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Synthesis and Polymerization of *p*-Bromomethylstyrene and *p*-Iodomethylstyrene

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SUMMARY

Synthesis of p-bromomethylstyrene (3) and p-iodomethylstyrene (4) is reported. 3 was obtained by the bromomethylation of 2-phenylethyl bromide followed by dehydrobromination of the resultant p-(2-bromoethyl)benzyl bromide (2) with t-BuOK, as well as by cleaving p-vinylbenzyl methanosulfonate with LiBr in the presence of 18-crown-6. 4 was obtained from p-chloromethylstyrene (1) via the Finkelstein reaction. 3 was polymerized successfully in the presence of free-radical initiators, but 4 was found to be too unstable to give a well-defined polymer.

INTRODUCTION

Chloromethylated linear and crosslinked polystyrene is widely used as an intermediate for the synthesis of many functional polymers (FRÉCHET and FARRALL 1977). These products possess, however, several drawbacks: their chloromethyl groups are statistically distributed along the polymer chain and are substituted in either ortho- (~30%) or para- (~70%) positions (FREEMAN 1961); the chloromethylated poly(styrene-co-divinylbenzene) contains an unknown amount of additional crosslinks via methylene bridges (JONES 1952), and the reactivity of a chloromethyl group is too low in a number of substitution reactions (TANIMOTO et al. 1974, LUCA et al. 1980).

The drawbacks related to structural deffects have been overcome by synthesizing p-chloromethylstyrene (1) from p-cyanotoluene (ARCUS and SALOMONS 1962) and p(2-bromoethylbenzyl) chloride (2) (TANIMOTO et al. 1974, KONDO et al. 1979), but the so-obtained 1 was still characterized by a low reactivity in various nucleophilic substitution reactions.

Several authors have used the Finkelstein reaction to obtain functionalized linear or crosslinked polystyrene containing more reactive bromomethyl or iodomethyl groups (TAKAKI et al. 1979, KORSHAK et al. 1966, HIRSCH et al. 1970). To this end, a direct halomethylation of poly(styrene-co-divinylbeneze) also has been reported (ROGOZHIN et al. 1966), but both approaches led to poorly defined products, often containing the residual chloromethyl groups.

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The purpose of this preliminary report is to present convenient methods for the synthesis of two novel reactive monomers: p-bromomethylstyrene (3) and p-iodomethylstyrene (4) as well as their free radical polymerization.

Experimental

Materials: 2-Phenylethyl bromide was obtained from 2-phenylethyl alcohol and bromine in the presence of red phosphorus; its purity was better than 99% (by GLC). Chloromethyl methyl ether was distilled twice prior to use (b.p.58-60°C). *tert*-Butyl alcohol was dehydrated by storing it and distilling it over CaH_2. Initiators were recrystallized from methanol or chloroform. 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was obtained and purified exactly as reported by GOKEL *et al*. (1974).

Methods: NMR spectra were recorded using a Tesla BS 497 100 MHz spectrometer, using CCl_4 or $CDCl_3$ solutions and HMDSO as an external reference. IR spectra were obtained using a Specord 71 IR spectrophotometer and samples as CCl_4 solutions, neat liquid films or polymeric foils cast from benzene solutions. Halogen content was determined by the oxygen-flask method (DIXON 1968) using potentiometric titrations with a 0.01 N $AgNO_3$.

Procedures: *p*-(2-Bromoethyl)benzyl bromide (5). In a 500 ml flask there was placed 105 g (0.57 mol) of 2-phenylethyl bromide, 21.5 g (0.72 mol) of paraformaldehyde, 80 g (0.78 mol) of well-ground, dried NaBr, and 50 ml of glacial acetic acid. The mixture was stirred vigorously at 85°C, and over a period of 4 hr. a mixture of 75 ml of glacial acetic acid and 75 ml of conc. sulfuric acid was added dropwise. Heating and stirring was continued for an additional 4 hr., then the reaction mixture was cooled, neutralized with $NaHCO_3$, thoroughly washed with water, extracted with benzene, and dried over $MgSO_4$. Benzene was driven off, and the residual brown oil was distilled under reduced pressure to give 48 g (45.7%) of the unreacted 2-phenylethyl bromide and 64.0 g of a colorless, viscous liquid which solidified on standing; b.p. 120-155°C/3.5 mm Hg. The product was twice recrystallized from hexane to yield 26.5 g (16.8%) of a white, crystalline product; m.p. 66-68.5°C.

