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Polymer-supported aza-15-crown-5 as effective catalyst for phase-transfer reactions

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Summary

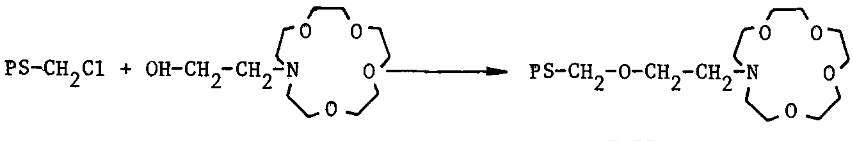
Immobilized aza-15-crown-5 were prepared by the reaction of chloromethylated polystyrene resin with N-(2-hydroxyethyl)-aza-15-crown-5. These polymer-supported crowns were very effective catalysts of nucleophilic substitution reactions carried out under the conditions of the two-phase (L-S) or three-phase (L-S-L) catalysis.

Introduction

The use of macrocyclic compounds as phase transfer catalysts has been known for a long time (1-4). In spite of the fact that they are much stabler than onium salts at elevated temperature and allow reactions to be carried out also in a strongly basic medium, their application is restricted due to the higher price. Only polymeric catalysts possessing high catalytic activity can be used for this purpose. Aza-15-crown-5 bound on a polystyrene matrix described below possesses a high catalytic activity for typical nucleophilic substitution reactions taking place under conditions of the two-phase (L-S) or three-phase (L-S-L) catalysis.

Results and discussion

The polymeric catalysts I-III with various contents of bound aza-15-crown-5 units were obtained by a reaction of N-(2-hydroxyethyl)-aza-15-crown-5 with chloromethylated polystyrene crosslinked with divinylbenzene (2 mole %) in the presence of sodium hydride by refluxing in tetrahydrofuran (5,6). At higher degrees of functionalization of the starting polymeric carrier the conversion reached is about 90 %.



I-III

The efficiency of polymeric catalysts I-III was tested in a reaction between 1-bromooctane and sodium phenoxide in 1,4-dioxane for L-S catalysis, or with potassium thiocyanate or sodium iodide for L-S-L catalysis in the toluene-water system.

$$C_8H_{17}Br + MX \xrightarrow[75^\circ C]{I\text{-}III} C_8H_{17}X + MBr \; ; \quad \begin{array}{l} M = Na,\ K \\ X = PhO,\ SCN,\ I \end{array}$$

To compare the catalytic activity of these polymer-supported crowns I-III

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*To whom offprint requests should be sent with that of polymeric catalysts prepared earlier (7-9), values of the specific rate constant, $k_s = k_o/c$, of the L-S system are given in Table 1, where k_o is the observed rate constant and c is the concentration of functional groups of the polymer present in the reaction mixture.

Table 1

Specific rate constants, k_s, of the catalyzed reaction between sodium phenoxide and 1-bromooctane in 1,4-dioxane at 75°C

Polymeric catalyst	Meq of functional unit per g of catalyst	$k_s.10^5$ $l^2mol^{-2}s^{-1}$
I	0.43	2300
II	1.64	3900
III	2.19	3000
PS-DMSO[a]	4.45[b]	2.32[b]
PS-NMP[c]	2.69[d]	28.8[d]

[a]Polymer analog of dimethyl sulfoxide based on poly(styrene-co-divinylbenzene) (98:2 mole %) prepared according to ref. 7. [b]Ref. 8. [c]Polymer analog of N-methyl-2-pyrrolidone based on poly(styrene-co-divinylbenzene) (98:2 mole %) prepared according to ref. 9. [d]Ref. 9.

Since the k_s values do not depend on the amount of the polymer, they characterize the effect of functional groups on the given polymeric carrier. With the same polymeric matrix the efficiency of the catalysts with bound aza-15-crown-5 units is higher by two or three orders of magnitude, compared with that of the so far most effective polymeric catalysts, i.e. polymeric analogs of N-methyl-2-pyrrolidone (PS-NMP) or dimethyl sulfoxide (PS-DMSO). The k_s values determined using polymeric catalysts I-III suggest that the accessibility of catalytic sites is probably affected by the degree of functionalization of the matrix. The efficiency of catalysts I-III remains the same also if they are reused, when on completion of the reaction the polymer is separated from the reaction mixture, washed with the solvent and reused in the reaction. Thus, e.g., also in the case of a third application of the catalyst III in reaction of 1-bromooctane with sodium phenoxide the conversion reached is virtually 100 % at 75°C within 13 min. Catalysts I-III can be equally readily used at room temperature because already after 24 h the conversion is 75 %.

