# A STUDY OF THE HYPOCHLORINATION OF STYRENE

## PREPARATION OF CHLOROHYDRINS IN AQUEOUS ACETONE

GENE SUMRELL,[1] BERT M. WYMAN, RONALD G. HOWELL, AND MACK C. HARVEY
*Research Department, El Paso Natural Gas Products Company, El Paso, Texas*

Received June 29, 1964

## ABSTRACT

A study has been made of the hypochlorination of styrene and of the by-products which accompany the formation of styrene chlorohydrin. A process was developed utilizing hypochlorination in aqueous acetone which gave a yield of 72% of the chlorohydrin. Application of this procedure was extended to several other olefins with good results.

Because of a need for substantial quantities of styrene chlorohydrin for use as an intermediate in other work, we have investigated in some detail its preparation from styrene. Frisch (1) claims the production of approximately equal quantities of the chlorohydrin and dichloride of styrene by the passage of chlorine into an aqueous suspension of styrene in the presence of sodium bicarbonate. The yield of chlorohydrin was determined indirectly by conversion to styrene oxide and fractionation to separate the oxide from accompanying styrene dichloride. Since the dichloride and chlorohydrin of styrene are readily separable by fractionation (1) and since the former may, in turn, be hydrolyzed to the chlorohydrin, the simple method of Frisch for converting styrene to the chlorohydrin was attractive to us and served as a starting point in our work.

We were disappointed to learn early in this work that a large percentage of the material reported as styrene oxide by Frisch was actually β-chlorostyrene, which distills at essentially the same temperature as styrene oxide, and that the yield of chlorohydrin was far less than reported by Frisch. A typical run gave the following yields of products: β-chlorostyrene, 20%; styrene dichloride, 59%; and styrene chlorohydrin, 6%.

The possibility occurred to us that better results in hypochlorinating styrene by directly adding chlorine in the presence of water might be achieved if we also had present an inert water-miscible organic material which would keep the styrene and water in one phase or, at least, greatly increase the amount of water present in the same phase with the styrene. A number of such solvents were investigated and all gave improved yields of styrene chlorohydrin. However, acetone proved to be far superior to the others. The yields of products from a typical run, described in the experimental section, were styrene chlorohydrin, 72%; styrene dichloride, 13%; and β-chlorostyrene, 7%.

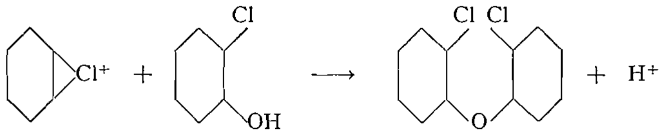
Similar work with cyclohexene gave a yield of 69% (isolated as the epoxide) of the chlorohydrin and 15% of the dichloride. Application of the aqueous acetone method to 1-pentene resulted in a yield of 66% of the mixed chlorohydrins (isolated as the epoxide) and 27% of the dichloride.

Investigation of the higher boiling residue from the cyclohexene chlorohydrin preparation showed it to be composed primarily of bis(2-chlorocyclohexyl) ether (II). This material undoubtedly results from the reaction of chlorohydrin already present with the chloronium intermediate, I, resulting from the initial reaction of olefin and chlorine (3) to give the ether, instead of the normal reaction with water to give the the chlorohydrin.

---

[1] *To whom inquiries should be directed. Present address: Southern Regional Research Laboratory, P.O. Box 19687, New Orleans, Louisiana, 70119.*

Canadian Journal of Chemistry. Volume 42 (1964)



I II

Attempts were not made in our work to isolate ethers analogous to II from the higher boiling residues obtained with 1-pentene and styrene. However, cursory investigation by infrared spectroscopy indicated the presence of ether linkages, suggesting that analogs of II were in all likelihood present.

A cursory investigation was made of the conversion of gaseous olefins to their chlorohydrins by the aqueous acetone technique described in this paper. Such chlorohydrins are conventionally prepared from the olefin and chlorine in sufficient water to give a 5% solution of the resulting chlorohydrin, with yields of 60–70% for the $C_4$-alkenes and 80% for propylene. We found that in the presence of acetone the volume of water could be greatly reduced without sacrifice of yield. For example, an 80% yield of the chlorohydrin was obtained when 1 mole each of propylene and chlorine were passed into a mixture of 200 ml of water and 300 ml of acetone, a combined volume of only a quarter that required for a similar yield of chlorohydrin with water alone.

