

POLY (P-N-CHLOROSTYRENESULPHONAMIDE): A NEW AND EFFICIENT CHLORINATING AGENT FOR AROMATIC RINGS

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(Received: Jun. 29th 1993 , Accepted: Jul. 17th 1995)

ABSTRACT : *Poly(p-N-chlorostyrenesulphonamide) synthesized via direct chlorination of poly [(p-styrene) sulphonamide], can be used for selective chlorination of aromatic compounds. Aromatic rings of the anisole, p-xylene, ethylbenzene and toluene are chlorinated with good yields. The polymer can be recovered, rechlorinated and reused several times.*

KEY WORDS : *Selective chlorination, Polymer supported halogenation, Chlorinated poly (p-styrenesulphonamide).*

INTRODUCTION

A major problem following an organic synthesis is the isolation of the desired product free from contamination due to solvents, catalysts, by-products and starting materials. This has been solved in a number of cases in recent years by using polymer based reagents. Numerous examples of these are now known and many reviews [1-7] and reports [8-11] available which provide, full coverage of this modern area of organic synthesis.

Polymer supported halogenation agents are

investigated in many reviews, [12-24]. Among them the poly-N-halo compounds are very important. One of the interesting advantages of the poly-N-halo compounds is that it reacts as a selective agent and specially increases the yield of the reaction. While, halogenation of the alkyl aromatic compounds with N-chlorosuccinimide in the absence of solvents and free radical initiators leads to the formation of a mixture of compounds including chlorinated aromatic rings and side chains. Under the same conditions only

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the aromatic rings of compounds are chlorinated by poly-N-chlorosuccinamide [16]. N-Chloro-nylon 6-6 is used for oxidation of alcohols [25] and sulfides [26]. N-F polymers are prepared from lithiated polystyrene [27]. This was proceeded to fluorinate the carbanion source $\text{Na}^+\text{PhC}^-(\text{CO}_2\text{Et})_2$. The best yield of $\text{PhCF}(\text{CO}_2\text{Et})_2$ achieved was 23%. Perfluoro-[N-fluoro-N(4-pyridyl) methane sulphonamide] [28], synthesized via direct fluorination of sodium derivatives of perfluoro- [N(4-pyridyl) methanesulphonamide], readily converts diethyl sodio phenyl malonate and anisole to diethyl fluoro phenyl malonate and ortho plus para fluoroanisole, respectively, at ambient temperature.

These types of polymer supported halogenating agents being relatively expensive and hard to synthesize, so the authors decided to prepare chlorinated poly-styrenesulphonamide, which is relatively inexpensive and easy to prepare. The novel chlorinated polymer was proved to be capable of effecting arene compounds.

RESULTS AND DISCUSSION

Treatment of poly (p-styrene sulphonamide) in dry Tetrahydrofuran (THF) at 80°C with an excess- molar equivalent of the Cl_2/CCl_4 was found to yield the corresponding chlorinated poly (p-styrenesulphonamide) in excellent yield. Work up of the product by standard procedures gave a semi- solid, which was identified by its $^1\text{H-NMR}$ and IR spectra. Iodometric titration was used to determine the amount of chlorine. This new compound proved to be a very powerful chlorinating agent, and was found to be easily recovered, regenerated and reused. This new polymer reagent converted p-xylene to 2- chloro-4-methyltoluene in high yield. Conversion of anisole to p-chloroanisole was achieved by this reagent in excellent yield. A mixture of ortho- and para- chloroethylbenzene was obtained from reaction of this polymer with ethylbenzene at 45°C. At 70°C 2,3,4,5,6-penta chloro ethylbenzene was obtained in high yield. A mixture of ortho- and para- chlorotoluene was obtained

from reaction of this polymer with toluene at 75°C in high yield. All attempts for chlorination of benzene were not successful. Therefore, the reagent is not able to chlorinate aromatic compounds, except those with donating substituents.

EXPERIMENTAL

Instruments

IR spectra were recorded using a *Perkin-Elmer* model 267 spectrometer, NMR spectra were recorded using a *Varian T.60 A* spectrometer, mass spectra were recorded on a *Varian Model MATMS-311* spectrometer (70ev.). NMR chemical shifts were measured relative to TMS (internal standard).

