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PHASE TRANSFER CATALYSED POLYMER-SUPPORTED WITTIG REACTIONS

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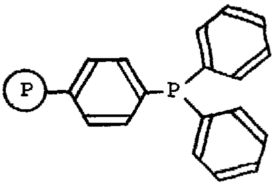
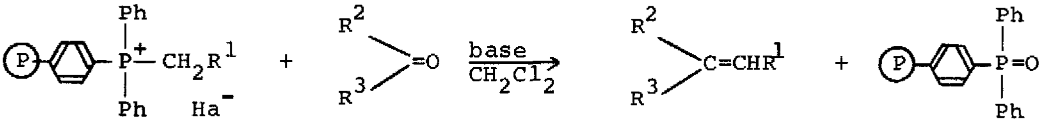
ABSTRACT: Arylsubstituted olefins can be prepared in high yield using phase transfer catalysed polymer-supported Wittig reactions.

In recent years there has been a great deal of interest in phase transfer catalysed reactions[1] and in polymer-supported reactions.[2] Wittig reactions using various alkyltriphenylphosphonium halides and aldehydes have been carried out successfully under phase transfer conditions.[3,4] These reactions have the attraction of using cheap bases (e.g. aqueous NaOH or K_2CO_3) and solvents such as methylene chloride or benzene which need not be dried and which are easily removed in the work up.[1] Polymer-supported Wittig reactions have the advantage of simplified work up procedures, in particular the easy removal of the polymer-bound phosphine oxide by-product,[5] which can, if necessary, be re-cycled.[6] We wish to report some novel Wittig reactions that combine the advantages of both of the above experimental techniques, i.e. some phase transfer catalysed polymer-supported Wittig reactions. The preparation of polymer-supported sulphonium ylids using phase transfer catalysis has been reported recently by Fréchet's group.[7]



(I)

Polymers containing phosphine residues (I) were prepared both from crosslinked and linear polystyrenes as previously described.[8] Reaction with organic halides in chlorobenzene (crosslinked polymers) or dimethylformamide (linear polymer) gave the corresponding phosphonium salts in high yield. The Wittig reactions (1) were carried out by vigorously stirring a mixture of the phosphonium salt, the carbonyl compound, methylene chloride, and 50% aqueous sodium hydroxide, with in most cases, an added phase transfer catalyst. When crosslinked polymers were used the reactions were worked up simply by filtering off the polymer and washing the organic phase. The latter was dried and the solvent removed. With linear polymers the reaction mixture was added to an excess of ether, the precipitated polymer filtered off and the filtrate washed, dried, and the solvent evaporated to give the olefin.



.....(1)

A selection of our results is given in the Table. It is clear that excellent yields of olefin were obtained from aralkylphosphonium salts and various aldehydes. In several cases the product isolated using the above work up procedures was essentially pure olefin. Allylphosphonium salts reacted satisfactorily with reactive aldehydes but alkylphosphonium salts did not react satisfactorily with any aldehyde. As expected,[3] ketones failed to react.

Several other points merit comment. First, although Wittig reactions using crosslinked polymers were best carried out using an added phase transfer catalyst, reaction did take place, albeit more slowly, in the absence of an added catalyst. The processes occurring in these reactions are probably closely related to those involved in 'triphase catalysis'.[9] Linear polymers reacted satisfactorily without an added catalyst. Secondly, in a few instances the proportions of cis and trans-olefins were measured by 'H nmr spectroscopy. These were not significantly different from those obtained in conventional phase transfer catalysed reactions.[4] Finally, as expected, hydrolysis of the phosphonium salt was a side reaction. For example, the reaction producing 4-t-butylstyrene also produced some 4-t-butyltoluene. In general, however, this did not make isolation of the olefins difficult.

TABLE: Reactions of Polymer-supported Phosphonium Salts with Carbonyl Compounds under Phase-transfer Conditions[a]

Halide used to prepare Phosphonium Salt	Polymer[b]	Carbonyl Compound	Catalyst[c]	Reaction Time	Yield of Olefin[d]
Benzyl chloride	C	9-formylanthracene	C	2h.	98%[e]
Benzyl chloride	C	9-formylanthracene	none	2h.	35%[f]
Benzyl chloride	L	9-formylanthracene	none	2h.	92%[e]
Benzyl chloride	C	$C_6H_5\cdot CHO$	C	16h.	92%
Benzyl chloride	C	$p\text{-}CH_3\cdot C_6H_4\cdot CHO$	C	16h.	100%[g]
Benzyl chloride	C	$p\text{-}Cl\cdot C_6H_4\cdot CHO$	T	4h.	97%[h]
Benzyl chloride	C	furan-2-aldehyde	C	16h.	90%[f]
Benzyl chloride	L	$C_6H_5\cdot CH{=}CH\cdot CHO$	none	2h.	75%[f]
Benzyl chloride	C	$n\text{-}C_7H_{15}\cdot CHO$	T	3h.	93%[f]
Benzyl chloride	C	cyclohexanone	T	3h.	0
4-t-Butylbenzyl chloride	C	formaldehyde	C	3h.	95%[i]
2-Bromomethylnaphthalene	C	β-naphthaldehyde	C	3h.	65%[j]
2-Bromomethylnaphthalene	C	formaldehyde	C	3h.	67%[k]
2-Bromomethylnaphthalene	L	9-formylanthracene	none	2h.	100%
Allyl bromide	C	$p\text{-}Cl\cdot C_6H_4\cdot CHO$	none	17h.	78%
Allyl bromide	C	9-formylanthracene	T	4h.	trace
n-Hexyl bromide	X	$p\text{-}Cl\cdot C_6H_4\cdot CHO$	T	4h.	trace
Methyl iodide	C	$p\text{-}Cl\cdot C_6H_4\cdot CHO$	T	19h.	0

Notes for Table:

a. A mixture of the phosphonium salt (1.5 mmol.), the carbonyl compound (1.0 mmol.), methylene chloride (10ml.), 50% aqueous sodium hydroxide (3ml.), and, if necessary, a catalyst (0.03 mmol.) was vigorously stirred under N_2 at 20°.

b. C = Polystyrenes crosslinked with 1% DVB with 3.0-3.5 mmol/g of phosphine
L = Linear polystyrene, MW = 150,000, with 2.7 mmol/g of phosphine
X = Amberlite XE-305, a macroporous polystyrene, with 2.3 mmol/g of phosphine.

c. C = Cetyltrimethylammonium bromide. T = Tetrabutylammonium iodide.

Notes continued

d. Unless indicated otherwise the yields are based on the carbonyl compound and are of isolated material with satisfactory ^{1}H nmr spectrum and/or physical properties.

e. Only *trans*-olefin formed.

f. Determined by ^{1}H nmr analysis.

g. *Cis*: *trans*-ratio, 43:57.

h. *Cis*: *trans*-ratio, 56:44.

i. Plus 16% 4-t-butyltoluene)

j. Plus 4% β-methylnaphthalene) Yields based on phosphonium salt.

k. Plus 12% β-methylnaphthalene)

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