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The preparation and attempted polymerization of beta-chlorostyrenes

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THE PREPARATION AND ATTEMPTED POLYMERIZATION
OF α -CHLOROSTYRENES

by

Curtis Usher Coleman

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the require-
ments for the degree of Bachelor of Science with a Major
in Chemistry.

By Curtis U. Coleman
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Accepted by R. W. Finholt
R. W. Finholt

May 28, 1949.

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INTRODUCTION

The polymerization of unsubstituted styrenes has been studied by a number of workers, among them Wheland (11), Stoermer and Kootz (9), and Ziegler and Bahr (13), but none of these workers have studied the effect of halogen substitution on the side chain. This has been studied by Worrall (12), and he concluded that such substitution blocked polymerization.

It was the purpose of the present work to prepare α -chlorostyrene, and to carry the work of Worrall a step further by seeking some reagent which would bring about the polymerization of α -chlorostyrene. A further purpose was to prepare a new α -chlorostyrene, determine the physical constants, and study its ability to polymerize.

HISTORICAL ASPECTS

Among the first workers to effect the preparation of α -chlorostyrene by the equimolar reaction of acetophenone and phosphorus pentachloride were Dufraisse and Viel (3). They observed that the hydrogen chloride given off would add across the ethylene linkage of the α -chlorostyrene formed in this reaction, if the hydrogen chloride was allowed to remain in the reaction vessel. They found that this addition could be prevented by carrying out the reaction in a solvent in which the hydrogen chloride was insoluble and by running the reaction at a slightly elevated temperature. The same workers also reported that α -chlorostyrene decomposed at room temperature into formaldehyde and chlorobenzene with subsequent resinification, and recommended storage at reduced pressures.

Emerson and Agnew (4) reported the preparation of several chloro substituted styrenes, those of particular interest being the α - and β -chlorostyrenes which were synthesized by the removal of hydrogen chloride from 1-phenyl-1,2-dichloroethane by the use of an alcoholic solution of sodium hydroxide.

It was noted by Worrall (12) that halogens on the side chain of styrene tended to block polymerization, and in his paper he reported that no reaction took place in the absence of water, and that wet reagents produced only unchanged components, products resulting from hydrolysis, or destructive decomposition.

More recently it has been reported by Bachman and Hellman (1) and by Briggs and Wolfstirn (2) that the substitution of a methyl group on the alpha carbon atom of styrene gave a compound (α -methylstyrene) which co-polymerized in emulsion systems with styrene, methyl methacrylate, and maleic anhydride, but did not polymerize alone with peroxide catalysts. It has also been found by Walling, Briggs, Wolfstirn, and Mayo (10) that bromine, as well as other groups, when substituted on the benzene ring of styrenes, increased the reactivity of the double bond.

APPARATUS

Because of the large quantities of hydrogen chloride evolved, both in the preparation of α -chlorostyrene and of p-bromoacetophenone, it was found necessary to use the following gas trap proposed in Gilman and Blatt (7), rather than the usual one which consists merely of a glass tube dipping beneath the surface of water in a flask.

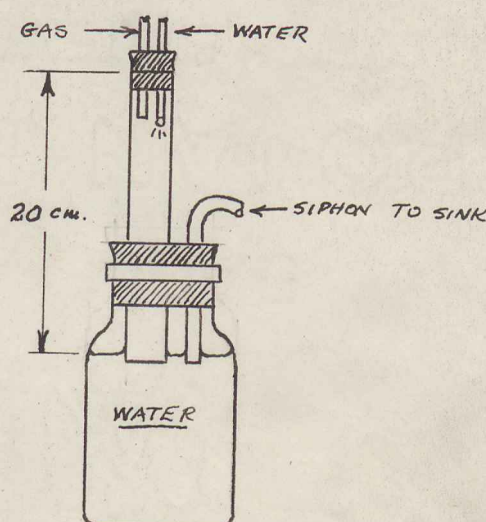


Figure 1. Gas Trap for Hydrogen Chloride.

