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PREPARATION OF 2,5-DICHLOROSTYRENE AND SOME RELATED COMPOUNDS

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The polymer of 2,5-dichlorostyrene has recently found fairly wide application in plastic compositions, due to its favorable mechanical and dielectric properties (9). For the preparation of the monomer, however, no satisfactory method was available when the present investigation was undertaken; with the exception of a paper by Brooks (3), pertinent data were only to be found in the patent literature (2, 4, 5, 7, 13). Only recently (15), Pollock and Davis gave a detailed description of the preparation of 2,5-dichlorostyrene by Friedel-Crafts acetylation of *p*-dichlorobenzene, reduction of the ketone obtained with aluminum isopropoxide and subsequent dehydration over activated alumina in the vapor phase. The over-all yield was 43%.

In the present investigation, the method described by Pollock and Davis had also been employed, but was abandoned in favor of another one which gave a smaller over-all yield, but required simpler operations. In the presence of aluminum chloride, *p*-dichlorobenzene reacts with ethylene to give a 36% yield of 2,5-dichloro-1-ethylbenzene. Bromination at about 100° yields 95% of the theoretical amount of 2,5-dichloro-1-(α-bromoethyl)benzene, which is dehydrobrominated with alcoholic sodium hydroxide solution in 80% yield. The over-all yield of 2,5-dichlorostyrene is, therefore, 27%.

In the reaction between *p*-dichlorobenzene and ethylene which was studied about 70 years ago by Istrati (11), a low-boiling liquid by-product (35% yield) has been observed. Its analysis corresponded to that of a dichlorobenzene, and its ultraviolet spectrum (series of bands between 250 and 280 mμ) and conversion into the well-known (14) 4,6-dichloro-1,3-dinitrobenzene proved that it was mainly the *m*-compound. The infrared spectrum revealed that the product was not pure *m*-dichlorobenzene; it may have contained some *o*-isomer, which is virtually undistinguishable from the *m*-compound in the ultraviolet spectrum. The results are in accord with recent observations by Fitzpatrick (8) on the isomerization of *o*- and *p*-dichlorobenzene to the *m*-compound in the presence of aluminum chloride and a trace of water. The corresponding *p*-dibromo compound also rearranges to a complex mixture (6, 12).

In addition to the dichlorobenzene fraction and the desired 2,5-dichloro-1-ethylbenzene, a small (8.5%) higher-boiling fraction was obtained, which gave the same analytical results as 2,5-dichloroethylbenzene. As its physical constants are different from those of the "normal" compound, it is assumed that it may be an ethyl derivative of *m*-dichlorobenzene. However, no attempt has been made to elucidate its structure.

The side-chain bromination of 2,5-dichloroethylbenzene which can be achieved either with elementary bromine or with N-bromosuccinimide, occurs undoubtedly in the α-position of the ethyl group. Indeed, the infrared spectrum of the product shows the deformation frequency of the methyl group (17) at 1375 cm^{-1} while for (α-bromoethyl)benzene the peak lies at 1373 $cm.^{-1}$ For the purpose of comparison, α- and β-bromo-2,5-dichloro-ethylbenzene have been prepared by unambiguous methods: 2,6-Dichlorophenyl methyl carbinol (15) was converted by means of hydrobromic acid to the corresponding (α-) bromide. 2,6-Dichloroacetophenone (15) was subjected to the Willgerodt-Kindler reaction and the butyl ester of the 2,6-dichlorophenylacetic acid so formed was treated successively with lithium aluminum hydride and phosphorus tribromide. The α- and β-bromo-compounds absorbed at 1378 and 1395 cm^{-1}, respectively (methyl and methylene frequency).

EXPERIMENTAL

Ethylation of p-dichlorobenzene. In a three-necked flask, mounted with stirrer, thermometer, and gas inlet, was suspended 200 g. of aluminum chloride in 200 g. of dichlorobenzene. At a temperature of 135–140° (in the liquid) and with slow agitation, there was introduced 28.5 l. of gaseous ethylene (measured at 24°) at the rate of 0.4 liter per minute. It has proven advantageous not to use more than this quantity of ethylene, which amounts to 80% of the theoretical.

At the end of the operation which does not take longer than 60–75 minutes, the aluminum chloride was allowed to settle and the supernatant liquid was decanted into a mixture of ice and concentrated hydrochloric acid. The organic layer was separated, dried, and fractionated, the following fractions being obtained:

(*a*) *m*-Dichlorobenzene, b.p. 48.5°/8 mm. Yield, 92 g. (35%). n_D^{20} 1.5439; d_{20}^{20} 1.2838; MR, Calc'd: 36.10; MR, Found: 36.30 (1, 10, 16).

Anal. Calc'd for $C_6H_4Cl_2$: C, 49.0; H, 2.7; Cl, 48.3.
Found: C, 49.1; H, 2.9; Cl, 47.8.

This fraction was converted to a dinitro derivative (from ether-alcohol, m.p. 101°) which did not depress the melting point of an authentic specimen of 4,6-dichloro-1,3-dinitrobenzene (14).

(*b*) 2,5-Dichloroethylbenzene, b.p. 80.5/8 mm.; 102°/30 mm. Yield, 94.5 g. (36%). n_D^{20} 1.5394; d_{20}^{20} 1.2090. MR, Calc'd: 45.28; MR, Found: 45.44.

Anal. Calc'd for $C_8H_8Cl_2$: C, 54.8; H, 4.6; Cl, 40.6.
Found: C, 54.9; H, 4.5; Cl, 40.5.

(*c*) Isomeric dichloroethylbenzene (?), b.p. 128°/30 mm. Yield, 22.4 g. (8.5%). n_D^{20} 1.5479; d_4^{20} 1.2447. MR, Calc'd: 45.28; MR, Found: 45.18.

