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Poly [4-vinyl-*N*,*N*-Dichlorobenzenesulfonamide], a Useful Reagent for Chlorination of Various Carbanionic Substrates

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Poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide], prepared in high yield, acts as site-selective electrophilic chlorinating agent towards carbanionic substrates. β-Ketoesters and β-diketones were chlorinated by this reagent without using any bases. The reagent can be recovered, rechlorinated and reused several times.

Key Words: Poly[4-vinyl-*N*, *N*-dichlorobenzenesulfonamide], Chlorination, Carbanions.

INTRODUCTION

The introduction of chlorine into organic molecules is of broad interest, being used extensively in physical, theoretical and mechanistic studies, but the chlorination of carbanions remains limited. Various reagents have been applied for chlorination of organic compounds. These contain tetrachloromethane and hexachloroethane for chlorination of indenes,[1] hydrochloric acid and potassium permanganate in acetonitrile for the chlorination of simple ketones, α-ketoesters and 1,3-diketones,[2,3] *N*-chlorosuccinimide for preparation of aryldichloromethane and trichloromethane-sulfonate esters[4] and chlorination of phenylacetylene,[5] triphenylphosphine in CCl_4 and phosphorus trichloride for chlorination of β-diketones,[6] chlorine for chlorination of 1,5-diketones,[7–9] oxalyl dichloride[10,11] and thionyl chloride[12] were also applied for chlorination of organic compounds. All these reagents have some disadvantages such as low yield, toxicity, lack of selectivity and tedious work-up. In view of this, in the present work, we choose poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] as a chlorinating agent for various carbanionic substrates.

EXPERIMENTAL

IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometry (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively. NMR chemical shifts were measured relative to TMS (int, 1H). poly[4-vinyl-*N*, *N*-dichlorobenzenesulfonamide] was prepared as reported earlier.[13]

(a) Chlorination of acidic organic compound in the presence of base: A solution of carbanion in anhydrous tetrahydrofuran [prepared in conventional fashion by adding an 80% dispersion of NaH (12 mmol) in oil to acidic organic compound (10 mmol) in THF (10 mL)] was added under dry nitrogen to a stirred slurry of reagent **II** (10 mmol) in CH_2Cl_2 (15 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and then diluted with diethyl ether (50 mL); the insoluble polymer **I** was removed by filtration and washed with diethyl ether (10 mL). The mixture was then washed with 0.5 M oxalic acid (30 mL), 10% aqueous potassium hydrogen carbonate (30 mL) and saturated brine (30 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was purified by F.C.C. (silica : 30% methylene chloride in hexane). The pure product was obtained in 40–95% yield (Table-1).

TABLE-1
CHLORINATION OF CARBANIONS WITH POLY[4-VINYL-*N*,*N*-DICHLOROBENZENESULFONAMIDE]

Entry	Substrate	Product	Base	Temp. (°C)	Time (min)	Yield (%)
1.	$CH_3CHNO_2CH_3$	$CH_3CClNO_2CH_3$	NaH	0	40	92
2.	$PhC\equiv CH$	$PhC\equiv CCl$	NaH	0	50	87
3.	$C_4H_9C\equiv CH$	$C_4H_9C\equiv CCl$	NaH	0	50	88
4.	$CH_3COCH_2COCH_3$	$CH_3COCCl_2COCH_3$	—	40	250	95
5.	$PhCOCH_2COPh$	$PhCOCCl_2COPh$	—	40	210	80[a]
6.	$CH_3COCH_2COOC_2H_5$	$CH_3COCH_2COOC_2H_5$	—	50	270	90
7.	$CH_2(COOC_2H_5)_2$	$CCl_2(COOC_2H_5)_2$	NaH	0	60	89
8.	$CH_3CH(COOC_2H_5)_2$	$CH_3CCl(COOC_2H_5)_2$	NaH	0	50	95
9.	$CNCH_2COOC_2H_5$	$CNCCl_2COOC_2H_5$	NaH	0	50	93
10.	$PhCOCH_3$	$PhCOCH_2Cl$	NaH	RT	90	40
11.	$PhCOCH_2CH_3$	$PhCOCHClCH_3$	NaH	RT	90	45

[a] Purified by column chromatography on silica gel; RT—Room temperature.

Rechlorination of recovered poly (*p*-styrenesulphonamide)

The recovered polymer I (2.0 g) was rechlorinated for 1 h; 2.1 g of rechlorinated dark brown polymer was obtained. Iodometry showed the presence of 2.9 mmol of N—Cl/g of polymer (95%).