A slight modification was made on the design as found in Gilman and Blatt, in that the end of the water-carrying tube was crimped slightly to provide a spray rather than a solid stream of water. It was felt that this would provide for more rapid absorption of the gas, and such seemed to be the case, for no escape of hydrogen chloride was noted at any time after this trap was put into operation.

The short column called for by Gilman and Blatt in their preparation of *p*-bromoacetophenone (6) was not available, therefore the modified column shown below was used and proved completely satisfactory.

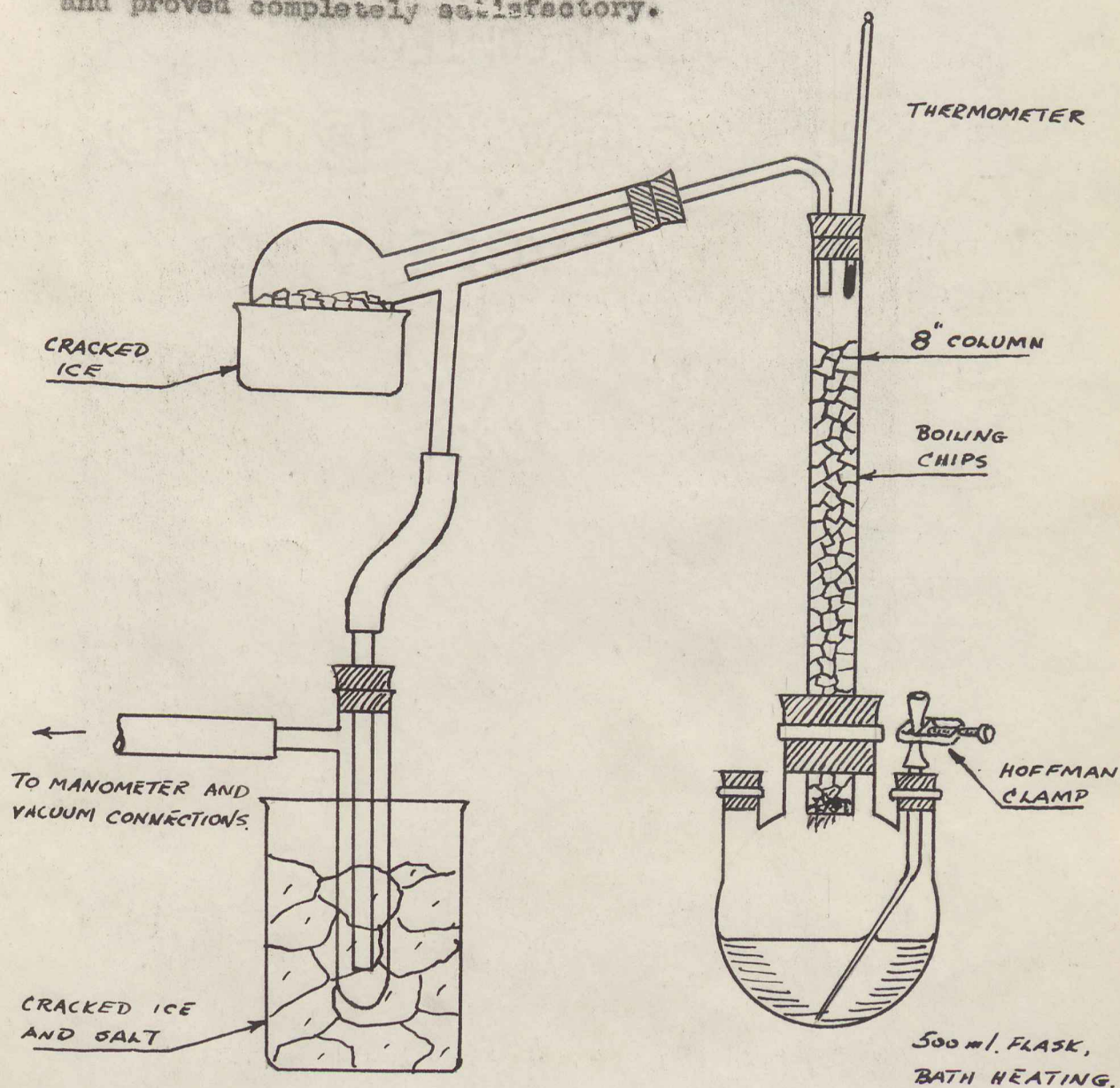