Commercial p-styrenesodiumsulphonate (*Fluka*, A.G, Switzerland) was used as received. p-styrenesulphonamide and poly (p-styrene sulphonamide) were prepared on 30g scale from p-sodium styrenesulphonamide, PCl_5 , ammonia and sodium t-butoxide according to the published procedure [29].

Methods

Poly (p-N-chloro styrenesulphonamide)

A sample of white finely- divided powdered poly (p-styrenesulphonamide) (8.0g) was dissolved in dry THF (50mL). Cl_2/CCl_4 was passed through the system for 30 minutes under ice-cooling. The color of the solution was not changed. The mixture was refluxed for 2 hours, until a dark brown color was produced. The solvent was evaporated, and the residue freed from the last traces of solvent in vacuum, to give the product (18.5g). The compound was identified by NMR, IR, and molecular weight determination (functional groups titration). The mole number of Cl bond chlorine (3mmol/g of N-Cl) was determined by iodometric titration [30].

Chlorination of anisole

Anisole (1.5mL, 13mmol) was dissolved in CCl_4 (50mL). The chlorinated polymer (4.33g) was added. The mixture was stirred at 0°C (1 hour) and then was heated to reflux for 2 hours.

The reaction mixture was filtered and the filtrate was dried under vacuum. This gave an oily residue (95%), NMR and mass spectrometry was shown to be p-chloroanisole.

The solid polymer was removed by filtration and recrystallized with ethanol and water. The yield of the recovery of polymer was 82%.

Rechlorination of recovered poly (p-styrene sulphonamide)

The recovered polymer (2.0g) was rechlorinated for 1 hour; 2.1g of rechlorinated dark brown polymer was obtained. Iodometry showed the presence of 2.9mmol of N-Cl/g of polymer (95%). The IR spectrum (KBr. disc) of recovered polymer was the same as before.

Reaction of recovered rechlorinated polymer with anisole

Recovered rechlorinated polymer (4.33g) was treated with anisole (1.5mL, 13mmol) in the usual way to give p-anisole in 84% yield.

Chlorination of ethylbenzene under mild conditions

Ethylbenzene (2mL, 19mmol) was dissolved in CCl₄ (40mL). The chlorinated polymer (6.33g) was added. The mixture was stirred at 0°C (1 hr) and then was heated at 40-45°C for 1 hour. The mixture was filtered and the filtrate was heated to remove solvent. The oily residue was identified by ¹H-NMR and IR to be a 1:2 mixture of ortho- and para- chloroethylbenzene.

Exhaustion of chlorination of ethylbenzene

Ethylbenzene (2mL, 19mmol) was dissolved in CCl₄ (40mL). The chlorinated polymer (32.0g) was added. The mixture was stirred at 0°C (1 hr) and then was heated at 70°C for 2 hours. The mixture was filtered and the filtrate was heated to remove solvent. The oily residue which was identified to be penta chloro ethylbenzene was obtained in 87% yield.

Chlorination of p-xylene

P-Xylene (2mL, 19mmol) was dissolved in

CCl₄ (40mL). The chlorinated polymer (6.33g) was added. The mixture was stirred at 0°C (1 hr) and then was heated to 50°C for 1 hour. The mixture was filtered and the filtrate was heated to remove solvent. It was identified by NMR (CDCl₃): 2.17(s, 3H, CH₃); 2.23(s, 3H, CH₃); 6.8(d, J=6), 6.9(d, J=6), 7.05(s).

Chlorination of toluene

Toluene (2mL, 19mmol) was dissolved in CCl₄ (30mL). The chlorinated polymer (6.5g) was added. The mixture was stirred at 0°C (1 hr) and then heated to 75°C for 1 hour. The mixture was filtered and the filtrate was heated to remove solvent. It was identified by NMR be a 1:2 mixture of ortho and para chlorotoluene. NMR(CDCl₃): 2.05(s, 3H, para CH₃); 2.2(s, 3H, ortho CH₃); 7.0(m, Ar).

ACKNOWLEDGEMENTS

The financial support of Bu-Ali Sina University is highly acknowledged.

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