Reaction of recovered rechlorinated polymer with 2-nitropropane

Recovered rechlorinated polymer (10 mmol) was treated with 2-nitropropane (10 mmol) in the usual way to give 2-chloro-2-nitropropane in 92% yield.

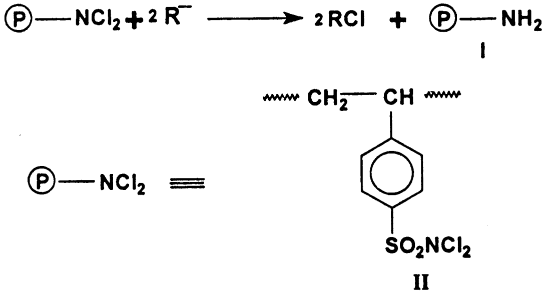
(b) Chlorination of β-ketoesters and β-diketones without base: A mixture of β-diketone of β-ketoesters (10 mmol) and reagent (10 mmol) in THF was heated (Table-1). After the completion of the reaction the mixture was evaporated under reduced pressure. The crude product was purified by F.C.C. (silica : 30% methylene chloride in hexane). The pure product was obtained in 40–95% yield (Table-1). All products were characterized by spectral methods (IR, ^1H NMR).

Reaction of recovered rechlorinated polymer with ethyl acetoacetate

Recovered rechlorinated polymer (10 mmol) was treated with ethyl acetoacetate (10 mmol) in the usual way to give dichloroethyl acetoacetate in 90% yield.

RESULTS AND DISCUSSION

We have previously reported a convenient method for chlorination of carbanions[14] and the deoximation of ketone and aldehyde oximes to their corresponding carbonyl compounds with poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide].[13] Herein, we now report that poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] **I** is effective reagent for the selective chlorination of a broad variety of carbanions under mild conditions **(Scheme-1)**. The poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] is in general a stable compound and easily prepared.[13–15] Treatment of carbanions with poly[4-vinyl-*N*,*N*-dichlorobenzenesulfonamide] results in transfer of chlorine from nitrogen to carbon.



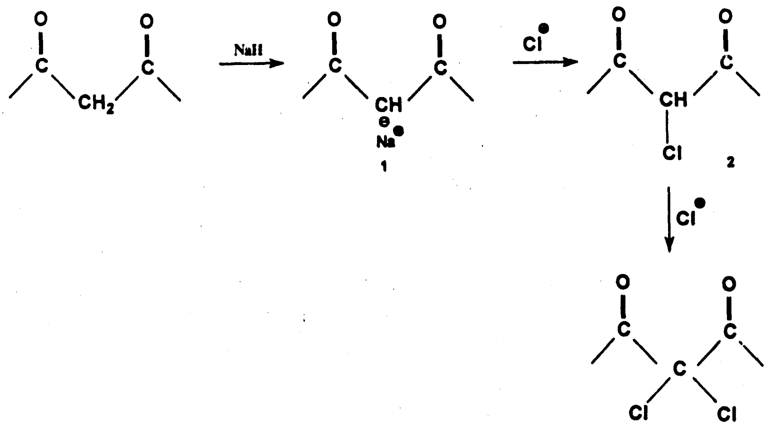
Scheme-1

A broad variety of anions, including malonates, nitroalkanes, alkynes, β-ketoesters and β-diketones can be chlorinated in high yield (Table-1). The products of the reactions with poly[4-vinyl-*N*,*N*-dichlorobenzensulfonamide] **II** were isolated simply by filtering off the solid polymer **I** and subsequent evaporation of the solvents from the filtrates. This method has advantages in terms of yields, simplicity of reaction conditions, and no side-products. The recovered starting polymer **I** was chlorinated and used many times without any reduction in its efficiency.

Since this polymer reagent **II** contains two chlorine atoms which are attached to nitrogen atom, it is quite possible that this reagent upon heating releases *in situ* Cl^+ which could act as electrophilic species. An evidence for this claim has been reported in which Cl^+ was generated *in situ*.[16, 17] Therefore we wish to propose the following mechanism for chlorination of carbanions with this polymer reagent **II (Scheme-2)**. This Cl^+ will react with intermediate **1** and **2**, respectively, and finally will give chlorinating compounds in high yield.

In the case of β-dicarbonyl compounds (*e.g.*, 2,4-pentanedione) dichlorinated products were obtained in excellent yields.

It should also be mentioned that β-diketones are chlorinated at 50°C, without using any base. The polystyrenesulfonamide **I** formed in this reaction is easily recovered, rechlorinated and reused several times.



Scheme-2

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