During our work with styrene, we learned that the styrene chlorohydrin, produced either by direct chlorination of styrene in the presence of water (1) or by hypochlorination using an alkali hypochlorite (4, 5), usually analyzed high in chlorine. We were able to isolate varying amounts of (1,2,2-trichloroethyl)-benzene from such material by treatment of the mixture with aqueous caustic which converted the chlorohydrin to the oxide while leaving the trichloroethylbenzene unchanged. These products were then easily separated by fractionation. The trichlorinated compound and styrene chlorohydrin distill at essentially the same temperature and cannot be separated by fractionation, which explains the fact that previous investigators have failed to observe the presence of (1,2,2-trichloroethyl)-benzene in their product. This material undoubtedly arises from addition of chlorine to the double bond of β-chlorostyrene. The latter appears to be invariably formed in varying amounts in preparations of styrene chlorohydrin. We found the ratio of styrene dichloride to β-chlorostyrene formed on a variety of preparations of styrene chlorohydrin to be of the order of 3:1 on a weight basis. This is the same ratio of dichloride and β-chlorostyrene as was reported by Emerson and Agnew (6) on the addition of chlorine to styrene in carbon tetrachloride solution at 40–50°. We also investigated the preparation of styrene dichloride by chlorinating styrene at 0–10° in a variety of solvents and at varying concentrations without greatly changing the ratio of addition to substitution from that reported by Emerson and Agnew.

## EXPERIMENTAL

Melting and boiling ranges are uncorrected. Fractionations were carried out using a 60 cm Podbielniak-type column with heated jacket and partial reflux head similar to that described by Cason and Rapoport (7). Gas chromatographic studies were done with an F & M Model 720 chromatograph using a 6 ft column packed with 20% Dow 9N9 nonionic surfactant on Chromasorb P of 30–60 mesh.

### *Hypochlorination of Styrene in Aqueous Acetone*

A mixture of styrene (1.25 moles), sodium carbonate (0.5 mole), acetone (1 000 ml), and water (250 ml) was placed in a 2 l, three-necked flask which was fitted with a mechanical stirrer, thermometer, and inlet tube for chlorine gas. One mole of chlorine was allowed to vaporize during approximately 4 h from a cold trap and pass into the mixture. No cooling or heating was resorted to, and the temperature of the reaction mixture rose to 41° during this time. The mixture was present as one phase initially (with the carbonate out of the solution), but a lower aqueous phase separated soon after the chlorine addition was started. The aqueous layer grew in size during the addition and, at the end, contained most of the water in the reaction mixture as a nearly saturated sodium chloride solution. The latter was separated and acetone was removed from the organic layer by distillation. Fractionation of the residue gave a recovery of 24 g of styrene, followed by 9.8 g (7% based on the styrene consumed) of $\beta$-chlorostyrene at 69–70° (5 mm), $n_D^{25}$ 1.5744 (lit. (8) b.p. 89–90° (15 mm), $n_D^{13}$ 1.5781), 23 g (13%) of styrene dichloride at 93–95° (4 mm), $n_D^{25}$ 1.5492 (lit. (2) b.p. 90° (4 mm), $n_D^{15}$ 1.5544); and 113 g (72%) of styrene chlorohydrin at 108–109° (4 mm), $n_D^{25}$ 1.5506 (lit. (4, 9) b.p. 110–111° (6 mm), $n_D^{20}$ 1.5525).

### *Chlorination of Styrene in Aqueous Suspension*

Chlorine (1 mole) was added as described in the preceding paragraph to an agitated mixture of water (500 ml), styrene (1 mole), and sodium bicarbonate (1 mole) with cooling to maintain the reaction mixture at approximately 10°. The heavy oil layer was separated, dried, and fractionated, yielding 28 g (20%) of $\beta$-chlorostyrene at 68–70° (5 mm), 103 g (59%) of styrene dichloride at 93–95° (4 mm), and 10 g (6%) of impure styrene chlorohydrin at 105–110° (4 mm), $n_D^{25}$ 1.5520. The polymeric residue amounted to 19 g.

### *Separation of (1,2,2-Trichloroethyl)-benzene from the Styrene Chlorohydrin Runs*

A sample of 150 g of impure styrene chlorohydrin was accumulated from a number of runs similar to that described in the preceding paragraph. This material was carefully fractionated and a cut of 109 g taken at 107–109° (3.5 mm), $n_D^{25}$ 1.5522. The latter material analyzed 27.20% chlorine (theory for styrene chlorohydrin, 22.64%). A sample of 100 g of this cut was treated with 20% aqueous sodium hydroxide (0.6 mole), with stirring at room temperature, and then maintained at 50° for 1 h. The organic phase was separated, dried, and fractionated. After a very small forerun, 57 g of styrene oxide was taken at 67° (5 mm), $n_D^{25}$ 1.5329 (lit. (2) b.p. 70° (5 mm)). After an intermediate cut of 3.5 g of material, $n_D^{25}$ 1.5526, there was obtained 10 g of (1,2,2-trichloroethyl)-benzene at 108–110° (3 mm), $n_D^{25}$ 1.5592 (lit. (8) b.p. 130° (17 mm)).

Anal. Calcd. for $C_8H_7Cl_3$: C, 45.86; H, 3.37; Cl, 50.77. Found: C, 45.70; H, 3.30; Cl, 50.50.

