

31. The Preparation of Styrene Chlorohydrin.

By W. E. HANBY and H. N. RYDON.

Methods for the conversion of styrene into styrene chlorohydrin have been studied; the best of these for preparative purposes is the reaction of styrene with *tert.*-butyl hypochlorite in dilute acetic acid. An improved method for the preparation of *tert.*-butyl hypochlorite is described.

STYRENE chlorohydrin (β -chloro- α -phenylethyl alcohol; $\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$) was first prepared by Detoef (Bull. Soc. chim., 1922, 31, 176), who obtained it by the action of monochlorourea on styrene in the presence of acetic acid; repetition of this work did not give the high yield (70%) claimed, the best yield in our experiments being only 52% (or 58%, allowing for recovered styrene). We therefore investigated a number of other reagents for the conversion of styrene into its chlorohydrin. The use of free hypochlorous acid for this purpose was not satisfactory; negligible yields were obtained by passing chlorine into suspensions of styrene in 10% sodium chloride solution at 90° (cf. the analogous preparation of styrene bromohydrin; Read and Reid, J., 1928, 1487), in 8% sodium carbonate solution at 40–50°, or in water containing suspended calcium carbonate; somewhat better yields (32%; 36% allowing for recovered styrene) were obtained by adding dilute nitric acid to a stirred suspension of styrene in sodium hypochlorite solution (cf. the preparation of 2-chlorocyclohexanol; Coleman and Johnstone, Org. Synth., 1925, 5, 31).

A better reagent than monochlorourea for our purpose was found to be *tert.*-butyl hypochlorite, which has been used for the addition of hypochlorous acid to many olefins (Irwin and Hennion, J. Amer. Chem. Soc., 1941, 63, 858; Emling, Vogt, and Hennion, *ibid.*, p. 1624); using this reagent in dilute acetic acid, the yield of styrene chlorohydrin varied between 60% and 70% (73% and 84%, respectively, allowing for recovered styrene) and the process, described in detail below, appears to be the most convenient available for the preparation of the chlorohydrin.* Omission of the acetic acid in this preparation leads to the formation of the *tert.*-butyl ether, $\text{Ph}\cdot\text{CH}(\text{O}i\text{Bu})\cdot\text{CH}_2\text{Cl}$, by direct addition; the *p*-nitrobenzoate and acetate of styrene chlorohydrin were also prepared and characterised. The purity of the various samples of styrene chlorohydrin was assessed by the yield of ω -chloroacetophenone obtained from them by chromic acid oxidation.

The original procedure of Chattaway and Backeberg (J., 1923, 123, 2999) for the preparation of *tert.*-butyl hypochlorite gave very variable yields in our hands; a modified method, employing calcium carbonate in place of sodium hydroxide and giving good and reproducible yields, is described below.

EXPERIMENTAL

Preparation of Styrene Chlorohydrin.—The following procedure gave the best yield of styrene chlorohydrin. Redistilled *tert.*-butyl hypochlorite (25 g.) was added during 1 hour to a stirred suspension of styrene (25 g.) in water (250 c.c.) and acetic acid (25 c.c.), the temperature being kept below 25° by cooling in ice. The reaction was complete after stirring for a further 15 mins.; the product was then extracted with ether, dried and distilled, yielding: (i) recovered styrene (4 g.), b. p. below 108°/6 mm.; (ii) styrene chlorohydrin (26.5 g.), b. p. 110–111°/6 mm., $d_4^{20.5}$ 1.1646, $n_D^{20.5}$ 1.5400, $[R_L]_D$ 42.16 (calc. 41.95) (Found: Cl, 22.2. Calc. for $\text{C}_8\text{H}_9\text{OCl}$: Cl, 22.7%). The yield was 70% (84% allowing for recovered styrene) and the material was of good quality, giving an 83% yield of ω -chloroacetophenone on oxidation. In another typical experiment using crude *tert.*-butyl hypochlorite (87 g.), styrene (92 g.), water (880 c.c.), and acetic acid (120 g.), the yield of chlorohydrin was somewhat lower (60%; 73% allowing for recovered styrene); the product gave a 77% yield of ω -chloroacetophenone on oxidation.

