Heterogeneous Phase-transfer Catalysts: Onium Salts, Crown Ethers, and Cryptands Immobilized on Polymer Supports

By Mauro Cinouini, Stefano Colonna, (Miss) Henriette Molinari, and Fernando Montanari*
(*Centro C.N.R. e Istituto di Chimica Industriale dell'Università, Via C. Golgi* 19, *Milano* 20133, *Italy*)
and Pietro Tundo*
(*Istituto di Chimica Organica dell'Università, Via Bidone* 36, *Torino* 10125, *Italy*)

Summary Typical phase-transfer catalysts, namely organophilic onium salts, crown ethers, and cryptands, when immobilized on a polymer matrix retain most of their catalytic activity, thus permitting catalyst recycling by simple filtration from the reaction medium.

Reactive groups bonded to insoluble polymer supports have been widely used not only in repetitive sequential-type syntheses, but also for a growing number of simple one-step reactions.[1] A procedure using polymer supports has been used in the immobilization of enzymes;[2] however, in the field of chemical catalysis, the applicability of such procedures has apparently been limited to organic photosensitizers and organometallic homogeneous catalysts.[1] In these cases one of the main advantages of the immobilization of the catalysts is their easy removal from the reaction

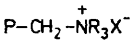
TABLE

Nucleophilic substitutions in n-octyl bromide[a] by KI and KCN in the presence of catalysts (I)—(IV).

Catalyst	Frequency of functionalised monomeric units[b]	Mol. equiv. of catalyst	T/°C	KI[c]		KCN[c]	
				Time/h	Yield (%)[d]	Time/h	Yield (%)[d]
(Ia)[e]	1:2	0·1	90	16	—	16	19
(Ib)	1:15	0·1	60	5	76		
(Ic)	1:10	0·1	60	6·5	73		
(II)	1:10	0·1	60	5	77		
,,	1:15	0·1	90	1·5	90	1·5	68
,,	1:10	0·1	90	1·5	90	1	86
,,	1:2	0·1	90	2·5	73		
,,	1:2[f]	0·1	90	16	—		
,,	1:10	0·01	90	5·5	89	3·5	90
,,	1:2	0·01	90	7	85	4	95
,,	1:2[f]	0·01	90	5	—		
(III)	1:20	0·01	90	5	⩾95		
,,	1:10	0·01	90	3	⩾95		
,,	1:3	0·01	90	5·5	⩾95	8	⩾95
,,	1:5[f]	0·01	90	6	⩾95	7	⩾95
(IV)	1:40	0·01	90	3·5	⩾95	2	⩾95
,,	1:20	0·01	90	3	⩾95		

[a] In toluene (1:3 v/v). [b] Approximate values; 2% divinylbenzene. [c] Saturated aqueous solution, 2·5 mol. equiv. [d] By g.l.c. analysis. [e] AG 1-X2 (Bio-Rad). [f] 4% Divinylbenzene.

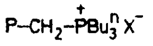
products, with minimum loss. In order to exploit these advantages we bound some typical phase-transfer catalysts such as ammonium and phosphonium salts,[3] crown ethers,[4] and cryptands[5] to a polymer matrix.



$\mathrm{P{-}CH_2{-}\overset{+}{N}R_3X^-}$

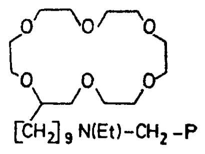
(I)

a; R = Me
b; R = Bu^n
c; R = Oct^n

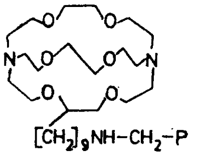


$\mathrm{P{-}CH_2{-}\overset{+}{P}Bu^n_3X^-}$

(II)



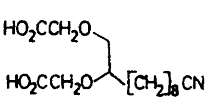
(III)



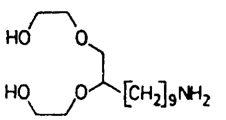
(IV)

$CH_2{=}CH[CH_2]_8CN$

(V)



(VI)



(VII)

The catalysts examined are of type (I)—(IV) and were prepared by reaction of the corresponding amines or phosphines with chloromethylated polystyrene resin (**P**–CH_2Cl) cross-linked with 2 or 4% *p*-divinylbenzene and different amounts of chloromethylated sites (0·7—3·7 mequiv. of Cl per g of polymer).

Reactions were carried out in anhydrous dimethylformamide at 60 °C for 5 days in the case of (Ib and c), at 110 °C for 4 days for (II), and at 60—65 °C for 7 days in the presence of $NaHCO_3$ for (III) and (IV) (65—75, 100, and 30—90% yields, respectively, depending also on the percentage of chloromethylated groups in the resin; see Table).