Figure 2. Apparatus for Vacuum Distillation of *p*-Bromoacetophenone

The distillation of p-bromo- α -chlorostyrene required special condensers shorter than those which were available, for it was felt that the losses in a condenser of standard length would be too high, therefore the following apparatus was made and used successfully.

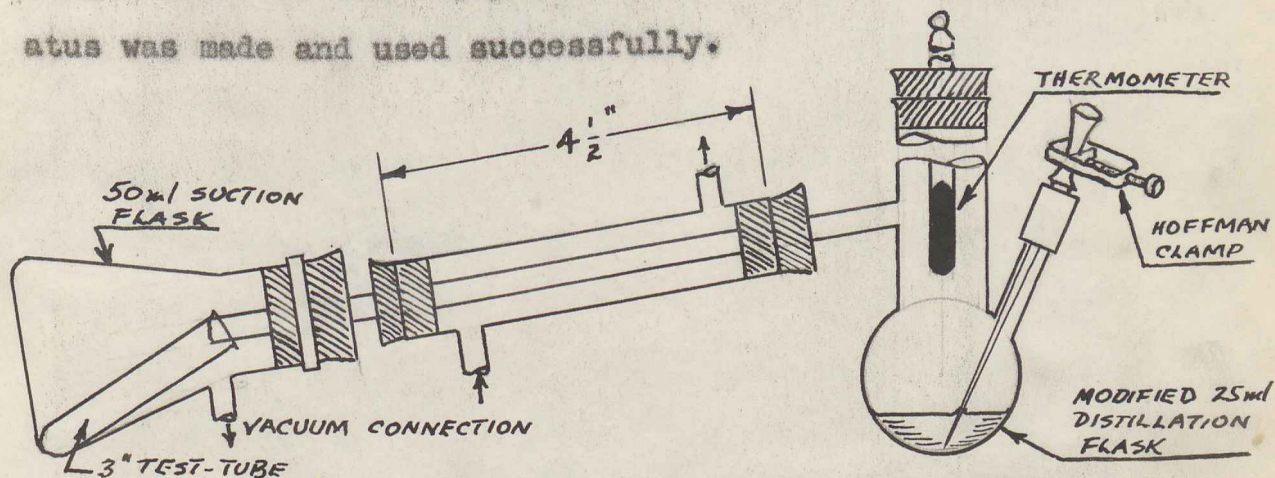


Figure 3. Distillation Apparatus for 5-10 ml. Samples.

The above equipment was found to be too large for distillation of samples of 1-2 ml., therefore the following condenser was made for samples this size and smaller, and proved quite satisfactory,

