

Preparation of some Polymer-supported Crown Ethers and their use as Phase-transfer Catalysts

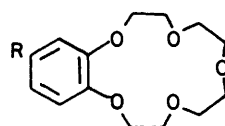
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Benzo-15-crown-5 and dibenzo-18-crown-6 have been formylated. The products were then bound to diol-containing crosslinked polystyrenes *via* acetalisation and to crosslinked polymers containing benzyltriphenylphosphonium chloride residues (obtained by treating chloromethylated polystyrenes with triphenylphosphine) *via* phase-transfer catalysed Wittig reactions. The various polymer-supported crown ethers have been found to be satisfactory phase-transfer catalysts for the reactions of *n*-octyl bromide in toluene with aqueous potassium iodide at 90 °C and with aqueous sodium *p*-methylthiophenolate at 80 °C, but not for the reaction of *n*-octyl bromide in toluene with aqueous potassium cyanide at 90 °C. The crosslinked polymers containing benzyltriphenylphosphonium chloride residues were also satisfactory catalysts for the first two reactions.

Polymer-supported (PS) quaternary ammonium^{1,2} and phosphonium salts,¹⁻³ poly(ethyleneglycol)s,^{1,4-6} crown ethers,^{1,5,7-11} and cryptands^{1,8,10,12} have all been used as phase-transfer (PT) catalysts. Like other PS catalysts they have the attractive features that they are easily removed from reaction mixtures and, in many cases, they can be re-used.¹³⁻¹⁶ The preferred types of PS PT catalysts for re-use are those derived from poly(ethyleneglycol)s, crown ethers, and cryptands, these groups being chemically more stable than the 'onium salts.^{1,5,10,17,18} PS Crown ethers are usually prepared either from crown ethers containing polymerisable groups⁷ or from crown ethers containing functional groups which can be used to bind covalently the crown ether to a pre-formed polymer.^{5,8-10} The latter approach is generally preferred because of the complexity of polymerisation processes.¹⁹ We report two convenient methods for binding readily available crown ethers to pre-formed polymers and the use of the products as PT catalysts.

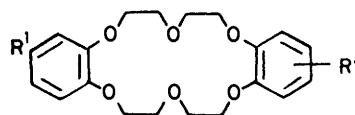
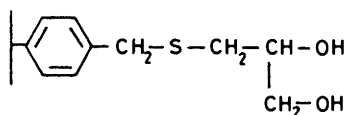
Preparation of PS Crown Ethers.—Formylation of mono-benzo-15-crown-5 (1) and dibenzo-18-crown-6 (3) as described by Wada *et al.*²⁰ gave the monoformyl compound (2) and the diformyl compound (4) respectively. Under milder conditions dibenzo-18-crown-6 (2) gave a mixture of the monoformyl compound (5) and starting material (mole ratio, 1:3).

Crosslinked polystyrenes containing diol residues (6) were prepared by treating 1% crosslinked chloromethylated polystyrenes (7) with 1-thioglycerol and base under PT conditions,²¹ then each of the formyl crown ethers were separately bound to one of the diol-containing polymers by acetalisation.²¹ This gave the PS crown ethers (8), (9), and (10) (see Table 1, entries 1-3). In each case the amount of bound crown ether was determined by detaching the crown ether using acid.²¹ Several points about these attachment reactions are noteworthy. First, it was not necessary to use pure formyl crown ether (5) for the attachment because after acetal formation the dibenzo-18-crown-6 could be easily washed from the polymer. Second, previous work on the binding of dicarbonyl compounds to the polymer (6) suggested that a substantial fraction of the diformyl crown ether (4) would be bound *via* both formyl groups, as in formula (9).²¹ The i.r. spectrum of the product, which showed only a very small carbonyl band at 1685 cm⁻¹, was consistent with this. Finally, although these PS crown ethers are easily prepared they clearly cannot be used under acidic conditions and any remaining diol residues (6) could cause problems in some applications.



