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POLY(STYRYLMETHYLTHIOL) AS AN EFFICIENT DEBROMINATING REAGENT OF 1,2-DIBROMIDES

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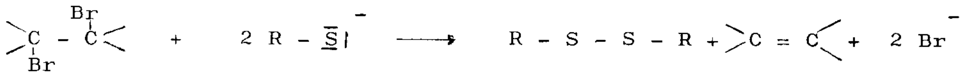
Summary Dibromides are readily debrominated by means of poly(styrylmethyl thiolate) with formation of the respective olefins. The polymeric reagent with a high content of sulphhydryl groups can be easily prepared from chloromethylated polystyrene, it extends possibilities of protection-deprotection reactions of the double bond.

In reactions of vicinal dihalogen derivatives with nucleophiles, halogen is eliminated along with substitution reactions and elimination of hydrogen halide.[1] The dehalogenation reaction was investigated in presence of halide ions[2-4], thiosulphates[5], thiolates[6,7], thiourea[8], selenides[9], tellurides[10], derivatives of trivalent phosphorus[11,12], and organometallic compounds[1] Alkenes may also be prepared by reacting dibromo derivatives with Cr^{2+} [13a,b], V^{III} [14] or Fe^{2+} ions and metals[1]. As regards the stereochemistry of these reactions, they were found to be[15] considerably stereospecific in polar solvents (ethanol, DMSO, DMF) and to proceed via an antielimination mechanism.

A disadvantage of the application of thiolates as dehalogenation agents consists in the unattractive work with thiols and in difficulties which may arise during the separation of dehalogenated products from the disulphide formed in the reaction



$$\underset{Br}{>C} - \overset{Br}{C}< \; + \; 2\,R-\overline{\underline{S}}|^{-} \longrightarrow R-S-S-R + >C=C< + \; 2\,Br^{-}$$

On the other hand, sulphhydryl groups attached to an insoluble polymeric carrier may overcome difficulties involved in the use of low-molecular weight thiols (easy manipulation with solid thiol, simple treatment of the reaction mixture by a simple filtration of one reaction component).

Ⓟ - CH_2SH Ⓟ = poly[styrene (99)-co-divinylbenzene (1)]

Crosslinked poly(styrylmethylthiol)(I) with an extremely high content of sulphhydryl groups was prepared from commercially available chloromethylated polystyrene (1% divinylbenzene as the crosslinking agent) by a reaction with thiourea followed by hydrolysis of the isothiuronium salt. Polymeric thiol (I) can readily be transformed by means of sodium methoxide in anhydrous methanol into the thiolate form active in the debromination reaction. This form is in a highly swollen state in methanol, so that reaction sites are easily accessible in the polymeric matrix. Although the debromination reaction gives rise to a polymer extremely crosslinked by disulphidic bonds, the reaction can nevertheless be carried out with satisfactory results by using an equivalent number of thiol groups on the polymeric carrier.

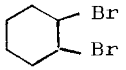
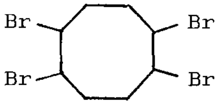
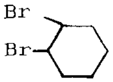
Thus, for instance, polymeric thiol I (6.50 mmol SH/g, 98% r.s.) was prepared as follows: 6.000 g of chloromethylated polystyrene (1% DVB, 23.30% Cl, 100% r.s., 40 mequiv.) were preswollen in 40 ml of 1,4-dioxan at 80°C, 1 h. After that, a solution of 4.940 thiourea (65 mmol) in 40 ml of a 1,4-dioxan - ethanol (4:1) mixture was introduced. The mixture was left to stand at 90°C for 24 h. The solution above the polymer was removed by suction, the polymer in the flask was washed with the dioxan-ethanol (4:1) mixture, and the polymeric isothiuronium salt was hydrolyzed with 15 ml of NaOH at 90°C for 10 h in an N_2 atmosphere. Finally, the solution was separated from the polymer by suction, and the thiol form was obtained after acidifying with 40 ml of 2M HCl (10 h, r.t.), and washing with H_2O and CH_3OH.

The debromination reactions were carried out, e.g., thus: 0.640 g of polymer I (4.16 mmol of SH groups) was heated under N_2 with 4 ml of 1 M

CH_3ONa to 50°C for 1 h, and 0.656 g of 1,2-dibromo-1,2-diphenylethane (2 mmol) in 15 ml THF was added. After 1 h the solution was separated from the polymer, the solvent was removed by distillation, the residue was dissolved in CH_2Cl_2 which was subsequently removed by distillation, and 0.310 g I of trans stilbene 1.84 mmol, 92%) was isolated. After recrystallization from EtOH - 0.300 g, 84%, m.p. 120-122°C.

The results of debromination are summarized in the Table

Table Debromination of the di- and tetrabromo derivative with the polymeric thiolate I

Compound	c[a], (mol/l)	Temperature (°C)	Time	Yield of alkene (%)
	2.0	50	3.5	95
	0.1	50	5	100
$C_6H_{13}CHBrCH_2Br$	2.0	50	5	60[c]
 - $CHBrCH_2Br$	0.4	50	2	100
 -$CHBrCH_2Br$	0.3	50	4	62
$CH_2BrC(CH_3)BrCN$	1.0	50	0.5	50[d]
meso-EtOOCCHBrCHBrCOOEt	0.1	r.t.	1	90[e,f]
meso-$C_6H_5CHBrCHBrCOOEt$	0.13[g]	r.t.	1	92[e,f]

[a] 1.0 mmol of the bromo derivative in methanol solution of the given concentration c was added to an equivalent amount of the polymerⓅ-CH_2SH (6.50mmol SH/g, 1% DVB) transformed in advance into the thiolate form by reacting with and equivalent amount of 1 M CH_3ONa in CH_3OH at 50°C for 1 h. [b] Yield according to GLC. [c] 1-Bromo-1-octene and 2-bromo-1-octene are the side products of the dehydrobromination reaction. [d] Consecutive addition of methacrylonitrile to the polymer takes place along with debromination. [e] Yield of the isolated product, original amount 2.0 mmol of the dibromo derivative. [f] Trans-isomer, a product of the antielimination mechanism, is formed in the reaction.

[g] A solution of the dibromo derivative in THF was used, cf. text.

It should be pointed out that the course of debromination of 1,2-dibromooctane is surprising although side dehydrobromination reactions were observed with dibromo derivatives which by debromination give rise to an alkyl substituted terminal olefin if low-molecular weight thiolates are used, the extent of these side reactions decreases with increasing chain, and with 1,2-dibromooctane they have not been observed at all[7] Compounds with a 1,2-substituted double bond are formed without any complications being involved.

Further aspects of the application of polymeric thiols in the debromination reaction are being investigated and will be reported

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