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Phase-Transfer Catalysts

Polymer-Supported Dimethyl Sulfoxide as Phase-Transfer Catalyst

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Summary

Crosslinked polystyrenes with pendant $-CH_2SOCH_3$ grouping are efficient phase-transfer catalysts in liquid-liquid reactions of 1-bromooctane with several inorganic nucleophiles. Direct introduction of $-CH_2SOCH_3$ grouping into polystyrene by the reaction of a halogenated polystyrene with methylsulfinylmethylsodium is described.

Introduction

Dipolar aprotic solvents are widely used in organic syntheses for anion activation. They were expected to retain their activating properties even on immobilization on an insoluble polymeric matrix. It has been proved indeed that polymer-supported hexamethylphosphoramide (1-4), oligoethylene glycol ethers (5-8), N,N-dimethylacetamide(9) or N-methylpyrrolidone (10) catalyze reactions of inorganic nucleophiles with organic halides in a two-phase system water - organic solvent or solid - organic solvent. Such polymeric catalysts are adequately called solid solvents (2) or solid phase cosolvents (5), and the reactions proper represent special cases of three-phase catalysis (11).

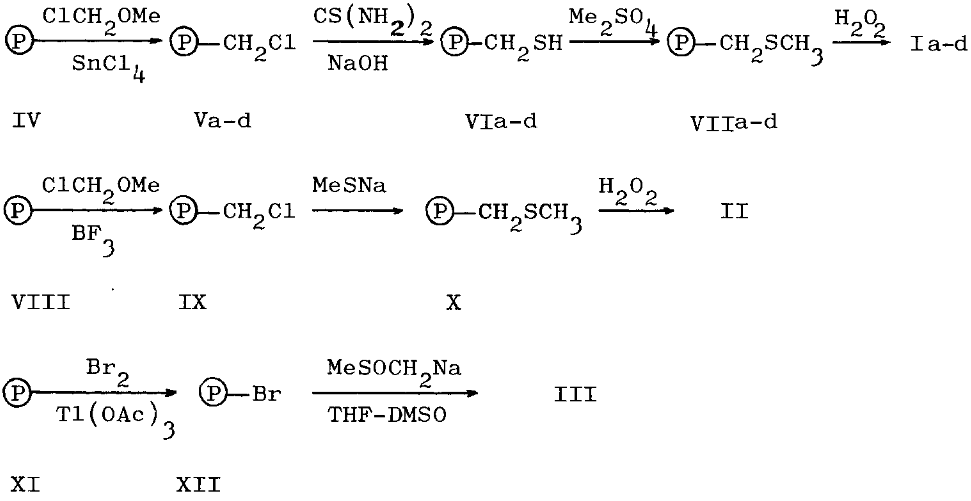
Polymer-supported dimethyl sulfoxide has been used as a phase-transfer catalyst only quite recently (12,13) though polymeric sulfoxides have been known for a long time. Up to now, sulfoxide polymers have been prepared (a) by polymerization of vinyl monomers bearing sulfoxide grouping (14-16), (b) by oxidation of sulfides chemically bound onto a polymer matrix (12,17), (c) by the reaction of chloromethylated copolymer styrene - divinylbenzene with methylsulfinylmethylsodium (18), this reaction, however, yields a mixture of products (19), (d) by the reaction of poly(methyl methacrylate) with methylsulfinylmethylsodium leading to poly(β-ketosulfoxides) (20).

In this communication the catalytic activity of crosslinked polystyrenes with pendant methylsulfinylmethyl grouping (Ⓟ$-CH_2SOCH_3$) was studied in a two-phase reaction of 1-bromooctane with several inorganic nucleophiles in the toluene - water mixture.

Experimental

Synthesis of polystyrene-supported dimethyl sulfoxides

Ⓟ$-CH_2SOCH_3$ (I-III, see Table I) were prepared by three procedures:



$$\textcircled{P} \xrightarrow[SnCl_4]{ClCH_2OMe} \textcircled{P}-CH_2Cl \xrightarrow[NaOH]{CS(NH_2)_2} \textcircled{P}-CH_2SH \xrightarrow{Me_2SO_4} \textcircled{P}-CH_2SCH_3 \xrightarrow{H_2O_2} Ia\text{-}d$$

IV Va-d VIa-d VIIa-d

$$\textcircled{P} \xrightarrow[BF_3]{ClCH_2OMe} \textcircled{P}-CH_2Cl \xrightarrow{MeSNa} \textcircled{P}-CH_2SCH_3 \xrightarrow{H_2O_2} II$$

VIII IX X

$$\textcircled{P} \xrightarrow[Tl(OAc)_3]{Br_2} \textcircled{P}-Br \xrightarrow[THF\text{-}DMSO]{MeSOCH_2Na} III$$

XI XII

Preparation of III

90 ml THF and 5.55 g XII swollen in 20 ml THF were slowly added to a solution of methylsulfinylmethylsodium prepared from 65 ml DMSO and 9.9 g NaH in 55 % oil dispersion (molar ratio CH_3SOCH_2Na : Br = 7.4 : 1). The reaction mixture was stirred under argon at laboratory temperature for 70 hours, then decomposed with ethanol, and filtered. The polymer was washed in turn with water, THF, and methanol. If the reaction was performed in neat DMSO, the product contained only 0.7 % S.