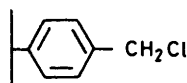
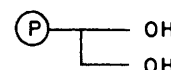
(1) R = H

(2) R = CHO

(3) R¹ = R² = H(4) R¹ = R² = CHO(5) R¹ = CHO, R² = H

(6)

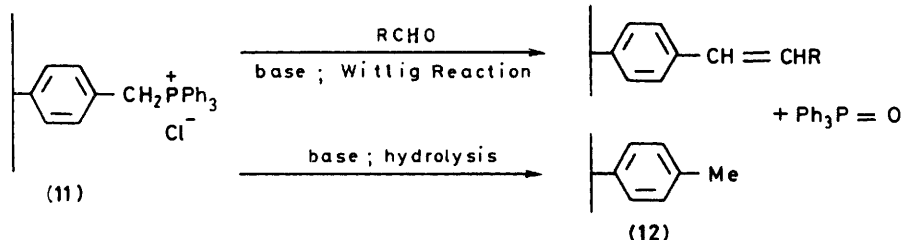
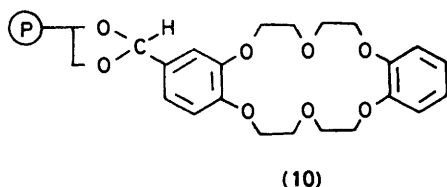
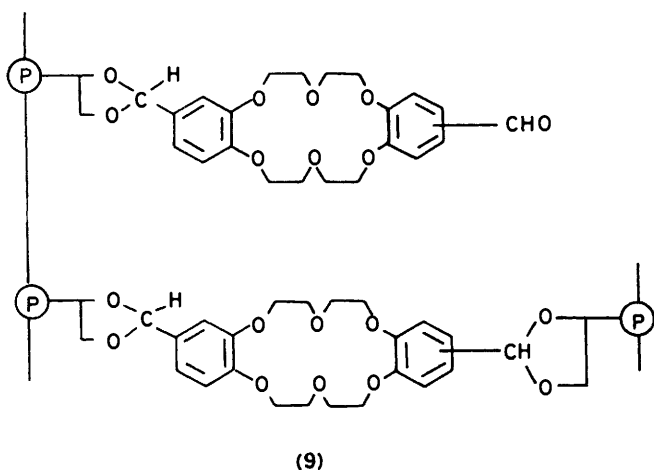
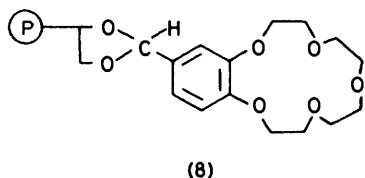
Which can be abbreviated to



(7)

A more satisfactory method of attaching the formyl crown ethers to crosslinked polystyrene which avoids the limitations noted above, utilises the PT catalysed Wittig reaction outlined in the Scheme.²² Crosslinked polymers containing residues (11) were readily prepared by treating chloromethylated crosslinked polystyrenes (7) with triphenylphosphine. Each of the formyl crown ethers (2), (4), and (5) in methylene chloride were separately treated with a crosslinked polymer (11) and aqueous sodium hydroxide under PT conditions. This gave the PS crown ethers (13)-(15) and (17) (see Table 1, entries 4-7) in which the crown moieties were bound *via* ethylene linkages. By using long reaction times the residues (11) that did not take part in the Wittig reaction were hydrolysed to residues (12).²² In each case the amount of crown ether bound to the polymer was estimated from the change in weight of the polymer that occurred as a result of the attachment reaction. The i.r. spectra of the products lacked bands due to phosphonium salt residues (11), but showed strong bands due to ether groups. As before, the crown ether (4) appeared to be mainly 'double bound'.

