

Sulfur Ylides Attached to Some Condensation Polymers

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In the present paper the syntheses of polymer-bound sulfonium salts and oxosulfonium salt using a dichloromethyl derivative of methyl phenyl sulfide, 2, 4-bis(chloromethyl)thioanisole, and the epoxidation reactions by use of polymeric sulfur ylides derived from them are described.

INTRODUCTION

In recent years the reactions of polymer-bound reagents with organic substrates have been involved as an active area of chemical research. The first example of a polymer-bound sulfur ylide was provided by us.¹⁾ That is, a cross-linked copolymer of methyl *p*-vinylphenyl sulfide and divinylbenzene gave an insolubilized dimethylsulfonium methylide on treatment with methyl sulfate and *t*-BuOK, and the ylide could be used to convert benzaldehyde to styrene oxide.

As an extension of our work, it seemed interesting to examine the possibility of substituting condensation polymer for the copolymer of the styrene derivative and divinylbenzene. Thus, we have taken three approaches for the synthesis of condensation polymers containing sulfonium methylide groups which may be used for similar purpose. All these attempts were successful to some extent and led to condensation polymers having sulfur ylides and consequently, effective on the conversion of benzaldehyde to styrene oxide. These polymer-bound sulfur ylides have been derived from the corresponding polymeric sulfonium salts or oxosulfonium salt by treatment with the appropriate strong base such as *t*-BuOK or NaH.

In this paper we wish to report the syntheses of the polymer-bound sulfonium salts and oxosulfonium salt using a dichloromethyl derivative of methyl phenyl sulfide and the epoxidation reactions by use of the polymeric sulfur ylides (**3**, **6**, and **9**) derived from them.

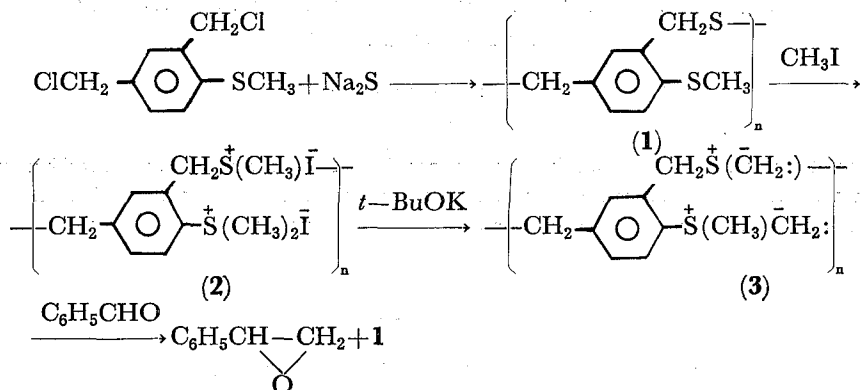
RESULTS AND DISCUSSION

Though relatively few reliable methods are currently available for the monochloromethylation of methyl phenyl sulfide,²⁾ many descriptions of the synthesis of its dichloromethyl derivative, 2, 4-bis(chloromethyl)thioanisole, are known since ages ago.³⁾ The easily available 2, 4-bis(chloromethyl)thioanisole was condensed with Na₂S·9H₂O in *N,N*-dimethylformamide to give a linear polysulfide (**1**). Reaction

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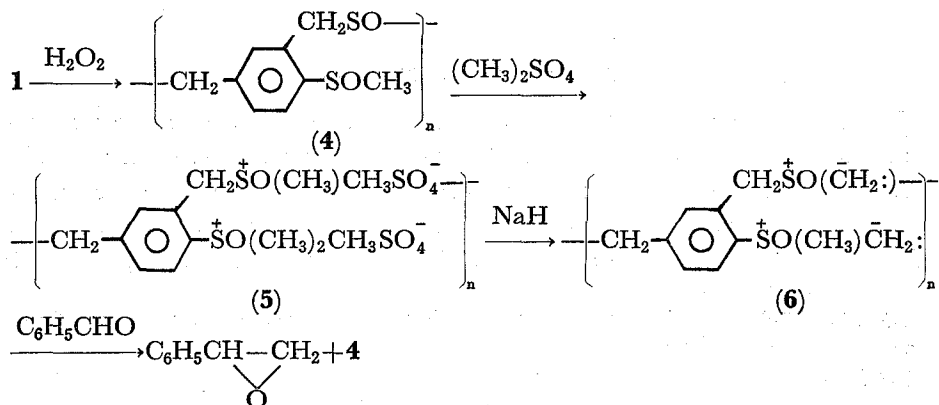
of **1** with an excess of methyl iodide gave a hygroscopic polymeric sulfonium iodide (**2**) in quantitative yield. Elemental analysis indicates that both sulfur atoms in **2**, one of which is that of the pendant methylthio group and the other constructs the backbone of the polymer, are equally converted to sulfonium iodide.