$C_9H_{10}Br_2$ (277.90) Calcd. Br 57.50, Found Br 57.36
IR (CCl_4): 3080, 3054, 3045, 2993, 1905, 1793, 1616, 1514 1263, 1228, 1201, 1023, 891, 647, 617 cm^{-1}
^{1}H-NMR (CCl_4): δ = 3.33-3.85 (m; 4H, $-CH_2CH_2Br$), 4.69 (s; 2H, $-CH_2Br$), 7.38-7.64 (m; 4H, arom.).

3. In a 250 ml flask containing 50 ml of anhydrous *t*-BuOH and 50 ml of anhydrous diethyl ether there was dissolved 5.50 g (0.14 mol) of metallic potassium. The suspension was cooled to -5°C, then 26.0 g (0.0936 mol) of 5 was added in small portions. Stirring was continued for 30 min., then the mixture was poured into 500 ml of water, extracted twice with diethyl ether, dried over $MgSO_4$, and dis-

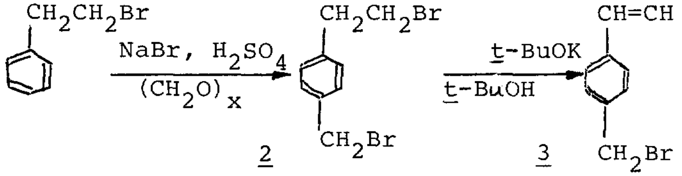
tilled under reduced pressure to give 14.6 g (79.2%) of a pale-yellow liquid; b.p. 72-75°C/1.5 mm Hg, lachrymator.
IR(neat): 2971, 1630, 1515, 1414, 1238, 1212, 1115, 1004, 927, 858, 823, 737 cm^{-1} (see Fig. 1).
^1H-NMR ($CDCl_3$): δ = 4.58 (s; 2H, $-CH_2Br$), 5.42 (dd; 1H, H_b), 5.89 (dd; 1H, H_a), 6.84 (dd; 1H, H_x), 7.48 (s; 4H, arom.).

Poly(3). A 2.996-g (15.2 mmol) portion of 3 and 24.5 mg of 2,2'-azoisobutyronitrile was sealed in a glass vial under argon and heated at 95°C for 20 hr. The resultant viscous product was dissolved in a small volume of benzene and precipitated into methanol, then filtered off and dried under reduced pressure to yield 1.53 g (51.1%) of a white polymer; m.p. 77-81°C.
$(C_9H_9Br)_x$ (196.98) Calcd. Br 40.57 Found Br 40.71
IR (film): 2970, 2922, 1894, 1810, 1610, 1513, 1481, 1446 1425, 1235, 1212, 1111, 1050, 1033, 850, 695 cm^{-1}.

4. In a 250 ml flask there was placed 130 ml of dry acetone, 29.5 g (0.198 mol) of dry NaI, and to the resultant solution 20.0 g (0.131 mol) of 1 (TANIMOTO et al. 1974) was added. The mixture was stirred at 50°C for 40 min., cooled and filtered. Acetone was driven off under reduced pressure at room temperature, and to a solid residue 100 ml of water and 150 ml of ether was added. The aqueous layer was extracted additionally with ether, the combined extracts were washed with water containing a small amount of sodium thiosulfate, dried over $MgSO_4$, and ether was evaporated under reduced pressure. The orange-yellow oil was dissolved in 50 ml of hexane, cooled to -20°C, and the crystalline, pale-yellow solid was fast separated on a cooled filter to yield 26.0 g (84.1%) of 4; m.p. 9-10°C.
IR (neat): identical with 3 except for the 1100-1300 cm^{-1} region 1300, 1229, 1169, 1136, 1100 cm^{-1} (Fig.1)
^1H-NMR ($CDCl_3$): δ = 4.64 (s; 2H, $-CH_2I$), 5.48 (dd; 1H, H_b), 5.94 (dd; 1H, H_a), 6.89 (dd; 1H, H_x), 7.53 (s; 4H, arom.).

Results and Discussion

In view of a similar reactivity of both the bromomethyl and the bromoethyl group in 2 toward nucleophilic reagents, the synthesis of 3 via dehydrobromination of 2 seemed to present a challenge to us (scheme 1):



(1)

However, the competitive test carried out by following chromatographically the course of reaction of a mixture of benzyl bromide and 2-phenylethyl bromide with t-BuOK showed that the rate of elimination reaction is much higher than the rate of substitution.