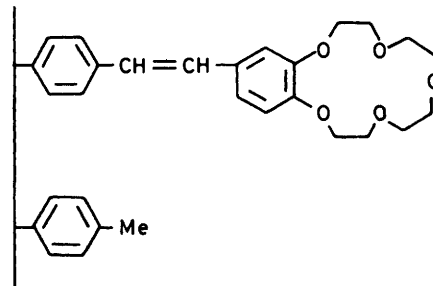
An alternative procedure for the Wittig reaction which was



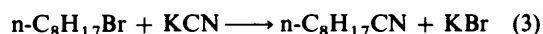
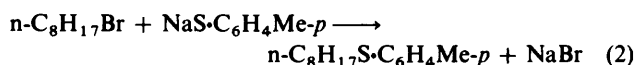
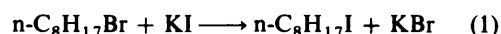
Scheme.

used to attach the diformyl crown ether (4) was to treat this compound in tetrahydrofuran with polymer (11) and solid potassium carbonate, followed by treatment with aqueous sodium hydroxide under PT conditions to hydrolyse any remaining salt residues (11) (see Table 1, entry 8). Interestingly the crown ether may well have catalysed its own attachment to the polymer. The product (16) appeared to have most of the crown ether 'double bound'.

Use of PS Crowns and PS Salts (1) as PT Catalysts.—The various PS crown ethers were used as liquid-liquid PT catalysts for one or more of the nucleophilic displacement reactions (1)–(3). For comparison, reactions were also carried out in the presence of unsubstituted crosslinked polystyrene, crown ethers (1) and (3), polymers (6) and (11), and the classical PT catalysts (18) and (19). Although polymers containing phosphonium salt residues (20) have often been used as PT catalysts,^{1–3} polymers containing residues (11) do not appear to have been used in this



way. It was therefore considered of interest to study several such polymers with different loadings. One of these was conveniently prepared by partially hydrolysing the residues (11) in a more highly loaded polymer.



The following points are clear from the results summarised in Table 2, though much more extensive studies would be needed to quantify relationships.

(i) Neither unsubstituted polystyrene beads nor the PS diol (6) which was used to prepare some PS crown ethers were effective catalysts for any of the reactions studied.

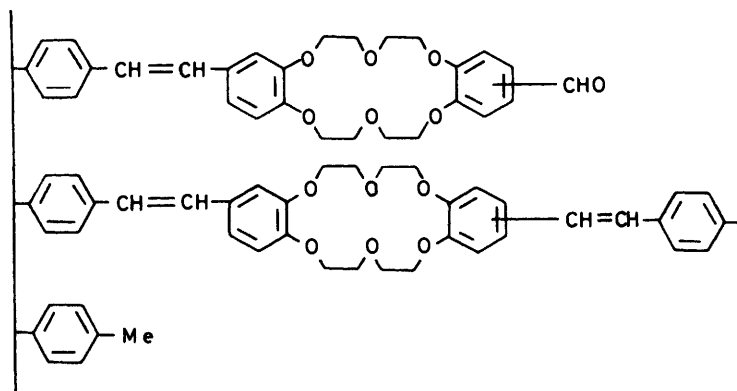
(ii) All the PS crown ethers catalysed reactions (1) and/or (2),

but none of those tried effectively catalysed reaction (3). Regen *et al.* have also found that several types of PS crown ethers which satisfactorily catalysed reaction (1) gave poor results with reaction (3).⁵ The reasons for this are not clear. Although dicyclohexyl-18-crown-6 is known to be a less efficient catalyst for liquid-liquid PT reactions involving cyanide than it is for those involving iodide,²³ other workers using different PS crown ethers obtained satisfactory results with reaction (3).^{8,10,11} Onium salts (18) and (19) satisfactorily catalysed reaction (3).

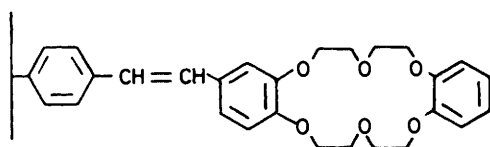
(iii) The PS crown ethers prepared from the diformyl crown ether (4) appeared to be of comparable activity to the others despite the 'double binding' which is equivalent to a crosslink.

(iv) Several PS crown ethers were recovered and re-used successfully (see footnotes in Table 2).

(v) Surprisingly, the PS crown ethers were generally more effective catalysts than the low molecular weight crown ethers (1) and (3). The reasons for this are not clear.