Table 2

S_N2 reactions under conditions of L-S-L catalysis: 2 mmol of starting compound, 1 ml of 60 % aqueous potassium hydroxide, 12 mg of the catalyst III

Starting compound	Product	Time h	T °C	Yield of product, %
Methyl benzoate	Benzoic acid	40	45	99[a]
1-Bromohexane	1-Hexanol	60	105	90[b,c]
1-Bromooctane	1-Octanol	120	105	90[d]

[a]Conversion 25 % without catalyst III. [b]10 % of 1-hexene. [c]Without catalyst III conversion 25 % (1-hexene undetected). [d]Conversion 30 % without catalyst III.

Under the conditions of L-S-L catalysis, polymeric catalysts also possess a high catalytic activity. Thus, e.g., with II used in a reaction between 1-bromooctane and potassium thiocyanate at 75°C the conversion after 48 h is 78 %, and in a reaction with sodium iodide the conversion is 94 %, already after 24 h; on the other hand, if the polymeric analog of dimethyl sulfoxide is used, a conversion of merely 38 % is attained only at 100°C within the same time, while in the reaction with iodide at 90°C the conversion is 20 % within 24 h (7). Variability of the possibilities with catalysts I-III used is documented in Table 2 by examples of dehydrohalogenation and hydrolysis under the conditions of L-S-L catalysis.

Experimental part

Anhydrous 1,4-dioxane, toluene and tetrahydrofuran were distilled from sodium in the nitrogen atmosphere. Sodium phenoxide was prepared by reaction equivalent amounts of phenol and sodium ethoxide in ethanol and recrystallized from ethanol. 1-Bromooctane was redistilled before use. N-(2-hydroxyethyl)-aza-15-crown-5: Oxirane (5 ml) was added under cooling with ice to a solution aza-15-crown-5 (11 g) in methanol (40 ml). The mixture was refluxed (3 h), methanol was evaporated and the residue was distilled, yielding 7.6 g (58 %) of the product (b.p. 139-143°C/6.7Pa). Chloromethylated polystyrene (200-400 mesh), crosslinked with divinylbenzene (2 mole %) and with 0.82, 2.98 and 5.00 mmol Cl/g, was prepared by the described procedures (10).

In the reactions for L-S catalysis or for L-S-L catalysis the temperature of the reaction mixture was maintained by means of Term-O-Watch with an accuracy 0.5°C. GLC analyses of the reaction mixtures were carried out using a CHROM 5 apparatus (Laboratory Instrument, Prague; column 0.3×250 cm, SP 2100 (5 %) on Inerton AW-DMCS, carrier gas N_2, FID).

Reaction of N-(2-hydroxyethyl)-aza-15-crown-5 with chloromethylated polystyrene resin

The mixture of chloromethylated polystyrene corresponding to 1 mmol of chlorine with 1.2 mmol of N-(2-hydroxyethyl)-aza-15-crown-5 in tetrahydrofuran (50 ml for 1 g of polymer) and 2 mmol of 80 % NaH was refluxed for 4 days. Then the polymer was washed with water, methanol and diethyl ether and dried at 40°C/25 Pa for 24 h. The content of crown units in the polymer was calculated from an elemental analysis of the samples.

Reaction of 1-bromooctane with nucleophiles

To a solution of 1-bromooctane (1 mmol in 0.5 ml of 1,4-dioxane, or 0.6 mmol in 1 ml of toluene) was added polymer (20-50 mg) and the mixture was magnetically stirred (600 r.p.m.) at 75°C for 30 min. After that, the solution of a nucleophilic compound was added (0.5 ml 0.5M sodium phenoxide in 1,4-dioxane for L-S conditions; 1 ml aqueous 3.4M sodium iodide or 17.5M potassium thiocyanate for L-S-L conditions) and the mixture was analyzed by GLC (dodecane as an internal standard).

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