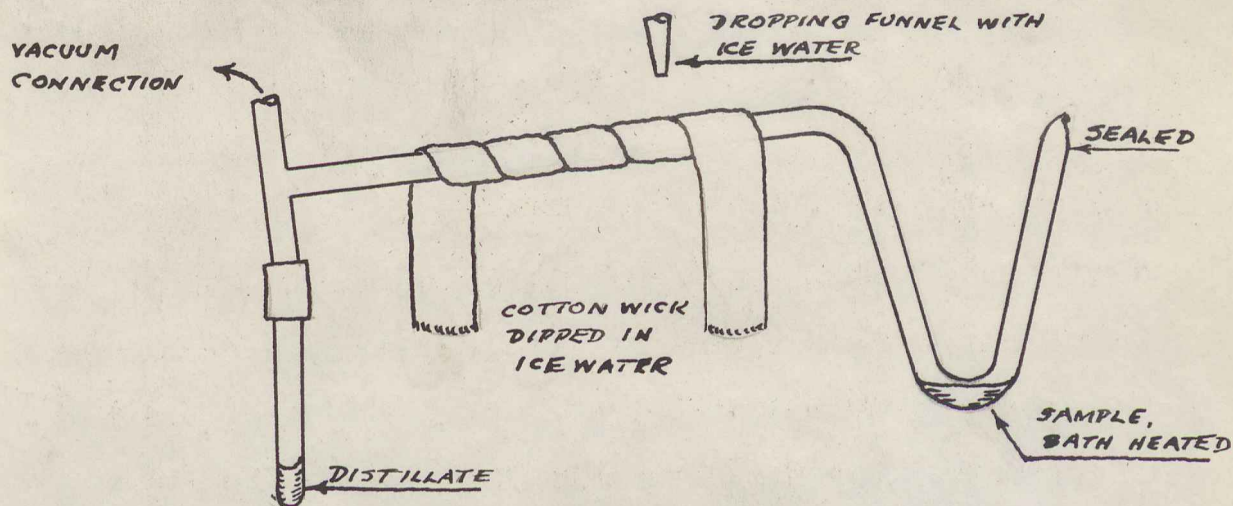


Figure 4. Distillation Apparatus for 0.5-1.5 ml. Samples.

EXPERIMENTAL WORK

The first attempted preparation of α -chlorostyrene following the procedure of Dufraisse and Viel (3) gave a poor yield due to inexperience, therefore this run was discarded, and a new start was made. In the second run, 120 g. (1 mole) of acetophenone was added to 206 g. (1 mole) of phosphorus pentachloride and 300 ml. of petroleum ether. The mixture was refluxed for two and one-half hours at a temperature of 57-63°C. in a one liter, three-necked flask fitted with reflux condenser and thermometer. The liquid was filtered, and the solid, unreacted phosphorus pentachloride was discarded. The liquid portion was vacuum distilled and the fraction boiling over a temperature range of 87-96°C., at a pressure of 18-25 mm. of mercury was collected. The weight of the distillate was 82.5 g. for a yield of 59.5%. The distillate was stored in the presence of 0.1 g. of hydroquinone, in an attempt to prevent decomposition and polymerization. It was found that the inhibitor failed to prevent oxidation, for the originally colorless compound turned black in the space of one day, therefore repurification was necessary. Since there were many faults to be found with the apparatus available for vacuum distillation, advantage was taken of the difference in melting points of acetophenone (M.P. 20.5°C.) and α -chlorostyrene (M.P. - 23.0°C.), and they were separated by crystallization, using dry ice to lower the temperature. At the conclusion of this crystallization, 82.5 g. of the α -chlorostyrene still remained, as practically

no acetophenone was present.

The physical constants of α -chlorostyrene were determined, and it was found to have a boiling point range of 197-198°C. (Lit.; 199°C.) at atmospheric pressure, and a refractive index at 20°C., of 1.5585 when referred to the sodium "D" line (Lit.; $n_D^{20.5}$ 1.5584)

In an attempt to overcome the need for daily distillation of the α -chlorostyrene, storing it at a pressure of 20-25 mm. of mercury was attempted, and this proved to be quite some help, though it was far from perfect. In this way the α -chlorostyrene would remain reasonably free from oxidation for a period of a week, but after that time, it was necessary to distill whenever pure compound was desired.

Several different methods of polymerization of α -chlorostyrene were attempted, all of them being carried out in tightly stoppered three inch test-tubes. The first attempts were made at room temperature, using in one case 0.1 g. potassium persulfate as accelerating agent, and in the second case, 0.1 g. of benzoyl peroxide, with 1 ml. samples of α -chlorostyrene. When both of these attempts gave no apparent polymer, the same reagents were used and the mixtures were heated to boiling, with the same results. Similar attempts were made at co-polymerization between α -chlorostyrene and the following: styrene, methyl methacrylate, vinyl acetate, diallyl phthalate, and vinyl isopropyl ether. The runs were made both at room temperature and at temperatures up to 100°C., using 1 ml. of α -chlorostyrene and 1.0 ml. of each monomer, plus 0.1 g. of benzoyl peroxide. No polymerization

was noted in any case.