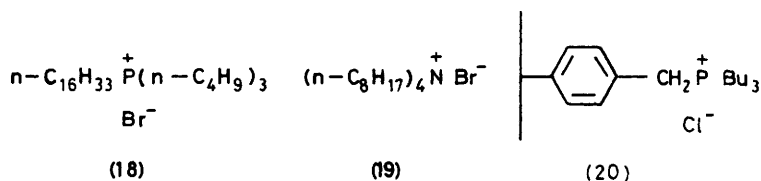
(15), derived from 1% crosslinked polystyrene using procedure C
(16), as (15) but using procedure D



(17), derived from Amberlite XE-305

(vi) The PS phosphonium salts (11) were effective catalysts for reactions (1) and (2) and, as expected,^{3,24} the activity per salt residue increased as the loading decreased, though the effect was not large. Ultimately this effect will be counteracted by there being insufficient ionic sites present in the polymer to allow effective ion transport in the beads. It should be noted that all the PS crown ethers (13)–(17) contained <3 mole %, if any, of the original residues (11).

(viii) For reaction (1) the PS crown ethers and the PS phosphonium salts (11), the latter of which were comparable in catalytic activity with their low molecular weight analogue $\text{Ph}_3\text{P}^+\text{CH}_2\text{Ph Cl}^-$, were all substantially less effective than the lipophilic onium salt catalysts (18) and (19). The reasons for this are not clear, but diffusional limitations almost certainly adversely affect the activity of the PS catalysts.



(ix) For reaction (2) the PS crown ethers and PS phosphonium salts had similar activity to the classical PT catalysts (18) and (19).

(x) PS Crown ethers (8) and (10) also catalyse reaction (1) under solid-liquid PT conditions.²⁵ Other PS crown ethers catalyse other displacement reactions.⁷

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. Tetrahydrofuran was dried over calcium hydride, distilled, and stored over molecular sieves. The particle sizes of the 1%

crosslinked polystyrene, Amberlite XAD-2, and Amberlite XE-305 beads were 200–400, 20–60, and 20–50 mesh respectively. I.r. spectra were measured for KBr discs on a Nicolet MX-1 FT-IR instrument. G.l.c. was carried out with a Pye 104 machine (flame ionisation detector) and 5 ft columns containing either SE30 or PEGA as the stationary phase. Peak areas were determined by triangulation and authentic samples of the products were used to determine retention times and response ratios. Polymer samples were dried to constant weight in a vacuum oven (2 mmHg) at 60 °C. Weighing, transferring, and drying of polymers were treated as analytical operations when the yields of reactions were based on changes in the weight of the polymers.

Formylation of the Crown Ethers (1) and (3).—Commercial samples of benzo-15-crown-5 (1) and dibenzo-18-crown-6 (3) were formylated as described by Wada *et al.*²⁰ The products were 4-formylbenzo-15-crown-5 (2) (85% yield), m.p. 79–80 °C (lit.²⁰ 80–81.5 °C), and 4,4'-diformyldibenzo-18-crown-6 (4) (79%), m.p. 230–232 °C (lit.²⁰ 231–233 °C), respectively. Both products had satisfactory i.r. and ¹H n.m.r. spectra. The formylation of the crown ether (3) to give a mixture of 4-formyldibenzo-18-crown-6 (5) and starting material has been described previously.²¹

Preparation of the Polymer-supported Diol (6).—Samples of the polymer-supported diol (6) were prepared from chloromethylated 1% crosslinked polystyrenes using the literature procedure.²¹ The products had S = 8.9 and 7.25% corresponding to 2.80 and 2.27 mmol of diol residues (6) per g respectively.

Attachment of Formyl Crown Ethers to Polymer-supported Diol (6).—The following reaction is typical of the two summarised in Table 1 which used procedure A. Procedure B differed only in the molar proportions of the crown ether and diol used (0.56:1.00) and has been described before.²¹

Table 1. Binding of formyl crown ethers to polymers (6) and (11) and capacities of the products

