Allylic Halogenation of α-Methylstyrene. Preparation of α-Chloromethylstyrene[1a]

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N-Bromosuccinimide[2] (NBS) has been used extensively in allylic bromination reactions while N-chlorosuccinimide (NCS) has been employed to a much lesser extent. Very few studies have been reported which compare the relative effectiveness of these reagents in allylic halogenation reactions. Ucciani and Naudet[3] have shown that in the reaction of these reagents with methyl oleate the allylic bromide was obtained in an 87% yield compared with a 9% yield of the allylic chloride. Other comparative studies[4] have been concerned mainly with halogenation in aromatic or heterocyclic side chains and in saturated hydrocarbons. As a part of another program the need for both α-bromomethylstyrene and α-chloromethylstyrene arose and prompted the present study.

α-Bromomethylstyrene has been prepared by reacting α-methylstyrene with NBS[5] in a reaction yielding α-methyl-β-bromostyrene as a secondary reaction product. The reaction of NCS with α-methylstyrene has not been reported, although α-chloromethylstyrene has been prepared by other methods.[6] Conditions employed in the present reactions with either NBS or NCS were similar to those described by Pines[5] with the exception that the refluxing mixtures were not cooled immediately in an ice–water bath, but rather, cooled slightly below the reflux temperature and then allowed to cool slowly to ambient temperature. After removal of the succinimide by filtration, the reaction products were isolated by distillation. In the reaction with NBS the allylic and vinyl bromides were obtained in yields of 73 and 5%, respectively, whereas, in the earlier study[5] the corresponding yields were 47 and 17%. In contrast the NCS reaction gave the allylic and vinyl chlorides in yields of 57 and 19%, respectively, along with 2% of an unidentified product.

It would appear from the results of the present study that there is little difference in the total halogenating efficiency of these reagents on α-methylstyrene. The ease and convenience of the halogenation reactions present an attractive method for the laboratory preparation of the allylic halides.

Experimental[7]

α-Methylstyrene. A. NBS Reaction.—A mixture of 94.4 g. (0.8 mole) of α-methylstyrene, 90.0 g. (0.5 mole) of NBS, and 50.0 ml. of carbon tetrachloride contained in a flask fitted with a reflux condenser and magnetic stirrer was heated in an oil bath at 160–170° until the mixture was refluxing and the NBS was dissolving at which point a very vigorous exothermic reaction was noted. The reaction was moderated by intermittent cooling in an ice–water bath in order to maintain a gentle reflux until the NBS had completely dissolved (approximately 3–4 min.). As the exothermic reaction subsided, the temperature dropped below the reflux temperature and the mixture was allowed to cool slowly over a period of 3 hr. The precipitated succinimide was separated by filtration and the carbon tetrachloride and the excess α-methylstyrene were removed under reduced pressure. The residue was examined by gas chromatography and found to contain a small quantity of α-methylstyrene and two unidentified components. Distillation of the mixture yielded 84.8 g. of bromides, b.p. 56–64° (1 mm.). Separation of the bromides was accomplished by fractional distillation on an 18-in. spinning-band column to give 5.1 g. (5%) of α-methyl-β-bromostyrene, b.p. 60–61° (0.9 mm.), n^{20}_D 1.5892 [lit.[5] b.p. 98° (10 mm.), n^{20}_D 1.5891], and 71.6 g. (73%) of α-bromomethylstyrene, b.p. 66–67° (0.9 mm.), n^{20}_D 1.5924 [lit.[5] b.p. 104–105° (10 mm.), n^{20}_D 1.5925].

B. NCS Reaction.—A mixture of 94.4 g. (0.8 mole) of α-methylstyrene, 66.8 g. (0.5 mole) of NCS, and 50 ml. of carbon tetrachloride contained in a flask fitted with a reflux condenser and magnetic stirrer was heated to reflux in an oil bath at 160–170°. An exothermic reaction occurred which required intermittent cooling to maintain gentle reflux conditions. These conditions were maintained until the NCS had completely dissolved (approximately 10–12 min.) at which point the mixture was cooled slightly below reflux with the ice–water bath and then allowed to cool slowly over the next 3 hr. The mixture of chlorides, b.p. 46–54° (0.6 mm.), was isolated as described for the bromides. Gas chromatography showed the presence (2%) of a third component, which was not separated sufficiently pure for characterization. From this mixture 14.5 g. (19%) of α-methyl-β-chlorostyrene, b.p. 76° (4.0 mm.), n^{20}_D 1.5623 [lit.[8] b.p. 102–105° (14 mm.)], and 43.5 g. (57%) of α-chloromethylstyrene, b.p. 53° (0.65 mm.), n^{20}_D 1.5633 [lit.[6a] b.p. 87–88° (5 mm.)], were obtained by fractional distillation on an 18-in. spinning-band column. The proton n.m.r. spectra were obtained in carbon tetrachloride solution using a Varian Associates A-60 n.m.r. spectrometer employing tetramethylsilane as an internal standard. The proton n.m.r. spectrum of α-chloromethylstyrene showed signals for the methylene group (τ 5.66), the proton *trans* to the methylene group (τ 4.63), and the proton *cis* to the methylene group (τ 4.53). The coupling constants were $J_{CH_2-H\ trans} = 1.09 \pm 0.1$ c.p.s., $J_{CH_2-H\ cis} = <0.1$ c.p.s., and $J_{H-H} = 0.94 \pm 0.01$ c.p.s. In the n.m.r. spectrum of α-methyl-β-chlorostyrene the methyl group appeared at τ 7.85 and the vinyl proton at τ 3.76 with a coupling constant of $J_{CH_3-H} = 1.51 \pm 0.02$ c.p.s. These data are in agreement with that expected of the two isomers.

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Reaction Products Formed by the Pyrolysis of Substituted Dibenzyl Sulfones

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A previous paper in this series[1] described the pyrolysis of dibenzyl sulfone and a number of *para*-disubstituted dibenzyl sulfones. These pyrolyses led to 35–90% yields of the corresponding diarylethanes. The present paper reports the extension of sulfone

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