Table I Characteristics of polystyrene-supported dimethylsulfoxides $\textcircled{P}-CH_2SOCH_3$ [a,b]

$\textcircled{P}-CH_2SOCH_3$	Polymer matrix	S %	CH_2SOCH_3 mmol/g	Degree of functionalization[c]
Ia	gel,1 % DVB[d]	17.48	5.53	0.98
Ib	gel,2 % DVB[d]	17.39	5.45	0.96
Ic	gel,2 % DVB[d]	13.05	4.01	0.62
Id	gel,2 % DVB[d]	8.80	2.75	0.33
II	macroreticular[e]	4.39	1.37	0.12
III[f]	gel,2 % DVB[d]	12.06[g]	3.80	0.70[h]

[a] Ia-d and II were prepared by the oxidation of polymeric sulfides VIIa-d and X according to (12); the synthesis of III is given above. [b] All the polymers possess characteristic infrared absorption of sulfoxides at 1020-1050 cm^{-1}. [c] Calculated from "ring average molecular weights" neglecting crosslinking (21). [d] Divinylbenzene. [e] Amberlite XAD-2 (Rohm and Haas Co.). [f] Swelling ratios (swollen volume/dry volume) in H_2O, MeOH,

THF and DMSO are 1.6, 1.6, 1.7 and 2.3, resp. [g] Br content 11.96 %. [h] 0.68 (ex S), 0.73 (ex Br).

Synthesis and characteristics of intermediate polymers

IV: 1 or 2 % divinylbenzene crosslinked polystyrene, beads 0.2-0.4 mm.
Va-d: Prepared according to (22); Cl content 23.70, 23.20, 16.90, 10.50, resp. (D.F. 1.01, 1.0, 0.63, 0.33, resp.).
VIa-d: Prepared according to (12); S content 20.85, 20.78, 14.77, 8.97 %, resp. (D.F. 0.98, 0.97, 0.61, 0.33, resp.).
VIIa-d: Prepared according to (12); S content 19.50, 19.13, 14.31, 8.84 %, resp. (D.F. 1.00, 0.95, 0.62, 0.34, resp.).
VIII: Amberlite XAD-2 (Rohm and Haas Co.) dried to constant weight in vacuo at 90°.
IX: Prepared according to (23), Cl content 9.06 % (2.55 g-atom Cl/g).
X: IX was refluxed under argon with methanolic solution of CH_3SNa (molar ratio Cl:S 1:5.6) for 8 hours, washed with water and methanol. S content 4.70 % (1.47 mmol S/g), Cl content 2.46 %. Conversion 58 % (ex S).

XI: 2 % divinylbenzene crosslinked polystyrene beads $<$0.5 mm, washed according to (24).
XII: Prepared according to (24), Br content 45.14 % (5.65 g-atom Br/g), D.F. 1.04. Swelling ratios (swollen volume/dry volume) in MeOH, THF and THF-DMSO 1:1 are 1.2, 2.9, and 2.0, resp.

General procedure for triphase-catalytic nucleophilic reactions of 1-bromooctane

1 ml of 0.6 M solution of 1-bromooctane in toluene and corresponding amount of Ⓟ—CH_2SOCH_3 were equilibrated at 100° in a closed tube while stirring magnetically for 15 min. Then 1 ml of an aqueous solution of inorganic salt was added. The mixture was stirred at 100°C for 48 hours and analyzed by gas chromatography (Chrom 51, flame ionization detector, 2.5 m x 3 mm column with Chromaton N-AW HMDS - 6 % methyl phenyl silicone oil OV 17, temperature program 70-180°C) using chlorobenzene as an internal standard. Infrared spectra of the products of the reactions performed to total conversions correspond to those of the authentic substances. The results are given in Table II.

Results and Discussion

Polystyrene-supported dimethyl sulfoxides Ia-d and II were obtained from chloromethylated copolymers styrene - divinylbenzene by successive building up the sulfoxide groupings by known reactions (12). Polystyrene-supported dimethyl sulfoxide III, on the other hand, was prepared by direct introduction of the dimethyl sulfoxide moiety on the polymeric matrix via the reaction of brominated copolymer styrene - divinylbenzene with methylsulfinylmethylsodium. This reaction using halogenated polystyrene as the starting material represents a new way of polystyrene functionalization.

