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PHASE TRANSFER CATALYSTS ANCHORED TO POLYSTYRENE

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Summary: Quaternary phosphonium and ammonium salts attached to polystyrene resins by short (2 - 3 atom) carbon chains are highly active phase transfer catalysts for a variety of nucleophilic substitution reactions.

Benzyltrialkylammonium and phosphonium salts are highly active phase transfer catalysts[1,2]. Regen[3-5] has made detailed studies of a variety of these catalysts attached to cross-linked polystyrene resins and found them to be reactive "triphasic catalysts," although they appear to be considerably less active than their nonpolymeric analogues[3-6]. Insertion of very long carbon chains (11-33 atoms) between the polystyrene backbone and the catalytic center allows reactions to proceed at rates comparable to nonpolymeric systems[7-8]. In this report we describe the effect on catalytic activity of the systematic insertion of 1, 2, and 3 methylene units between the polystyrene backbone and the catalytic center (catalysts **I** - **V**). In addition, we report on synthetic applications of these polymeric catalysts.

$\text{Ⓟ} - (CH_2)_n - \overset{+}{P}Bu_3$

Ia $n = 1$ (65%)
Ib $n = 1$ (18%)

IIa $n = 2$ (37%)
IIb $n = 2$ (15%)

IIIa $n = 3$ (65%)
IIIb $n = 3$ (18%)

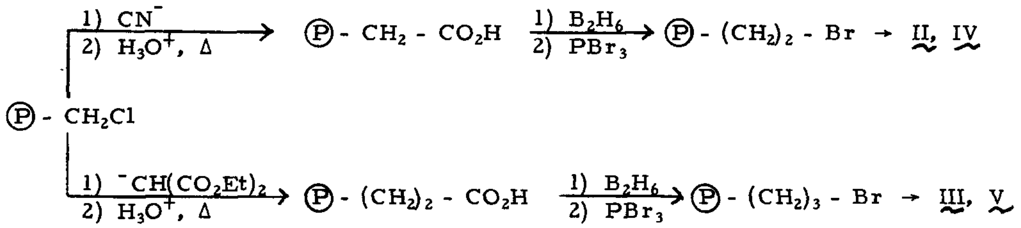
$\text{Ⓟ} - (CH_2)_n - \overset{+}{N}Bu_3$

IV $n = 2$ (34%)

V $n = 3$ (30%)

Values in parentheses represent per cent ring substitution.

The catalysts were prepared from commercially available chloromethylated polystyrene resins (cross-linked with 2% divinylbenzene, 200-400 mesh). Catalysts Ia, b were prepared according to literature procedures[6]. The others were synthesized according to the following scheme. The per cent ring substitution was determined by elemental analysis for phosphorus or nitrogen in the final polymer.



Results from studies of the reaction between cyanide ions and 1-bromopentane in the presence of these catalysts allow some conclusions to be drawn. (1) The phosphonium catalysts are more active than the related ammonium salts. (2) There is a gradual increase in activity with an increase in distance from the polystyrene backbone. (3) An increase in substitution of the polystyrene leads to an increase in activity (the reaction half life for IIIa = 0.25 hr, for IIIb = 0.33 hr). Our most active catalyst, IIIa, is equal or superior to other previously reported polystyrene supported catalysts (Table 1). It requires no conditioning prior to use and reactions catalyzed by it proceed rapidly to completion with no leveling of reaction rates with time. These data seem to indicate that it is not necessary to separate the catalytic center from the backbone by long carbon chains to achieve high activity. In fact, the reaction half lives for substitution reactions catalyzed by IIIa are very similar to those for hexadecyltributylphosphonium bromide[9].

Currently we are in the process of determining the factors (chain length, per cent ring substitution, alkyl groups on the quaternary atom, etc.) which will produce the greatest catalytic activity.

Table 1. Bromide Displacement from 1-Bromooctane by Cyanide

Catalyst	Solvent	Temp, °C	Time, hr.	Yield, %	Ref.
Ⓟ - CH_2 - NH - PO - $(NMe_2)_2$	none	80	8	95	10
Ⓟ - CH_2 - NEt - $(CH_2)_9$ - 18-crown-6	toluene	90	7	95	6
Ⓟ - CH_2 - $\overset{+}{N}Me_2Bu$	benzene	110	4	92	3
Ⓟ - $(CH_2)_6$ - $\overset{+}{P}Bu_3$	toluene	90	1.6	98	8
Ⓟ - CH_2 - NH - $CO(CH_2)_{10}$ - $\overset{+}{P}Bu_3$	none	90	1.5	[a]	7
IIIa	none	110	0.8	95	-

[a] Iodide used as the nucleophile instead of cyanide.

The synthetic utility of this catalyst has been explored by examining the reactions of a variety of nucleophiles with 1-bromopentane under phase transfer conditions. Reactions proceed rapidly and in high yield (Table 2). The catalyst can be recycled a minimum of five times with only a slight decrease in activity. A variety of organic substrates can be used as well. As with other phase transfer catalysts, alkyl bromides react more readily than chlorides or iodides. In addition reactivity of the substrate is governed by the same structural considerations as typical S_N2 reactions. Thus, 1-bromo pentane reacts more rapidly than 3-methyl-1-bromobutane which is in turn more reactive than 3,3-dimethyl-1-bromobutane.

Table 2. Nucleophilic Substitution Reactions Catalyzed by IIIa

$CH_3-(CH_2)_4-Br + Nuc^- \rightarrow CH_3-(CH_2)_4-Nuc + Br^-$

Nuc^-	Time[a] hr	Temp °C	Molar Ratios[b] Nuc^-/R-X/Cat.	Yield[c] %
CN^-	0.5	110	5/1/.01	79
I^-	1.0	110	5/1/.01[d]	82
$Ph-O^-$	1.0	110	3/1/.01	81
$Ph-S^-$	0.2	110	1.5/1/.01	87
N_3^-	0.5	110	2/1/.01	63
SCN^-	2.0	110	2/1/.01	94
S^{-2}	1.5	110	1.2/1/.01	98
$CH_3CO_2^-$	8.0	110	2/1/.01	70

[a] Time required for >95 % conversion of starting material. [b] Typically 33 mmoles of halide, 0.3 mmoles of catalyst, 25 ml of H_2O and the required quantity of nucleophile are stirred together. [c] Isolated and purified. [d] Catalyst **V** was used.

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