In order to obtain 2, we used KUBICZEK and NEUGEBAUER's (1950) procedure, since the absence of a Friedel-Crafts catalyst was expected to lower the content of higher condensation products in the reaction mixture. The yield of 2 was rather low (15-20% after crystallization), but it should be mentioned that the unreacted substrate (30-40% of the starting amount) is recovered during work up and can be used in subsequent syntheses. No attempt has been made to optimize the reaction parameters. The distillate containing 2 is a multicomponent mixture containing two main components. One of them, 2, can be separated easily by careful crystallization from hexane; the others, including *o*-(2-bromoethyl)benzyl bromide as the main component, remain liquid. The NMR spectrum of 2 was found to be very similar to that reported for *p*-(2-bromoethyl)benzyl chloride (TANIMOTO *et al*.1974, KONDO *et al*.1979). TLC and GLC analyses confirmed its purity, although a small amount of the *ortho* isomer was still present.

Pure 2 was dehydrobrominated at -5°C using *t*-BuOK,and no *p*-vinylbenzyl *tert*-butyl ether was found in the product.

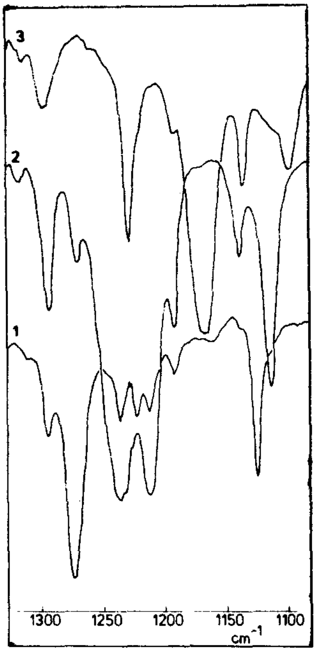


Fig.1. IR spectra of *p*-chloromethylstyrene (1), *p*-bromomethylstyrene (2), and *p*-iodomethylstyrene (3) in 1100-1300 cm^{-1} region

The so-obtained 3 was polymerized successfully in bulk and in benzene solution in the presence of typical freeradical initiators, e.g., benzoyl peroxide, acetyl peroxide, and 2,2'-azoisobutyronitrile to yield a white, soluble powder after precipitation into methanol, or a transparent and clear foil if cast from benzene solution. This monomer was copolymerized also with divinylbenzene to give an insoluble, transparent foil or beads. Preliminary results indicate, however, that the rate of polymerization of 3 is at least several times lower than that of 1 , whose polymerization properties were found to be similar to those of styrene (KONDO *et al*. 1979). At present, further studies are being carried out to elucidate this problem.

We also obtained 3 by another route, i.e., by the reaction of silver tosylate (FIESER and FIESER 1969), or its more reactive analog, silver methanosulfonate, which was obtained similarly, with 4 in acetonitrile solution.

The reaction was considerably slower with 1. This route has been chosen, since it is known that the direct Cl→Br or I→Br exchange reactions do not proceed to completion even in the presence of phase-transfer catalysts (LANDINI *et al*. 1974). However, even under relatively harsh reaction conditions used to carry out the cleavage of the mesylate 5 (2-molar excess of LiBr, 10-mole-% of 18-crown-6, DMF-dioxane solution, 100°C, 2 hr.), GLC analysis showed that a considerable amount of the ester was still present in the reaction mixture. In light of these results, further studies on this route have been discontinued. The ease of preparation of 5 by this method seems to suggest, however, that this compound may be used as an intermediate in the synthesis of other functional monomers.

Because *p*-(2-bromoethyl)benzyl iodide was wxpected to be difficult to obtain and, especially, to purify, another route was used to synthesize 4. Here, the application of the Finkelstein reaction gave excellent results, and preparative yields in the range 80-90% were obtained routinely. According to our expectations, this monomer proved to be very reactive. It was found to decompose slowly on heating and on exposure to light with the liberation of iodine. Attempted polymerization of this monomer failed to yield a well-defined polymer, even though a non-peroxide initiator (AIBN) and relatively low temperatures were used.The polymer so-obtained was always brown-colored and crosslinked. The exceptional thermal instability of 4 seems to indicate that the monomer itself is of limited value as a starting material for the synthesis of poly(4).

We have found, however, that 4 is an excellent starting material for the synthesis of a number of so-far unreported and potentially useful monomers having a *p*-vinylbenzyl moiety. Thus, a number of nucleophilic substitution reactions have been carried out using 4 as well as linear and crosslinked poly(halomethylstyrenes), but further details will be reported in a separate communication.

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