Further attempts at polymerization were made, again using tightly stoppered three inch test-tubes, into which were placed 1.0 ml. of α -chlorostyrene and 0.1 g. of aluminum chloride. The test-tubes were then placed in a beaker filled with cracked dry ice, which was replenished as needed during the eight to ten hours of the run. These attempts were also unsuccessful, though in one run a black, tarry substance was found in the bottom of one of the test-tubes. This substance was insoluble in both acetone and diethyl ether, forming a bright yellow, flocculent precipitate in the former, said precipitate also being insoluble in the ether. The tar dissolved in ethyl alcohol, and viscosity tests were made on this alcohol solution. A 5 ml. portion required 210.5 sec. to flow through an Ostwald viscometer at 25°C., while 5 ml. of the same alcohol required 230.4 sec. Therefore, it was concluded that the tarry substance was not a polymer, as polymers raise the viscosity of solutions. It was thought that the tar was quite probably some aluminum chloride addition compound. This would account for its solubility in a slightly polar solvent, and the increased density of the alcoholic solution of an aluminum chloride salt would account for the increased rate of flow through the viscometer.

The next phase of the work was to synthesize an α -chlorostyrene with a halogen substituted on the ring, since ring halogens were known to speed the polymerization of styrene (10). The preparation of p-bromo- α -chlorostyrene was carried out, again following the procedure of Dufraisse and

Viel (3). For this preparation p-bromoacetophenone was needed, and this compound was prepared according to the Procedure of Gilman and Blatt (6) as follows: into a one liter three-necked flask fitted with reflux condenser, dropping funnel, and mechanical stirrer were placed 78.4 g. (0.5 mole) of bromobenzene, 150 g. (1.12 moles) of aluminum chloride, and 200 ml. of carbon disulfide. The reflux condenser was connected to an efficient gas trap (see Figure 1, page 5), and 40.8 g. (0.4 mole) of acetic anhydride were placed in the dropping funnel. The mixture in the flask was heated on the steam bath until gentle refluxing started, following which the acetic anhydride was added over a period of one hour, and refluxing continued for one hour after the addition was complete. At the end of that time, the condenser was reversed, and the majority of the carbon disulfide was distilled off on the steam bath. The reaction mixture was allowed to cool, but while still warm was poured over approximately 750 cc. of a mixture of cracked ice and hydrochloric acid. The leavings in the reaction flask were also treated with the ice-acid mixture, and were added to the main product, bringing the total volume up to about one liter. Each 400 cc. portion was extracted twice with 60 and 40 ml. portions of diethyl ether, following which the extracts were combined and washed twice with 100 ml. portions of water, once with 100 ml. of 10% sodium hydroxide, and twice more with 100 ml. portions of water. The extract was dried overnight with 6-10 g. of calcium chloride, filtered, and the solvent distilled from the steam bath. The

residue was distilled at a pressure of 18-22 mm. of mercury, using a short column (see Figure 2, page 6). Some low boiling matter came over first, and was removed. After that, the temperature rose rapidly, and the distillate came over colorless, crystallizing to a white solid in the receiving flask. The yield was 27.2%, as 27.15 g. of p-bromoacetophenone with a melting point of 49-50° C. were obtained. (Lit.; 49-50.5° C.)