When **2** was treated with *t*-BuOK in dimethyl sulfoxide (DMSO) at room temperature, a polymeric sulfonium methylide (**3**) was produced, which was able to convert benzaldehyde to styrene oxide in much the same manner as dimethylsulfonium methylide or dimethylloxosulfonium methylide. The charged **2** for the reaction was recovered in the form of **1**, which could be reused for epoxidation reaction upon conversion to **2** by methyl iodide. There was, however, some loss in activity of the recycled polymer.

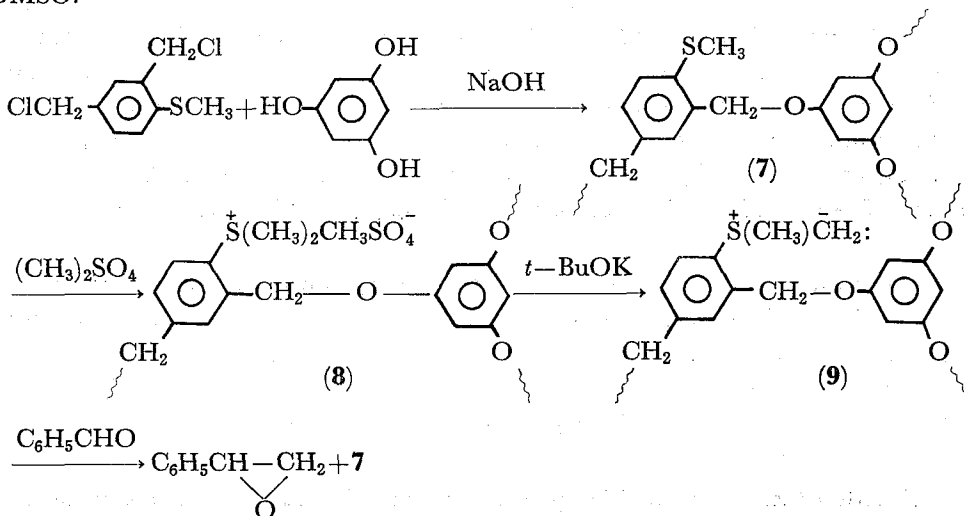
The epoxidation of benzaldehyde could be effected even more cleanly and efficiently (68%) using a polymeric sulfonium methylsulfate (prepared by heating **1** with an excess of methyl sulfate at 100°C for 6 hr) under the action of *t*-BuOK in DMSO.

On the other hand, treatment of **1** with hydrogen peroxide in acetone resulted in the formation of a polymeric sulfoxide (**4**), which when treated with methyl sulfate at 100°C with stirring is converted to a polymeric oxosulfonium methylsulfate (**5**). Elemental analysis and IR spectrum of **4** are in good agreement with the expected structure. In spite of recurring sulfoxide groups in the backbone and the pendant groups, **4** is insoluble in water, but the corresponding polymer-bound oxosulfonium methylsulfate (**5**) is water-soluble as expected.



By treatment with NaH in DMSO **5** was converted to a polymeric oxosulfonium methylene (**6**), which was able to use for the epoxidation reaction of benzaldehyde. However, the yield of styrene oxide in the reaction was extremely low.

