Tetrahedron Letters,Vol.24,No.15,pp 1661-1664,1983 0040-4039/83/151661-04$03.00/0
Printed in Great Britain

OPTIMIZATION OF POLYMER-SUPPORTED OLIGOETHERS AS SOLID-LIQUID PHASE TRANSFER CATALYSTS

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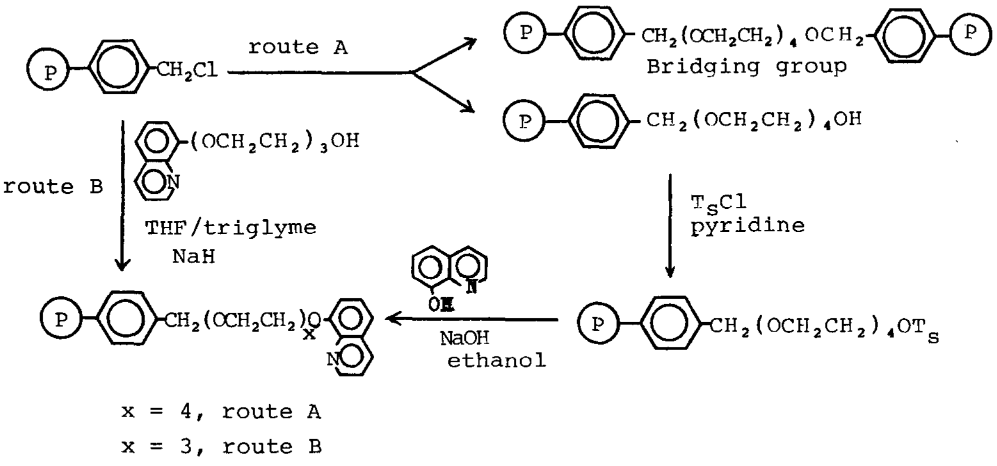
Summary. Oligoether residues with terminal 8-quinolyl donor groups have been loaded virtually quantitatively onto polystyrene resin supports and function more effectively than dibenzo-18-crown-6 as solid/liquid phase transfer catalysts in Williamson ether syntheses.

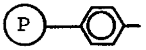
Oligoethylene oxide species are known to be useful and cheap phase transfer catalysts and their practical applicability can be improved by supporting them on polystyrene resins[2] when they function similarly to other 'triphase' catalysts[3]. If the oligomers are terminated with rigid donor groups their ability to complex group I and II metal ions is substantially enhanced[4] and their effectiveness as solid/liquid phase transfer catalysts similarly significantly improved[5]. Previous attempts to attach specifically mono terminally functionalized oligoethers to resins (via route A, Scheme) resulted in a relatively low loading of pendant aromatic groups and contamination by bridging oligoether groups whose catalytic activity was thought to be low[5].

We have now optimised the loading of such terminally functionalized oligoethers firstly using the original route (A, Scheme; Catalysts IIa,b,c;Table 1), secondly, and more successfully, using an approach similar to that reported by Manecke and his coworkers[5] (route B, Scheme) involving prior synthesis of a terminally mono-functionalized 8-quinolyl oligoether and direct attachment of this to chloromethylated polystyrene (catalysts, IId,e; Table 1). Also by employing a resin synthesised from chloromethylstyrene, rather than chloromethylating a non-functional resin, it has been possible to achieve virtually quantitative loading of all polymer aromatic groups with the specific oligoether group required (catalyst, IIe). Further attempts to minimise the production of bridging oligoether groups via route A did meet with some success, e.g. catalyst C, but for oligomers with n=4, the complete elimination of this side reaction proved elusive. Syntheses of IIa,b and c involved minor modifications to the procedure already described in detail[5]. The mono-8-quinolyl ether of triethylene glycol was prepared from triethylene glycol monochlorohydrin using the procedure described by Manecke[5] in synthesising analogous styryl monomers. This was then attached to a chloromethylated polystyrene resin (synthesised from chloromethyl styrene monomer) to yield catalysts IId and e as follows. A 500 ml round bottomed flask with indented flanges was charged with triethylene glycol mono-quinolyl ether (22.7g, 0.082 mole), tetrahydrofuran (100 ml) and triethylene glycol dimethyl ether (15 ml). Sodium hydride (4.5g, 0.092 mole) was carefully added and the flask heated to 40°C for 30 minutes to allow for the evolution of hydrogen gas to cease. Chloromethylated resin (6.2g, 0.041 mole Cl) was added and resultant slurry was heated to 100°C for 72 hours while the flask was gently rotated. The polymer beads were collected and washed well with toluene, acetone, water, acetone and toluene respectively. Finally they were extracted in a Soxhlet overnight using toluene, before being dried under vacuum at 50°C. Yield of pink coloured beads 8.36g. I.R. (KBr) 1260 cm^{-1} Ar-O-C, 1125-1055 cm^{-1} C-O-C. Elemental microanalysis: C 75.16; H 6.81; N 3.43; Cl 0.02.