For the chlorination of this compound, a 500 ml. three necked flask was used as the reaction vessel, and was fitted with a thermometer and reflux condenser with gas trap. In this were placed 18.20 g. (0.095 moles) of p-bromoacetophenone, 19.8 g. (0.095 moles) of phosphorus pentachloride, and 80 ml. of petroleum ether. The mixture was refluxed for two and one-half hours at a temperature ranging from 39-43° C., then cooled and filtered to remove any excess phosphorus pentachloride. The liquid portion was distilled and 4.40 g. of a straw colored liquid were obtained. A chlorine analysis was run on this solution, by boiling a 0.5100 g. sample of it with a 3% silver nitrate solution (alcoholic). The silver nitrate was added until no more precipitate was seen forming, then approximately 0.5 ml. was added in excess. The silver chloride formed was filtered through a weighed Gooch crucible, and the precipitate was washed with ether and water to ensure that there were no organic or soluble inorganic residues adhering to it, dried and found to weigh 0.3321 g. To find the percent of chlorine in the sample, these figures were substituted in the following equation

which gives the percent of chlorine directly:

$$\% \text{ Cl} = \frac{\text{Wt. AgCl} \times 0.2474}{\text{Wt. of sample}} \times 100$$

This was done, and the value found to be 16.1%. Since the calculated value for the chlorine content of p-bromo- α -chlorostyrene was 16.3%, it was concluded that the liquid was indeed p-bromo- α -chlorostyrene. The yield of this reaction was 18.3%. The compound was found to have a density of 1.203 g./ml. at 25° C., a boiling point of 211-212° C., and a refractive index of 1.67695 at 25° C. when compared with the "D" line of sodium. The density was found by weighing a 0.40 ml. sample as measured by a pipet, a procedure made necessary by the small amount of the compound available. Because of the small quantities, all necessary distillations were carried out in the apparatus shown in Figures 3 and 4 on page 7.

DISCUSSION

A search of Chemical Abstracts revealed several methods for the preparation of α -chlorostyrene, among them the method of Emerson and Agnew (4), and the method of Dufraisse and Viel (3). The second reaction gave promise of being the more interesting, and consequently was chosen. This preparation called for an equimolar reaction between acetophenone and phosphorus pentachloride in a solvent of petroleum ether. It is thought that the reaction proceeds through the formation of an intermediate dichloro addition product. This compound is probably thermally unstable, and at the temperature of the reaction, spontaneously decomposes to give the desired α -chlorostyrene as follows:

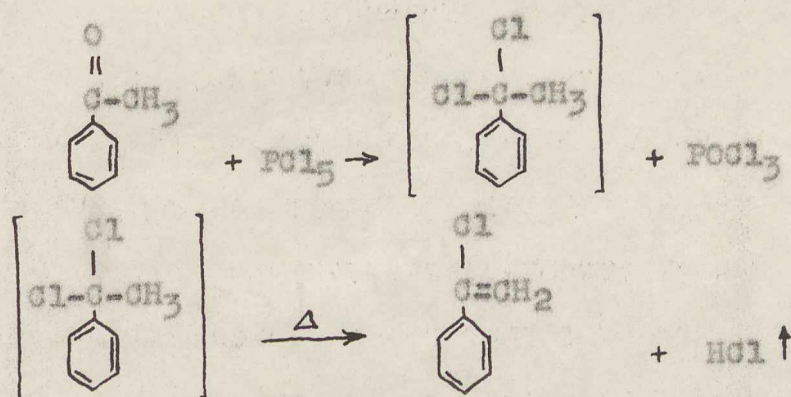


Figure 5.

The chief disadvantage of this reaction is that precautions must be taken to insure against the possibility of the addition across the double bond of the hydrogen chloride formed in the reaction. This fault was overcome by using an elevated temperature, and a solvent (petroleum ether) in which hydrogen chloride was insoluble. It was thought at

one time that the yield of 59.5% could be improved by the use of a larger quantity of phosphorus pentachloride, but such was not the case, for with the use of phosphorus pentachloride in an excess of equimolar proportions, there was a greater tendency to add across the double bond; in fact it was necessary to filter and remove the excess phosphorus pentachloride at the conclusion of the reaction.