Catalyst AG 1-X2 (Ia) is a commercial product (Bio-Rad). The ω-ethylaminononyl-substituted 18-crown-6, the intermediate for the preparation of (III), was prepared by conversion of undec-10-enenitrile (V) into the acid (VI), *via* oxidation to the glycol with performic acid followed by condensation with chloroacetic acid, reduction to (VII) with $LiAlH_4$–tetrahydrofuran, *N*-acetylation, cyclisation to the crown ether with triethyleneglycol ditosylate, and finally reduction of the acetylamino-group with $LiAlH_4$. Condensation of the dichloride of the acid (VI) with 1,10-diaza-18-crown-6 under high dilution conditions and subsequent reduction of the bicyclic diamide formed with B_2H_6 gave the ω-aminononyl substituted cryptand [222], the intermediate for the preparation of (IV).†

The catalysts (I)—(IV) were used for anion-promoted reactions under conditions similar to those classically employed in phase-transfer processes[3–5] between two immiscible aqueous and organic phases. Data reported in the Table refer to Br to I and Br to CN exchange reactions, carried out by stirring a saturated aqueous solution of the inorganic reagent (2·5 mol. equiv.) and a solution in toluene of 1-bromo-octane in the presence of 0·01—0·1 mol. equiv. of the resin-anchored catalyst.

The most relevant features of our present results are as follows. (i) Reactions with polymer-supported catalysts are relatively slower than those carried out in the presence of similar non-immobilized phase transfer catalysts.[3–5] However, the dependence of catalytic activity on the structure of the catalyst is very similar in both cases, and the presence of an alkyl chain capable of imparting a sufficient organophilicity to the system seems to be a determinant factor: for instance compound (Ia) shows a very poor catalytic activity, as does $Me_4N^+X^-$.[3,6]‡ (ii) Polymer-

---

† Elemental analyses, and i.r. and ^1H n.m.r. data for all these compounds were in agreement with the assigned structures.

‡ This is in line with the fact that catalytic activity of the recently described catalyst (S. L. Regen, *J. Amer. Chem. Soc.*, 1975, **95**, 5956) **P**–$CH_2{-}N^+Me_2Bu^nCl^-$ seems to be noticeably lower than those of (Ib and c).

anchored phosphonium salts, crown-ethers, and cryptands are better catalysts than the corresponding supported ammonium salts, not only in terms of their higher reactivity, but also in terms of their higher thermal stability; at least some ammonium salts become unstable above 80—90 °C. (iii) The reaction rates are only slightly sensitive to the frequency of active sites on the polymeric skeleton. (iv) In contrast to the previously observed behaviour[6,7] of non-immobilized phase-transfer catalysts, no direct relationship was found between conversion times and concentration of the anchored catalysts when the concentration increases from 1 to 10% with respect to the substrate. The fact that for high catalyst concentrations large amounts of the solvent are absorbed by the resin could be one cause of this behaviour. (v) When the amount of cross-linking is 4% instead of 2%, the activity of the phosphonium salt (II) is practically zero; the influence of cross-linking is small in the case of the crown ether (III). (vi) The catalyst can be recovered at the end of the reaction by simple filtration and directly used for another run (the catalytic activity was shown to be practically unaltered after 5 times).

(*Received*, 20*th February* 1976; *Com.* 183.)

[1] C. C. Leznoff, *Chem. Soc. Rev.*, 1974, **3**, 65; C. G. Overberger and K. N. Sannes, *Angew. Chem. Internat. Edn.*, 1974, **13**, 99; D. C. Neckers, *J. Chem. Educ.*, 1975, **52**, 695.

[2] R. Goldman, L. Goldstein, and E. Katchalski, in 'Biochemical Aspects of Reactions on Solid Supports,' ed. G. R. Stark, Academic Press, New York, 1971, p. 1; S. P. O'Neil, *Rev. Pure Appl. Chem.*, 1972, **22**, 133; W. Marconi, S. Gulinelli, and F. Morisi, *Chimica e Industria*, 1974, **56**, 417.

[3] C. M. Starks, *J. Amer. Chem. Soc.*, 1971, **93**, 195; J. Dockx, *Synthesis*, 1973, 441; E. V. Dehmlov, *Angew. Chem. Internat. Edn.*, 1974, **13**, 170.

[4] D. Landini, F. Montanari, and F. M. Pirisi, *J.C.S. Chem. Comm.*, 1974, 879; D. Landini, A. M. Maia, F. Montanari, and F. M. Pirisi, *Gazzetta*, 1975, **105**, 863; M. Makosza and M. Ludwikow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 665.

[5] M. Cinquini, F. Montanari, and P. Tundo, *J.C.S. Chem. Comm.*, 1975, 393; B. Dietrich and J. M. Lehn, *Tetrahedron Letters*, 1973, 225.

[6] A. W. Herriott and D. Picker, *J. Amer. Chem. Soc.*, 1975, **97**, 2345.

[7] C. M. Starks and R. M. Owens, *J. Amer. Chem. Soc.*, 1973, **95**, 3613; D. Landini, A. M. Maia, F. Montanari, and F. M. Pirisi, *J.C.S. Chem. Comm.*, 1975, 950.