCN$<br>+ $PhCH_2NCS$ | Bz | ref. | 3h | 56 |
| | | $PhCH_2Br$ | $PhCH_2SCN$ | $CH_2Cl_2$ | ref. | 3h | 93 |
| IIc | $NO_2^-$ | $PhCH_2Br$ | $PhCH_2NO_2$ | Bz | r.t | 24h | 89 |
| | | n-ButBr | $n\text{-}ButNO_2$ | Bz | r.t | 24h | 21 |
| | | $ClCH_2COOEt$ | $O_2NCH_2COOEt$ | Bz | r.t | 24h | 33 |
| IId | $PhSO_2^-$ | i-PrI | $PhSO_2Pr\text{-}i$ | Bz | r.t | 3h | 50 |
| | | $EtOCOCH_2Cl$ | $PhSO_2CH_2COOEt$ | Bz | r.t | 3h | 55 |
| IIIa | PhCO | i-PrI | PhCOOMe | Bz | 60° | 12h | 73 |
| IIIb | $O_2N\text{-}C_6H_4\text{-}CO$ | MeI | $O_2N\text{-}C_6H_4COOMe$ | Bz | r.t | 5h | 86 |
| IIIc | PhCH=CHCO | $PhCH_2CL$ | $PhCH{=}CHCOOCH_2Ph$ | Bz | 60° | 8h | 80 |
| IIId | Ph | MeI | $Me\text{-}C_6H_4\text{-}OH$ | Bz | r.t | 12h | 50 |
| IIIe | $O_2N\text{-}C_6H_4\text{-}$ | MeI | $O_2N\text{-}C_6H_4\text{-}OMe$ | EtOH | r.t | 12h | 50 |
| IIIf | β-naphthyl | MeI | 1-Me-2-OHnaph<br>2-OMenaph | EtOH | r.t | 20h | 43<br>57 ] 70 |

Bz = Benzene / ref. = reflux

Thus, the nucleophilicity of polymer-bound carboxylate ion is increased sufficiently to allow esterification with alkyl halides.

The results of the reactions of reagents IIId-f with alkyl halides show that O-alkylation products are predominant, except for reaction of methyl iodide with phenoxide ion bound to reagent IIId, in which C-alkylation of phenol was favoured. Thus, the polymeric reagents seem to increase the activities of the anions in a similar manner to low molecular catalysts. Regeneration of the polymeric by-product in the active form is readily accomplished by treatment with the sodium salts of the anions and were re-used in some examples without loss of activity.

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