The preparation of p-bromo- α -chlorostyrene necessitated the use of p-bromoacetophenone, and this compound was prepared by the use of a Friedel-Crafts synthesis outlined by Gilman and Blatt (6). As may be seen from the following equations, it was necessary to use an amount of aluminum chloride slightly in excess of two equivalents in order that free reagent be present to perform the function of a catalyst (5).

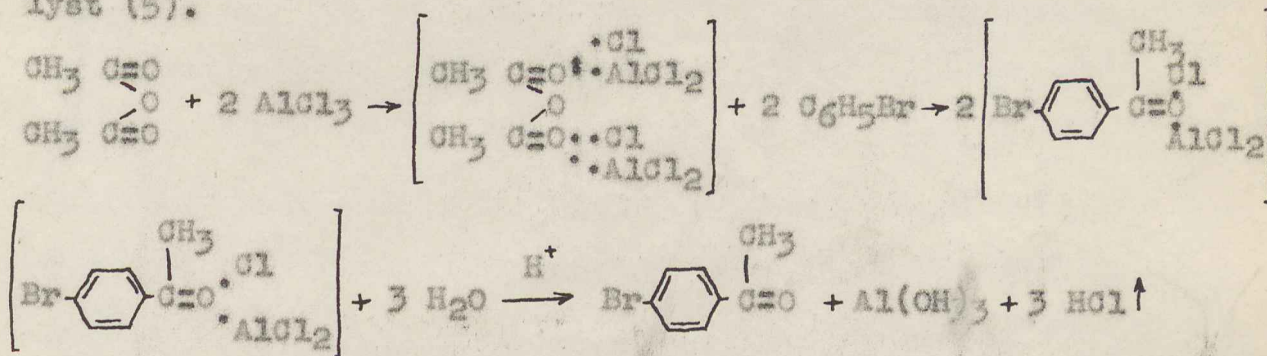


Figure 6.

With the p-bromoacetophenone available, the succeeding reaction for the preparation of p-bromo- α -chlorostyrene was carried out exactly as was the preparation of the unsubstituted α -chlorostyrene.

The procedure in Gilman and Blatt (6) called for the use of a five-to-four ratio of bromobenzene to acetic

anhydride, though as may be seen from Figure 6, the stoichiometric ratio should be two-to-one. Perhaps this serves to explain the low (27.2%) yield obtained.

It had been found by Worrall (12) that the substitution of halogens on the side chain of styrene tended very markedly to inhibit both addition reactions and polymerization, but it was not pointed out in his paper specifically what accelerators were used, nor under what conditions of temperature the reactions were carried out. Wheland (11) has pointed out that the polymerization of unsubstituted styrene could be brought about either by electrophilic, nucleophilic, or radical reagents, and Bachman and Hellman (1) noted that the co-polymerization of α -methylstyrene could be brought about by radical reagents, but that quite active nucleophilic reagents were required to cause this compound to polymerize with itself. Sparks, Kellog, and Field (8) discovered that styrene or a mixture of styrene and α -methylstyrene could be made to polymerize by the action of aluminum chloride at a temperature of -100°C . With the work of these men in mind, numerous investigations were made to ascertain the effect of benzoyl peroxide and aluminum chloride as accelerating agents upon the polymerization of α -chlorostyrene. The former decomposes thermally to give the active phenyl radical, while the latter is an electrophilic compound. Both reagents were tried at room temperature as well as at elevated temperatures, with no polymerization noted, and the aluminum chloride accelerator was tried at temperatures around -70°C . to -80°C ., also with

negative results. The benzoyl peroxide was not tried at low temperatures, as it requires heating to produce the active phenyl radical. The only conclusion that could be drawn from the above was that the substitution of a halogen, at least in the alpha position, completely prevented the polymerization of styrene under the influence of electrophilic or radical reagents. No trials were made with nucleophilic reagents, as none of sufficient activity such as triphenylmethyl sodium were available.

A possible explanation for the failure of α -chlorostyrene to either polymerize or co-polymerize may be had by comparing the electronic structures of styrene, α -methylstyrene, and α -chlorostyrene as seen in Figure 7.