Our approach has two advantages over the 'specialized monomer' route. Firstly, it eliminates the handling of sensitive (to spurious polymerization) styryl monomers, and secondly the resin catalysts have the usual spherically symmetric bead form, potentially useful in continuous flow applications. Suspension polymerization using specialized monomers in order to produce functionalized beaded resins is an alternative possibility. However, such polymerizations are difficult to establish and the stability of a well-tried suspension can be modified substantially on introduction of a functional comonomer. Considerable wastage of the latter is therefore possible in achieving successful suspension conditions.



Scheme

Table 1. 2% Crosslinked Polystyrene Resin Supported Oligoether Phase Transfer Catalysts,  $CH_2(OCH_2CH_2)_nOR$

Catalyst	Loading of Chloro-methylated Resin Precursor (%)	Loading of Terminal Hydroxyl Groups(%) (Bridging Groups)	Loading of Terminal Tosyl Groups (%)	n	-R	N-micro-analysis (%)	Loading of Terminal R Groups (%)
I	60[a]	-	-	3	$-CH_3$	-	60
IIa	40[a]	28(12)	28	4	8-quinolyl[c]	1.01	14
IIb	60[a]	40(20)	40	4	8-quinolyl[c]	1.20	16
IIc	60[a]	40(20)	40	4	8-quinolyl[c]	1.69	31
IId	96[b]	-	-	3	8-quinolyl[d]	2.98	87
IIe	96[b]	-	-	3	8-quinolyl[d]	3.43	∼100

a) From chloromethylation of Bio-Beads SX2, particle size ∼30-50µ.

b) From in-house suspension polymerization of 96% chloromethylstyrene(60% m-, 40% p-)4% commercial divinylbenzene, particle size ∼ 100-200µ.

c) Introduced via route A (Scheme).

d) Introduced via route B (Scheme).

e) Note loadings are orders of magnitude of % of pendant aromatic groups modified and are subject to error of ±3%.

Table 2. Phase Transfer Catalysed Solid/Liquid Williamson Synthesis of n-butyl phenyl ether[a)]

Catalyst	Loss of BuBr (%)(time, h)	Yield of PhOBu(%)	10^5 Initial Rate ($M\ s^{-1}$)
None	12(5)	9	slow
I	93(3)	-	10.0
IIa	92(2)	92	8.3
IIb	97(2)	97	10.5
IIc	94(-)	94	10.1
IId	∼100(2)	99	20.4
IIe	∼100(1)	99	24.0
IIc	∼100(1.5)	99	13.0[b]
Dibenzo-18-crown-6	∼100(1.5)	99	19.5

a) $[n\text{-}BuBr]_{initial}$ = 0.24M in toluene, K^+OPh^-(solid) = 2.0 mmol, catalyst = 1.16 mmole of donor atom on resin, temp. 105°C.

b) Resin finely powdered prior to reaction.

The effectiveness of each catalyst was assessed in the model solid/liquid reaction of potassium phenoxide with n-butyl bromide in toluene. Experimental conditions were as described before[2] and are summarised at the bottom of Table 2 Reactions were monitored and quantified by g.l.c. analysis again as previously reported[2]. The first quinolyl terminated species IIa yielded a reaction rate somewhat poorer than an analogous methyl terminated species, I. Comparisons were made using a fixed quantity of donor atom (O or O + N) in each catalyst and this result probably reflects the presence, in IIa, of those bridging oligoether groups whose activity is likely to be severly impaired. Increasing the loading of quinolyl terminated catalysts, IIb and c, does improve the reaction rate a little as does crushing IIc, but the most substantial effect arises with IId and e. Here bridging structures are completed eliminated and the loading of aromatic groups with the specifically terminally functionalised oligoether is more or less quantitative. Indeed with these species the reaction rate is superior to that using equivalent moles of dibenzo-18-crown-6 ether, and this represents one of the few examples where a supported catalyst is more active than an already highly active low molecular weight species.

Acknowledgement

We acknowledge the receipt of a CASE award for J.G.H. in collaboration with Polymer Laboratories Ltd., Church Stretton.

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(Received in UK 11 February 1983)