### *Chlorination of Styrene in Solution*

Chlorine (1 mole) was added during 4 h to a solution of styrene (1 mole) in carbon tetrachloride (1 035 ml), with cooling to maintain the temperature at 0–10°. The mixture was stirred for 1 h after the addition was complete. Then the solvent was flashed off under a column and the residue was fractionated, yielding 39 g (28%) of $\beta$-chlorostyrene at 68–70° (5 mm), 119 g (68%) of styrene dichloride at 93–95° (4 mm), and 4.2 g (2%) of (1,2,2-trichloroethyl)-benzene at 107–110° (3 mm).

### *Cyclohexene Oxide*

A mixture of acetone (250 ml), water (125 ml), and sodium carbonate (0.5 mole) was placed in a 1 l, three-necked flask which was fitted with a mechanical stirrer, dry ice – acetone condenser, dropping funnel, thermometer, and gas inlet tube extending below the surface. Chlorine (1 mole) was added through the inlet tube during 3 h while cyclohexene (1 mole) was concurrently added through the dropping funnel. Cooling was used to maintain the reaction mixture at 40–45°. After the additions were complete, the reaction mixture was filtered to remove precipitated salt. Then the acetone was removed at water-pump pressure under the column, and the two-phase residue was stirred for 1 h at room temperature with 20% aqueous sodium hydroxide (1 mole). The two phases were separated, and the organic phase was dried over sodium sulfate. Fractionation gave 68 g (69%) of cyclohexene oxide at 54–55° (50 mm), $n_D^{25}$ 1.4492 (lit. (10) b.p. 54–55° (50 mm), $n_D^{30}$ 1.4462), and 23 g (15%) of *trans*-1,2-dichlorocyclohexane at 52–53° (5 mm), $n_D^{25}$ 1.4875 (lit. (11), b.p. 88–89° (30 mm), $n_D^{20}$ 1.4904). After removal of an intermediate cut of 10 g of material at 53–137° (5–3.5 mm), $n_D^{25}$ 1.5050, without any indication of a stable boiling point, there followed 9 g (7%) of bis(2-chlorocyclohexyl) ether at 137–139° (3.5 mm), $n_D^{25}$ 1.5019. This material crystallized on standing and after recrystallization from acetone melted at 71–72° (lit. (12) m.p. 70–71°).

### *1,2-Epoxypentane*

1-Pentene was converted to the epoxide in the same manner described above for cyclohexene, with the exception that the sodium carbonate was added portionwise to the reaction mixture after the additions of chlorine and olefin were complete.[2] Fractionation gave 57 g (66%) of 1,2-epoxypentane at 80–81° (665 mm), $n_D^{25}$ 1.3932 (lit. (13) b.p. 89–90° (750 mm), $n_D^{20}$ 1.3963). After a small intermediate fraction, 38 g (27%) of 1,2-dichloropentane was obtained at 55–57° (30 mm), $n_D^{25}$ 1.4439 (lit. (14) b.p. 146° (739 mm), $n_D^{25}$ 1.4448), leaving 9 g of higher boiling residue.

---

[2] *This procedure was used to avoid loss of the more volatile 1-pentene in the evolving carbon dioxide. In the case of cyclohexene it was found that the yields of products were essentially identical whether the sodium carbonate was present initially or added to the acidic mixture after the chlorination. Under acidic conditions, however, there was some slight attack on the acetone by chlorine, yielding chloroacetone and a slightly lachrymatory reaction mixture.*

## REFERENCES

1. H. R. FRISCH. U. S. Patent No. 2,582,114; Chem. Abstr. **46**, 7590 (1952).
2. M. F. HANDLEY. U. S. Patent No. 2,776,982; Chem. Abstr. **51**, 8143 (1957).
3. H. J. LUCAS and C. W. GOULD, JR. J. Am. Chem. Soc. **63**, 2541 (1941).
4. W. E. HANBY and H. N. RYDON. J. Chem. Soc. 114 (1946).
5. W. S. EMERSON. J. Am. Chem. Soc. **77**, 516 (1945).
6. W. S. EMERSON and E. P. AGNEW. J. Am. Chem. Soc. **67**, 519 (1945).
7. J. CASON and H. RAPOPORT. Laboratory text in organic chemistry. Prentice-Hall, Inc., New York. 1950. p. 238.
8. F. BERGMANN, A. KALMUS, and E. BREUER. J. Am. Chem. Soc. **80**, 4543 (1958).
9. H. BODOT, E. DIEUZEIDE, and J. JULLIEN. Bull. Soc. Chim. France, 1086 (1960); Chem. Abstr. **55**, 18649 (1961).
10. F. C. FROSTICK, JR., B. PHILLIPS, and P. S. STARCHER. J. Am. Chem. Soc. **81**, 3355 (1959).
11. H. C. STEVENS and O. GRUMMITT. J. Am. Chem. Soc. **74**, 4876 (1952).
12. K. WIESNER, F. H. CLARKE, and S. KAIRYS. Can. J. Res. B, **28**, 234 (1950).
13. W. D. EMMONS and A. S. PAGANO. J. Am. Chem. Soc. **77**, 90 (1955).
14. C. F. KOELSCH and S. M. MCELVAIN. J. Am. Chem. Soc. **51**, 3393 (1929).