Table II Phase-transfer reactions of 1-bromooctane with nucleophiles catalyzed by polystyrene-supported dimethyl sulfoxide [a]

Run. no.	Ⓟ—CH_2SOCH_3	Bound sulfoxide mmol	Yield [b] %
KSCN (13 mmol)			
1	-	-	0
2	Ia	0.52	20
3	Ia	0.78	27
4	Ib	0.76	28
5	Ic	0.61	99, 83 [c]
6	Id	0.61	35
7	II	0.28	<1
8	III	0.56	74, 51 [c]
9	III	0.28	54, 40 [d]
NaI [e] (3.3 mmol)			
10	-	-	<1
11	Ia	0.28	50
12	Ib	0.25	48
13	Ic	0.20	70, 67 [c]
14	III	0.18	62, 64 [c]
KCN (7.7 mmol)			
15	-	-	0
16	Ib	0.50	20
17	Ic	0.40	46
18	III	0.19	58

[a] See general procedure in Experimental. [b] GLC yields of the products are based on chlorobenzene as an internal standard. [c] Reused catalyst. [d] Without stirring. [e] At 90°C.

The solid-solvent polymer mediates the contact between an inorganic and an organic reaction component present in different phases. The mechanism of catalytic activity of solid-solvent polymers has not been fully elucidated. In our case, it probably involves solvation interactions between sulfoxide groupings and alkaline metal cations in the aqueous phase and subsequent transfer of the ion-pair bound anion into the organic phase - and/or microhomogenization of the aqueous and organic phases inside the polymer in the region of balanced hydrophilic and hydrophobic effects (micellar mechanism).

Polystyrene-supported dimethyl sulfoxides I-III were tested as catalysts in reactions of 1-bromooctane with NaCN, KSCN and NaI in the toluene-water system. Their activity was evaluated according to the yields reached under defined and comparable conditions. The characteristics of the results obtained are (see Table II): (a) The easiness of anion transfer is roughly $I^- > SCN^- > CN^-$. (b) Reaction rates and/or yields rise with increasing amount of catalyst. (c) Macroreticular catalyst II is not active, obviously due to the heavily crosslinked matrix of the starting polymer - Amberlite XAD-2 (run No. 7). (d) Reaction rate is favourably affected by stirring. (e) On reuse, the activity of the catalysts depends on the nucleophile: iodides do not lower the activity while thiocyanates apparently cause partial deactivation of the catalyst (cf. runs No. 5,8,9 vs. 13,14). (f) Degree of crosslinking (1 or 2 % divinylbenzene) has no effect on the product yields (cf. runs No. 3 vs. 4 and No. 11 vs. 12).

Fully functionalized polymers Ia and Ib, as well as the little functionalized polymer Id give only low yields. Apparently, the catalysts with the optimum ratio of sulfoxide moieties to the hydrophobic polymeric matrix possess the highest activity. In our case, the optimum ratio is attained at the degree of functionalization 0.6-0.7 (polymers Ic and III). Not only the population of hydrophobic domain, but also its structure may determine the catalyst behavior in various nucleophilic reactions. Polymers Ic and III, though differing only little in the degrees of functionalization, contain hydrophobic domains of different structures. The former consists of styrene, the latter of bromostyrene units. While catalyst Ic is considerably more active than III in the reaction with KSCN (runs No. 5,8), the difference between them is already small in the reaction with iodide (runs No. 13,14). A dramatic reversal in the activity of both catalysts can be observed in the reaction with KCN (runs No. 17,18).

The increase in the active group concentration in linear polystyrene sulfoxides is accompanied by a monotonic decrease of their catalytic activity in the reaction of 1-bromooctane with KSCN (12). A similar decrease with increasing loading of the polymeric matrix was found with crosslinked polystyrene--supported glymes in the alkaline hydrolysis of 1-bromoadamantane (25).

The results reported in this communication for the crosslinked polystyrene sulfoxides suggest the existence of an optimum concentration of sulfoxide groups at which the yields of the products reach the maximum. Previously, we observed a great rise in the catalytic activity of polystyrene sulfoxides when the sulfoxide group was part of the crosslink (12). Apparently, in addition to other known factors, hydrophobic domains of the polystyrene matrix play an important role in the catalysis with solid-solvent styrene polymers. So far, this effect has been wrongly neglected.

For the organic synthesis, it is noteworthy that the reactions catalyzed with crosslinked polystyrene-supported dimethyl sulfoxides may be performed at high conversions and that the catalysts retain a satisfactory activity even after reuse. When compared with soluble non-crosslinked polymeric sulfoxides prepared by the copolymerization of the corresponding monomers with styrene (13), the crosslinked polystyrene-supported dimethyl sulfoxides I-III are readily accessible, their catalytic activity is similar, and they can be easily removed from the reaction mixture by mere filtration.

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