

Debromination of α -Bromo Ketones using Polymer-supported Triphenylphosphine†

J. Chem. Research (S),
1998, 56†

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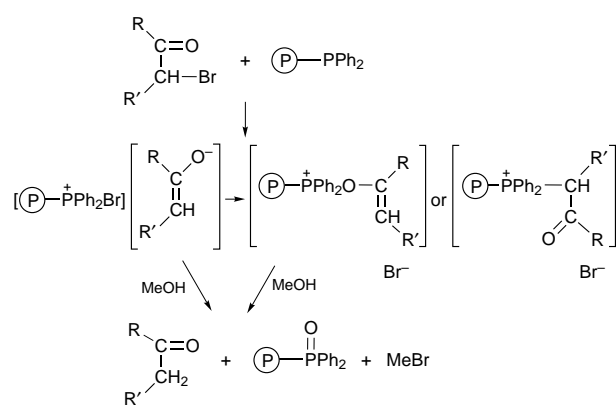
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An effective method for the debromination of α -bromo ketones using polymer-supported triphenylphosphine is described.

The use of polymeric reagents in organic synthesis has been a subject of substantial interest in recent years.¹ Among the several advantages offered by these reagents,² the one most frequently utilized is the ease of work-up, which often consists of a simple filtration. This feature is of more importance especially when the reaction products are toxic or noxious and when they are unstable to lengthy and tedious work-ups. We have developed a mild and high-yielding method for the debromination of α -bromo ketones using a polymer-supported reagent. Polymer-supported triphenylphosphine has been earlier used in a number of reactions such as in the conversion of alcohols into alkyl halides,³ the Wittig reaction⁴ and the conversion of aromatic disulfides into thiols.⁵ The polymeric phosphine oxide obtained as a by-product can be recycled after reduction to phosphine.^{3,4}

The debromination of α -bromo ketones has been extensively studied and the mechanism carefully detailed.⁶⁻⁸ However, separation of the ketone from the triphenylphosphine oxide by-product and any excess of phosphine is difficult. Also, the yields obtained in the above reactions are considerably low.

We report here the debromination of α -bromo ketones using polymer-supported triphenylphosphine as shown in Scheme 1. To a solution of the bromo ketone in anhydrous benzene is added the insoluble phosphine reagent. This results in the formation of the phosphonium salt which is decomposed by alcohol to yield the corresponding ketone. The yield of product and the rate of reaction, when carried out in toluene, acetonitrile, THF, etc. were found to be very low. Polymeric phosphine oxide is obtained as a by-product, which is separated by filtration. Removal of the solvent under reduced pressure yields the pure ketone.



Scheme 1

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Debromination of α -bromo ketones

α -Bromo ketones	Product	Time (t/min)	% Yield ^a
Phenacyl bromide	Acetophenone	45	96 (64)
<i>p</i> -Nitrophenacyl bromide	<i>p</i> -Nitroacetophenone	30	85 (53)
2-Bromocyclohexanone	Cyclohexanone	50	89 (62)
3-Bromocamphor	Camphor	40	97 (51)

^aFigures in parentheses indicate percentage yields in solution-phase reactions.

Various α -bromo ketones were investigated, as outlined in Table 1. The yields indicated are for isolated products without additional purification. In all cases the isolated products were found to be homogeneous by TLC and were characterised by IR and NMR spectroscopy.

In summary, the use of polystyryldiphenylphosphine represents a very effective procedure for the debromination of α -bromo ketones. The reaction offers improved yields and a convenient isolation procedure.

Experimental

General Procedure for the Debromination of α -Bromo Ketones.—The α -bromo ketone (0.125 mmol) was dissolved in anhydrous benzene (10 ml). Polymer-bound triphenylphosphine (50 mg; 2% crosslinked with DVB, 3 mmol g⁻¹) was added to form the phosphonium salt after which methanol (1 ml) was added and the reaction mixture was refluxed. When the reaction was complete (TLC), the reaction mixture was cooled, polymeric phosphine oxide was filtered off and the solvent was removed under reduced pressure to give the product ketone in pure form.

We are thankful to Dr N. V. Thakkar, Institute of Science, Mumbai, for helpful discussions.

Received, 7th July 1997; Accepted, 29th September 1997
Paper E/7/04778I

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