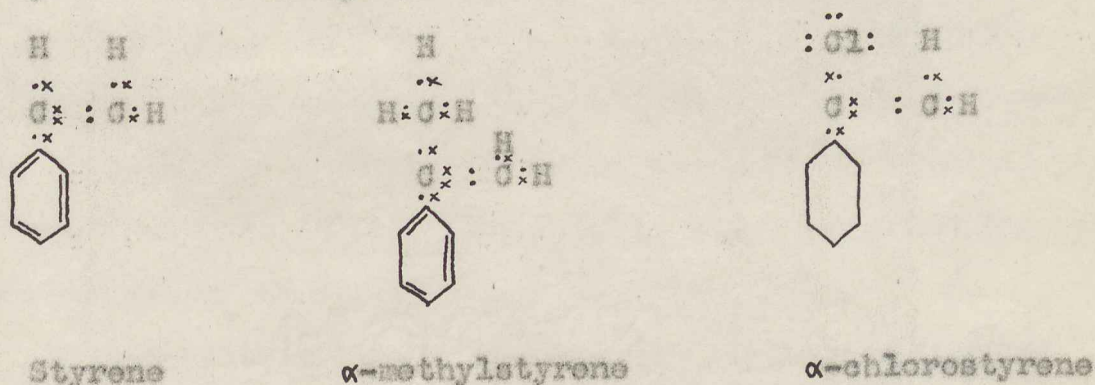


Figure 7.

It is known that styrene will polymerize and co-polymerize under the influence of electrophilic, nucleophilic, or radical reagents, while α -methylstyrene will polymerize only with nucleophilic reagents, though it will co-polymerize with radical reagents. As has been noted before, this present work found that α -chlorostyrene failed to polymerize or co-polymerize using either electrophilic or radical catalysts. Some explanation may be had by noting differences in

electronegativity of the various groups attached to the alpha carbon atom. Of the three, hydrogen is the least electronegative, and chlorine the most electronegative, with the methyl group occupying an intermediate position. Thus it is seen that while styrene's electron arrangement is such that polymerization is possible using all three types of reagents, in α -methylstyrene only anionic catalysts will produce the proper electronic configuration around the alpha carbon atom to permit polymerization. The α -methylstyrene will co-polymerize under the influence of radical catalysts, because it is the other monomer that becomes activated by the catalyst, and the α -methylstyrene has no trouble polymerizing once there is an activated complex present. However, the α -chlorostyrene presents a different problem. Here, the electronegativity of the chlorine atom may be so great as to prevent the formation of an activated center at the alpha carbon atom, consequently, no polymerization or co-polymerization can occur.

Another factor tending to inhibit polymerization of the substituted styrenes is the steric effects of the methyl group and of the chlorine atom. The size of the chlorine atom is about the same as that of the methyl group, therefore its hinderance would be expected to be about the same, which may be the case.

One further factor that needs to be taken into account in the discussion of α -methylstyrene is the possibility of hyperconjugation between a hydrogen atom of the alpha substituted methyl group and the beta carbon atom.

Such hyperconjugation increases the stability of the α -methylstyrene molecule, and makes more difficult the formation of the activated complex necessary in order that polymerization may take place.

SUMMARY

1) The preparation of α -chlorostyrene and of p-bromo- α -chlorostyrene by the equimolar reaction between the appropriate acetophenone and phosphorus pentachloride have been carried out, and the physical constants of these α -chloro-styrenes have been determined.

2) Both of these chloro substituted styrenes were found to be quite unstable in the presence of air, oxidizing during the space of one day even in the presence of an inhibitor. They were found to require storage under reduced pressures.

3) Unsuccessful attempts were made to bring about the polymerization of α -chlorostyrene by the use of aluminum chloride and benzoyl peroxide as accelerators. The attempted polymerizations were carried out at temperatures ranging from -80°C. to 200°C.

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