Entry	Starting polymer			Formyl crown	Reaction conditions Procedure ^d ; Time (h)	Amount of bound crown ether (mmol g ⁻¹)	Designation for catalyst
	Type of polystyrene ^a	Loading of diol residues (6) ^b mmol/g	Loading of salt residues (11) ^c mmol/g				
1	SX1	2.80		(2)	A; 20	0.85	(8)
2	SX1	2.80		(4)	A; 20	0.60	(9)
3	SX1	2.27		(5)	B; 9.5	0.74	(10)
4	SX1		1.32	(2)	C; 96	0.85	(13)
5	XAD-2		0.92	(2)	C; 96	0.60	(14)
6	SX1		1.32	(4)	C; 96	0.59	(15)
7	XE-305		1.38	(5)	C; 96	0.53	(17)
8	SX1		1.32	(4)	D; 96	0.67	(16)

^a SX1 = 1% Crosslinked polystyrene; XAD-2 = Amberlite XAD-2, a macroporous 20% crosslinked polystyrene; XE-305 = Amberlite XE-305, a macroporous 3% crosslinked polystyrene. ^b By elemental analysis for S. ^c By titration for chloride ion. ^d See Experimental section for details of typical procedures.

Table 2. Yields of products from reactions (1)–(3) using various phase-transfer catalysts

Catalyst ^a	Yields (%) of products after 5 h and 24 h					
	From reaction (1) ^b		From reaction (2)		From reaction (3)	
	5 h	24 h	5 h	24 h	5 h	24 h
1% Crosslinked polystyrene (8)	3					
(9)		36 (44)		54		0
(10)	15	42		35		
(13)	31	20	58	64	2	4
(14)		43		55		
(15)	32	75 (48)	55	62	2	4
(16)		51 (58)		26		
(17)	8	44		58		
Crown ether (1)	3	12		9	2	2
Crown ether (2)	11	28		6	2	2
Polymer (6) ^c		8		0		0
Polymer (11) ^d		43		52		
Polymer (11) ^e		51				
Polymer (11) ^f		65		61		
Polymer (11) ^g		23				
Ph ₃ P ⁺ CH ₂ Ph Cl ⁻ (18)	89	97	47	56	90	99
(19)	93	97	35	43	92	99

^a See Table 1 for details of polymer-supported catalysts (8)–(10) and (13)–(17). ^b Yields in brackets were obtained using recycled catalyst. ^c 1% Crosslinked polystyrene containing 2.80 mmol of residues (6) per g. ^{d–f} 1% Crosslinked polystyrenes containing 1.80, 1.32, and 0.90 mmol per g respectively of residues (11). ^g Amberlite XAD-2 containing 0.92 mmol per g of residues (11).

Entry 1. A mixture of the diol (6) (907 mg, 2.54 mmol), 4-formylbenzo-15-crown-5 (2) (806 mg, 2.72 mmol), benzene (40 ml), and toluene-*p*-sulphonic acid (38 mg) was vigorously stirred and heated under reflux for 20 h during which time water was removed azeotropically. The polymer was filtered off and washed successively with water, acetone, chloroform, and ether, and then dried. The product (8) (1.193 g) had ν_{\max} 1 134s cm⁻¹ (ether linkages).

A portion (298 mg) of the above product, toluene-*p*-sulphonic acid (20 mg), water (3 ml), and dioxane (30 ml) was vigorously stirred at 95 °C for 10 h. The polymer was then filtered off and washed with dioxane (30 ml). The combined

filtrate and washings were concentrated under reduced pressure, diluted with water, and then extracted with ether. Evaporation of the dried (MgSO₄) extracts gave the crown ether (2) (74 mg, 0.25 mmol) with i.r. and H n.m.r. spectra identical with those of the original sample, corresponding to an original loading of 0.85 mmol/g.

Preparation of Polymer-supported Phosphonium Salts (11).—Various chloromethylated crosslinked polystyrenes were treated with triphenylphosphine in chlorobenzene using the usual procedure.²¹ By Volhard titrations the final products from 1% crosslinked polystyrene, Amberlite XAD-2, and Amberlite XE-305 contained 1.32, 0.92, and 1.38 mmol of chloride [and hence residues (11)] per g respectively.

