Diphenylphosphinated Ethylene Oligomers as Polymeric Reagents for Synthesis of Alkyl Chlorides from Alcohols

David E. Bergbreiter* and James R. Blanton

Department of Chemistry, Texas A&M University College Station, Texas 77843, U.S.A.

Diphenylphosphinated ethylene oligomers can be used as homogeneous polymeric reagents at 90 °C in carbon tetrachloride to form alkyl chlorides from alcohols and since these functionalized ethylene oligomers precipitate quantitatively from solution at 25 °C, they can be easily recovered and separated from the reaction products and can be partially recycled.

The use of derivatives of insoluble organic polymers such as divinylbenzene (DVB) cross-linked polystyrene as reagents in organic chemistry is an established application of polymers in synthetic chemistry.[1] Here we describe our initial work to develop alternative polyethylene-like polymeric reagents which can be used homogeneously at 90 °C and which can be recovered and quantitatively separated from the products of a synthetic reaction at 25 °C by centrifugation or filtration.

In the course of other work directed toward development of new methods for synthesis of polyethylene derivatives,[2] we have found that ethylene oligomers derived from the oligomerization reaction (1) are insoluble in typical organic solvents at 25 °C if their M_v is greater than *ca.* 1000. However, heating suspensions of oligomers like (**1**) to 90—100 °C results in formation of solutions of (**1**). Since cooling solutions of ethylene oligomers like (**1**) and/or polyethylene results in selective, quantitative precipitation of (**1**) or of a polyethylene dispersion of (**1**) without incorporation of other low molecular weight species which may have been present in solution, we were encouraged to examine the utility of functionalized ethylene oligomers like (**1**) in synthesis.

$$\mathrm{H_2C{=}CH_2} \xrightarrow[\substack{\text{TMEDA}\\ \text{hexane}}]{\text{RLi}} \xrightarrow{\mathrm{ClPPh_2}} \underset{(\mathbf{1})}{-\mathrm{[CH_2CH_2]{-}CH_2CH_2PPh_2}} \qquad (1)$$

TMEDA = tetramethylethylenediamine

$$\mathrm{ROH} + (\mathbf{1}) \xrightarrow[\substack{\text{toluene}\\ 90\ ^\circ\text{C}}]{\mathrm{CCl_4}} \mathrm{RCl} \qquad (2)$$

To demonstrate the applicability of these polyethylene-bound reagents, we have chosen to examine their utility in alkyl halide synthesis from alcohols [reaction (2)]. Similar uses of diphenylphosphinated polystyrene reagents have been described.[3] In our case, we find that use of diphenylphosphinated ethylene oligomers proves to be a useful alternative to a more conventional polymeric phosphine reagent. A series of typical results are presented in Table 1 with some selected comparisons to a polystyrene-bound phosphine reagent (control) prepared from 1% DVB cross-linked chloromethylated polystyrene and $\mathrm{LiPPh_2}$ (containing *ca.* 0.7 mequiv. $-\mathrm{PPh_2}$/g of polymer).

Our polyethylene-bound reagents are comparable in activity to 1% DVB cross-linked polystyrene-bound phosphine reagents for these reactions. However, recovery of (**1**) and reaction of the recovered oligomer with $\mathrm{HSiCl_3}$ (to reduce phosphine oxide) does not completely restore the original activity of (**1**) possibly because of quaternary phosphonium salt formation.[3] These polyethylene-bound reagents feature easier characterization (*e.g.* by solution n.m.r. spectroscopy),

Table 1. Synthesis of alkyl chlorides from carbon tetrachloride and phosphinated ethylene oligomer (**1**) at 90 °C.

Alcohol	Polymeric reagent	Yield of alkyl chloride (%)[a]
Octan-1-ol	(**1**)	96
	(**1**)[b]	65
	(**1**)[c]	41
	(**1**)[d]	>99
	control[e]	93
Undec-10-en-1-ol	(**1**)	81
Cyclodecanol	(**1**)	61[f]
	control[e]	57[g]
Cyclohexanol	(**1**)	42[h]
Benzyl alcohol	(**1**)	91
Octadecan-1-ol	(**1**)	69[i]

[a] Yield based on alcohol as determined by g.c. unless otherwise indicated. The identity of the reaction products was verified by g.c.–mass spectroscopy in every case. Reactions (1 mmol scale) were carried out for 5 h at 90 °C in 50 ml of 1 : 1 (v/v) $\mathrm{CCl_4}$: toluene using a 2 : 1 molar ratio of polymeric reagent : alcohol. Reactions of primary alcohols typically contained <10% unreacted alcohol. [b] Second cycle using ethylene oligomer recovered from first cycle after having reduced the oligomeric phosphine oxide with $\mathrm{HSiCl_3}$ in toluene (ref. 4). [c] Third cycle using the same ethylene oligomer used in the second cycle after reduction of any phosphine oxide with $\mathrm{HSiCl_3}$. [d] When a 3 : 1 molar ratio of (**1**) : octanol was used, g.c. analysis indicated <1% unreacted alcohol remained. [e] 1% DVB cross-linked polystyrene-bound phosphine reagent (see text). [f] G.c. indicated formation of 26% cyclododecene. [g] An 8 h reaction time was required and 27% alkene by-product formed. [h] G.c. indicated formation of 42% cyclohexene. [i] Isolated yield of chloride characterized by ^{13}C and ^{1}H n.m.r. and i.r. spectroscopy and by g.c.–mass spectroscopy.

homogeneity during a reaction, and useful levels of functionality (up to 0.8 mmol $-PPh_2$/g of polymer or 0.2 M solutions).

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Texas A&M Center for Energy and Mineral Resources for support.

Received, 13th November 1984; Com. 1604

References

1 A. Akelah and D. C. Sherrington, *Chem. Rev.*, 1981, **81**, 557.

2 D. E. Bergbreiter, Z. Chen, and H.-P. Hu, *Macromolecules*, 1984, **17**, 2111.

3 C. R. Harrison, P. Hodge, B. J. Hunt, E. Khoshdel, and G. Richardson, *J. Org. Chem.*, 1983, **48**, 3721 and references therein.

4 C. A. Fyfe, H. C. Clark, J. A. Davies, P. J. Hayes, and E. Wasylishey, *J. Am. Chem. Soc.*, 1983, **105**, 6577.