Lastly, the preparation of an insolubilized polymeric sulfide (**7**) *via* the condensation of 2, 4-bis(chloromethyl)thioanisole with phloroglucinol and its conversion to the corresponding insolubilized sulfonium methylsulfate (**8**), and further the use of **8** in the epoxidation reaction were attempted. Thus, we were able to obtain moderately good yield of styrene oxide from the reaction of benzaldehyde with **8** that had been converted to the corresponding insoluble sulfonium methylene (**9**) with *t*-BuOK in DMSO.



The insoluble sulfonium methylene (**9**) could be regenerated from the recovered **7**. However, some loss in activity of the recycled polymer was unavoidable.

EXPERIMENTAL

Reaction of 2, 4-Bis(chloromethyl)thioanisole with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. 3.3 g (14.9 mmol) of 2, 4-bis(chloromethyl)thioanisole is dissolved in 60 ml of *N,N*-dimethylformamide and added to a solution of 4.8 g (20.0 mmol) of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 20 ml of water while maintaining the temperature at 20°C. The mixture is stirred at 100°C for 2 hr and further at 230–240°C for 2 hr, and then poured into a large quantity of water. The resulting precipitate is collected on a funnel. It is washed thoroughly with boiling water and then with warm ligroin. Yield 2.5 g (92%), mp 58–62°C, $\eta_{inh} = 0.29$ (0.3 g/100 ml hexamethylphosphoric triamide, 30°C). Found: C, 58.11; H, 5.71%. Calcd for $(\text{C}_9\text{H}_{10}\text{S}_2)_n$: C, 59.29; H, 5.53%.

Reaction of a Polysulfide (1) with Methyl Iodide. A mixture of 2.0 g of **1** and 100 g methyl iodide is boiled under reflux for 6 hr, and then poured into a large quantity of ether. The resulting precipitate is collected by filtration and washed thoroughly with ether. Yield 5.1 g (100%). Found: C, 27.04; H, 3.90%. Calcd for $(\text{C}_{11}\text{H}_{16}\text{I}_2\text{S}_2)_n$: C, 28.34; H, 3.46%.

Epoxidation Reaction Using a Polymeric Sulfonium Iodide (2) and *t*-BuOK.

To a mixture of 4.5 g of **2**, 1.0 g (9.4 mmol) of benzaldehyde and 30 ml of DMSO is added 3.2 g (28.5 mmol) of *t*-BuOK in 20 ml of DMSO while maintaining the temperature at 20°C. The mixture is stirred at 20–25°C for 3 hr, and then poured into a large quantity of water. The resulting precipitate (1.9 g), which is recovered **1**, is collected by suction filtration, and washed twice with small portions of ether. The combined filtrate and washings are extracted with ether. The ether solution is washed with water and dried over anhydrous MgSO₄. The solvent is removed on a rotary evaporator, and the residue is distilled to yield 0.60 g (53%) of styrene oxide.

Oxidation of a Polysulfide (1) by Hydrogen Peroxide. To a solution of 1.5 g of **1** in 40 ml of acetone is added 1.94 g (20.0 mmol) of 35% hydrogen peroxide, and the solution is stirred at room temperature for 24 hr. The mixture is poured into 40 ml of water, and the resulting precipitate is collected on a funnel. After thorough washing with water, 1.6 g (91%) of a light yellow powder, mp 90–98°C, is obtained. Found: C, 49.53; H, 6.30%. Calcd for (C₉H₁₀O₂S₂)_n: C, 50.44; H, 4.70%.

Reaction of a Polysulfoxide (4) with Methyl Sulfate. A mixture of 0.9 g of **4** and 30 ml of methyl sulfate is stirred at 100°C for 6 hr. The reaction mixture, which has become dark brown, is poured into a large quantity of ether. The resulting precipitate is collected and washed with ether. Yield 1.9 g (97%). Found: C, 32.81; H, 5.58%. Calcd for (C₁₃H₂₂O₁₀S₄)_n: C, 33.47; H, 4.75%.

Epoxidation Reaction Using a Polymeric Oxosulfonium Methylsulfate (5) and NaH. To a stirred mixture of 1.8 g of **5**, 0.60 g (5.7 mmol) of benzaldehyde and 50 ml of DMSO is added 0.2 g (8.3 mmol) of NaH in small portions. The NaH has been washed thoroughly with petroleum ether before use. The mixture is stirred at 25°C for 1 hr and further at 40°C for 1 hr, and then poured into a large quantity of water. Extraction with ether followed by vacuum distillation give styrene oxide. Yield 0.10 g (15%).