A 1% crosslinked polystyrene containing 1.80 mmol of residues (11) per g was prepared similarly. A polymer with a lower content of salt residues (11) was obtained by vigorously stirring a mixture of this polymer (4.002 g), methylene chloride (25 ml), 50% aqueous sodium hydroxide (10 ml), and cetyltrimethylammonium bromide (130 mg) at 20 °C under nitrogen for 4 h. The polymer was filtered off and washed successively with 2M-hydrochloric acid, water, tetrahydrofuran-water (1:1), tetrahydrofuran, and methylene chloride, and was then dried. By Volhard titration the product (2.940 g) contained 0.90 mmol of chloride per g.

Reactions of Formyl Crown Ethers with Polymer-supported Phosphonium Salts (11).—These are summarised in Table 1, entries 4–8. The following is typical of the experiments using procedure C.

Entry 4. 1% Crosslinked polystyrene containing phosphonium salt residues (11) (2.100 g, 2.77 mmol of salt residues), 4-formylbenzo-15-crown-5 (2) (1.020 g, 3.44 mmol), methylene chloride (25 ml), 50% aqueous sodium hydroxide (10 ml), and cetyltrimethylammonium bromide (72 mg) were vigorously stirred at 20 °C under nitrogen. The mixture soon became dark brown but after 48 h it had regained its initial pale colour. The polymer was then filtered off and washed successively with tetrahydrofuran-water (1:1), tetrahydrofuran, and methylene chloride, and was then dried. The i.r. spectrum of the product (1.803 g) had small bands at 1 440 and 1 000 cm⁻¹ indicating that some residues (11) remained. To hydrolyse these the above procedure was repeated except that no crown ether was added. The i.r. spectrum of the final product (13) (1.680 g) no longer showed bands characteristic of residues (11) but there were strong bands at 1 135 and 1 113 cm⁻¹ due to ether groups. By Volhard titration the product contained <0.02 mmol of

residues (11) per g. If all the residues (11) present in the original polymer had simply hydrolysed the weight of the final polymer would have been 1.281 g. However, it weighed 299 mg more than this which corresponds to a crown ether content of 1.425 mmol, equivalent to 0.85 mmol per g.

The reaction (entry 8) using procedure D was carried out as follows. A mixture of 1% crosslinked polystyrene containing residues (11) (4.010 g, 5.29 mmol of salt residues), 4,4'-diformyldibenzo-18-crown-6 (4) (2.316 g, 5.56 mmol), anhydrous potassium carbonate (887 mg), and dried tetrahydrofuran (35 ml) was vigorously stirred under reflux and under nitrogen for 48 h. The polymer was then filtered off, washed, and dried as above. To ensure that no residues (11) remained the product (3.396 g) was treated for 48 h with aqueous sodium hydroxide under phase-transfer conditions as above. The final product (16) (3.275 g) had v_{\max} 1 685vw (aldehyde) and 1 130s cm^{-1} (ether residues). There were none of the bands characteristic of residues (11). The product contained <0.02 mmol of residues (11) per g by Volhard titration. The weight changes correspond to a total crown ether content of 2.18 mmol, equivalent to 0.67 mmol per g of polymer.

Reactions Summarised in Table 2.—The following experiment is typical of those involving reaction (1). A mixture of 1-bromo-octane (193 mg, 1.0 mmol), potassium iodide (830 mg, 5.0 mmol), toluene (4 ml), water (2 ml), catalyst (14) (34 mg, 0.02 mmol), and n-hexadecane (113 mg, 0.5 mmol; internal standard for g.l.c. analysis) was stirred (>1000 r.p.m.) at 90 °C under nitrogen. After 24 h the mixture was cooled then analysed by g.l.c. (SE30 stationary phase at 160 °C). The yield of 1-iodo-octane was 40%. In a duplicate experiment the yield was 45%.

The experiments involving reaction (2) were carried out as above except that sodium *p*-methylthiophenolate (365 mg, 2.5 mmol) in water (3 ml) was used, the reaction temperature was 80 °C, and the temperature of the SE-30 stationary phase was 250 °C.

The experiments involving reaction (3) were carried out as for reaction (1) but using potassium cyanide in place of potassium iodide, and using a PEGA stationary phase at 140 °C for the g.l.c. analysis.

Acknowledgements

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