Anal. Calc'd for $C_8H_8Cl_2$: C, 54.8; H, 4.6.
Found: C, 54.8; H, 4.7.

Bromination of 2,5-dichloro-1-ethylbenzene. (*a*). In a three-necked flask (condenser, stirrer, thermometer) a solution of 175 g. of 2,5-dichloroethylbenzene in 300 ml. of carbon tetrachloride was heated at 95–100° and 160 g. of bromine was added dropwise with vigorous agitation. When the bromine was absorbed, the stirring was continued for a few minutes and then the solvent was removed *in vacuo*. The residue (239 g.; 95%) boiled at 141.5°/5 mm. with slight decomposition. Distillation at less than 0.1 mm. is not accompanied by loss of hydrogen bromide. n_D^{20} 1.5846; d_{20}^{20} 1.5783. MR, Calc'd: 53.38; MR, Found: 54.11.

Anal. Calc'd for $C_8H_7BrCl_2$: Br, 31.4. Found: Br, 30.8.

(*b*) The mixture of 87.5 g. of 2,5-dichloroethylbenzene, 81.0 g. of N-bromosuccinimide, 0.5 g. of dibenzoyl peroxide, and 250 ml. of carbon tetrachloride is refluxed for 2.5 hours. After cooling, the succinimide formed is filtered and washed with carbon tetrachloride, and the solvent is removed *in vacuo* from the filtrate. The residue (114.5 g.; 90%) boils at 141.5°/5 mm.

2,5-Dichlorostyrene. To a solution of 239 g. of the foregoing compound in 300 ml. of alcohol, a concentrated alcoholic solution of 80 g. of sodium hydroxide is added and the mixture is refluxed for two hours. After cooling, and neutralization with concentrated hydrochloric acid, the alkali halide precipitate is filtered and the filtrate is concentrated. The residue is poured into water and washed by decantation to a neutral reaction. Drying and distillation give 2,5-dichlorostyrene in 80% yield. B.p. 92–93°/5 mm. n_D^{20} 1.5798; d_4^{20} 1.246. MR, Calc'd: 44.80 (without exaltation); MR, Found: 46.19.

Anal. Calc'd for $C_8H_6Cl_2$: C, 55.5; H, 3.5.
Found: C, 55.0; H, 3.8.

α-(2,5-Dichlorophenyl)ethyl bromide. A mixture of 55 g. of 2,5-dichlorophenyl methyl carbinol (b.p. 119–121°/2 mm.; m.p. 61–62°)(15), 120 g. of potassium bromide, and 180 g. of sulfuric acid (55%) was heated for 15 minutes at 120°. The oily layer was separated after cooling, washed with water and 1% sodium carbonate solution, and dried. B.p. 112.5°/2 mm.; yield, 96.5 g. (95%); n_D^{20} 1.5866; d_{20}^{20} 1.5939; MR, Calc'd: 53.0; MR, Found: 53.8.

Anal. Calc'd for $C_8H_7BrCl_2$: C, 37.8; H, 2.8; Halogen, 59.4.
Found: C, 38.9; H, 3.0; Halogen, 58.2.

The analysis shows that the product has suffered slight decomposition (dehydrobromination), probably during the distillation.

Similar results were obtained, using phosphorus tribromide.

2,5-Dichlorophenylacetic acid. A mixture of 99 g. (0.5 mole) of 2,5-dichloroacetophenone (15), 24 g. (0.75 mole) of sulfur, and 66 g. (0.75 mole) of morpholine was refluxed for 15 hours and the hot reaction mixture was poured into 500 cc. of hot ethanol. The crystals of the thiomorpholide were filtered and washed with cold ethanol. The product (87 g.; 60%) melted at 126–127° and was immediately hydrolyzed with a mixture of aqueous acetic and sulfuric acids. Thus was obtained 31 g. (66%) of 2,5-dichlorophenylacetic acid which was recrystallized from benzene. M.p. 104°.

Anal. Calc'd for $C_8H_6Cl_2O_2$: C, 47.0; H, 2.9.
Found: C, 47.1; H, 2.6.

The *butyl ester* was prepared by esterification in the presence of sulfuric acid. B.p. 162°/7 mm.; yield, 90%; n_D^{20} 1.5190; d_{20}^{20} 1.1651. MR, Calc'd: 68.51; MR, Found: 68.00.

Anal. Calc'd for $C_{12}H_{14}Cl_2O_2$: C, 55.4; H, 5.2.
Found: C, 55.1; H, 5.6.

β-(2,5-Dichlorophenyl)ethanol. The foregoing ester (26.1 g.) was reduced with lithium aluminum hydride (5.4 g.) in dry ether (350 ml.). B.p. 121–122°/3 mm.; m.p. 26–28°; yield, 87 g. (90%).

Anal. Calc'd for $C_8H_8Cl_2O$: C, 50.3; H, 4.2; Cl, 37.2.
Found: C, 50.1; H, 4.6; Cl, 37.4.

β-(2,5-Dichlorophenyl)ethyl bromide. To a mixture of 17 g. of the alcohol in 250 ml. of carbon tetrachloride, there was added 30 g. of phosphorus tribromide with stirring. The stirring was continued for two hours and the solution was washed with water and sodium bicarbonate solution. The product distilled under 2 mm. pressure at 114°. n_D^{20} 1.5827; d_{20}^{20} 1.5936. MR, Calc'd: 53.00; MR, Found: 53.50.

Anal. Calc'd for $C_8H_7BrCl_2$: C, 37.8; H, 2.8; Halogen, 59.4.
Found: C, 37.9; H, 2.9; Halogen, 59.8.

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