Reaction of 2, 4-Bis(chloromethyl)thioanisole with Phloroglucinol. To a solution of 5.0 g (22.6 mmol) of 2, 4-bis(chloromethyl)thioanisole and 2.44 g (15.0 mmol) of phloroglucinol (C₆H₆O₃·2H₂O) in 30 ml of DMSO is added 2.0 g (50 mmol) of finely powdered NaOH. The mixture is stirred at 120°C for 3 hr. The resulting precipitate is isolated by filtration, washed successively with 10% NaOH aqueous solution, water, 10% HCl, and water, and then dried. Yield 4.0 g (76%), mp > 360°C. Found: C, 65.83; H, 6.98%. Calcd for (C₃₉H₃₆O₆S₃)_n: C, 67.21; H, 5.21%.

Reaction of an Insolubilized Polymeric Sulfide (7) with Methyl Sulfate. A mixture of 2.0 g of **7** and 40 g of methyl sulfate is stirred at 110–120°C for 3 hr. The resulting **8** is collected by suction filtration and washed thoroughly with ether; yield 3.2 g (100%). Found: C, 49.11; H, 6.81%. Calcd for (C₄₅H₅₄O₁₈S₆)_n: C, 50.27; H, 5.06%.

Epoxidation Reaction Using an Insolubilized Sulfonium Methylsulfate (8) and *t*-BuOK. To a stirred mixture of 4.0 g of **8** and 0.60 g (5.7 mmol) of benzaldehyde in 50 ml of DMSO is added 4.2 g (37.4 mmol) of *t*-BuOK. The mixture is stirred at 25°C for 1 hr and further at 50°C for 2 hr, and then poured into a large quantity of water. The polymeric material is removed by filtration and washed with ether, the ether being combined with an ethereal extract of the filtrate. After washing with water and brine, drying over anhydrous MgSO₄ and removing the solvent, styrene oxide is obtained by distillation; yield 0.35 g (52%). The recovered **7** weighs 2.5 g (97%).

REFERENCES AND NOTES

- (1) S. Tanimoto, J. Horikawa, and R. Oda, *Yūki Gōsei Kagaku Kyokai-shi (Journal of the Society of Organic Synthetic Chemistry, Japan)*, **27**, 989 (1969).
- (2) Pines and co-workers have recently devised a superior, direct synthesis of *p*-methylthiobenzyl chloride *via* a new chloromethylation of methyl phenyl sulfide. See S. H. Pines, R. F. Czaja, and N. L. Abramson, *J. Org. Chem.*, **40**, 1920 (1975). However, no description of the monochloromethylation of methyl phenyl sulfide using HCl, formaldehyde and Lewis-acid catalyst is to be found in the literature. We accomplished the monochloromethylation with H₃PO₄-catalyst in the following manner. A mixture of 10 g (0.081 mol) of methyl phenyl sulfide, 2.5 ml of 85% H₃PO₄, 125 ml of glacial acetic acid, 25 ml of water and 12.5 g (0.42 mol) of paraformaldehyde is stirred at 5°C for 8 hr, during which time a stream of HCl is introduced. The reaction mixture is then poured into a large quantity of water. The organic layer is separated, combined with a benzene extract of the aqueous phase and dried over anhydrous MgSO₄, and the benzene is removed. The oily residue is distilled *in vacuo* to afford *p*-methylthiobenzyl chloride (bp 92–97°C/0.42 mmHg) in 77% yield, which is suitable for synthetic reaction without further purification.
- (3) *e.g.* J. H. Wood, M. A. Perry, and C. C. Tung, *J. Am. Chem. Soc.*, **72**, 2989 (1950); General Aniline Works, U.S. 1,887,396 [*Chem. Abstr.*, **27**, 1359 (1933)]; I. G. Farbenind A.-G. Brit. 347,892 [*Chem. Abstr.*, **26**, 2750 (1932)].