Omission of the acetic acid gave mainly the *tert.*-butyl ether of styrene chlorohydrin as indicated. Crude *tert.*-butyl hypochlorite (87 g.), styrene (92 g.), and water (1000 c.c.) were stirred for 2 hours at 15°. The lower layer was separated and distilled, yielding 40.8 g. of a fraction, b. p. 100–103°/5 mm., n_D^{21} 1.5234. This material (30 g.) was heated for 45 mins. at 120°/2 mm. with boric acid (0.88 g.) (cf. Schmidt, Chem.-Ztg., 1928, 52, 898); unreacted, non-hydroxylic material (b. p. 92–93°/2 mm.) was then distilled away. On redistillation impure β -*tert.*-butoxy- β -phenylethyl chloride (β -chloro- α -phenylethyl *tert.*-butyl ether) (18.6 g.), b. p. 87–88°/1.5 mm., d_4^{13} 1.0549, n_D^{14} 1.5102, $[R_L]_D$ 60.27 (Calc. 60.53), was obtained (Found: Cl, 18.2. $\text{C}_{12}\text{H}_{17}\text{OCl}$ requires Cl, 16.7%). The product was contaminated with more highly chlorinated material which we were unable to remove.

Derivatives of Styrene Chlorohydrin.—*Styrene chlorohydrin p*-nitrobenzoate (β -chloro- α -phenylethyl *p*-nitrobenzoate), prepared in pyridine, crystallised from alcohol in parallelograms, m. p. 81° (Found: C, 59.1; H, 4.1. $\text{C}_{15}\text{H}_{12}\text{O}_4\text{NCl}$ requires C, 58.9; H, 3.9%).

The acetate was prepared by keeping styrene chlorohydrin (79 g.) with acetic anhydride (150 c.c.) for 1 hour at room temperature; the product was then refluxed for an hour, cooled, poured into water, and kept overnight. Distillation of the dried ether extract yielded β -chloro- α -phenylethyl acetate (65.8 g.; 66%) as an oil, b. p. 101–104°/3 mm., n_D^{22} 1.5182 (Found: C, 60.5; H, 5.8; Cl, 18.5. $\text{C}_{10}\text{H}_{11}\text{O}_2\text{Cl}$ requires C, 60.5; H, 5.5; Cl, 17.9%).

Oxidation of Styrene Chlorohydrin.—In a typical experiment, styrene chlorohydrin (26.5 g.) was added during 10 mins. to a stirred solution of sodium dichromate (35 g., 2.08 equivs.) in water (88 c.c.) containing sulphuric acid (17.5 c.c.). The temperature rose to 71°, falling again to 60° in 10 mins.; the stirred mixture was kept at 60° for 5 hours when it was poured on ice. The precipitated ω -chloroacetophenone was separated, washed, and dried in a vacuum desiccator (21.9 g., 84%; m. p. 51–53°).

Preparation of tert.-Butyl Hypochlorite.—Into a gently stirred suspension of calcium carbonate (50 g.) in water (1000 c.c.) containing *tert.*-butyl alcohol (74 g.) at 0–1° chlorine is passed until all the carbonate has dissolved (the rate of stirring is highly important; it should be just sufficient to keep the carbonate in suspension. If too fast, the yield falls considerably owing to hydrolysis). The upper layer is separated and washed once with water. This crude product

* Since this work was completed, early in 1942, an improved preparation of styrene chlorohydrin has been described by Emerson (J. Amer. Chem. Soc., 1945, 67, 516); Emerson's procedure appears to be more time-consuming than ours but may be preferable for large-scale working.

(87 g., 80%) is sufficiently pure for many purposes. Distillation gives pure *tert.*-butyl hypochlorite, b.p. 77—79° (65 g., 60%).

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CHEMICAL DEFENCE EXPERIMENTAL STATION,
PORTON, NR. SALISBURY.

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