The Synthesis of Aromatic Divinylogs and Aromatic Halogenated Vinylogs*

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The crosslinking of styrene with p-divinylbenzene was first described by Staudinger et al.¹ Relatively small amounts of p-divinylbenzene in these copolymers improve the thermal properties of these copolymers and render them insoluble in organic solvents. In addition to the above properties, styrene-p-divinylbenzene copolymers possess excellent electrical characteristics and have found industrial use primarily in form of castings.

Since p-divinylbenzene polymerizes very rapidly, it was found desirable to prepare difunctional compounds similar to p-divinylbenzene but polymerizing at a slower rate. The next higher homologues of p-divinylbenzene, i.e., p-allylstyrene, p-1-propenylstyrene, and p-isopropenylstyrene were selected for this purpose.

p-1-Propenylstyrene (p-1-propenylvinylbenzene) (V) was synthesized by the following series of reactions:



p-Bromoallylbenzene (II) was prepared by the method of Quelet.² The formation of the Grignard compound of p-bromoallylbenzene (III) proceeded considerably more slowly than that of p-dibromobenzene, as expected.

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Treatment of *p*-allyl- β -phenethyl alcohol (IV) with activated alumina at 300° C. caused not only dehydration of the carbinol to form the vinyl group but also brought about simultaneous rearrangement of the allyl to the 1-propenyl group.

Allylbenzene (VI) when subjected to identical conditions rearranged completely to 1-propenylbenzene (VII). A similar rearrangement of the allyl to the 1-propenyl group under the influence of activated alumina was previously demonstrated by Levina, Karelova, and El'yashberg³ in the case of *p*-diallylbenzene and 1-allylnaphthalene.

p-Allylstyrene (p-allylvinylbenzene) (VIII) was made by the reaction of p-allylphenylmagnesium bromide (III) with vinyl bromide in the presence of anhydrous cobaltous chloride:



No product was obtained without the catalyst. Anhydrous cobaltous chloride was first used by Kharasch and Fuchs⁴ to activate the halogen in vinyl halides to prepare styrene.

In order to prepare *p*-isopropenylstyrene (*p*-isopropenylvinylbenzene) the following series of reactions was carried out:



p-Bromoisopropanolbenzene (IX) was made according to the method of Ziegler and Tiemann.⁵ *p*-Bromoisopropenylbenzene (X) was prepared by dehydration of (IX) over activated alumina at 300°. However, attempts to prepare the corresponding Grignard compound of (X) did not give any significant yields. It is interesting to note that *p*-bromoallylbenzene and *p*-bromopropenylbenzene readily undergo the Grignard reaction, whereas *p*-bromostyrene and *p*-bromoisopropenylbenzene do not appear to react readily with magnesium alone and require the use of cohalides such as methyl iodide or ethyl bromide.⁶ Recently, Dreyfuss, and Notley⁷ reported the synthesis of *p*-isopropenylstyrene by the dehydrogenation of *p*-isopropylstyrene as well as by the dehydrohalogenation of the chloroalkylation product of bromoethylbenzene and propylene chlorohydrin. *p*-Bromostyrene (XII), an intermediate for the synthesis of difunctional aromatic crosslinking agents, was prepared by the following two methods:



The first method gave better yields but the second method is simpler, and the yields might eventually be improved. p-Bromostyrene had previously been prepared by various investigators using different methods.^{6,8}

p-Chloroallylbenzene (XIV), another intermediate in the synthesis of difunctional crosslinking agents, was made by reacting p-chlorophenylmagnesium bromide (XIII) with allyl bromide. This compound has previously not been reported in literature despite the fact that p-bromoallylbenzene was described as early as 1926.

Preliminary polymerization experiments were carried out with the above described difunctional crosslinking agents. Benzoyl peroxide-catalyzed bulk polymerization of *p*-allylstyrene, *p*-1-propenylstyrene, and *p*-divinyl-benzene indicated the following order of activity for the *p*-substituents in these crosslinking agents: vinyl > 1-propenyl > allyl. This order of reactivity is in accord with the findings of Whitby and Katz⁹ who found that the polymerization of β -methylstyrene derivatives proceeded at a faster rate than the corresponding allyl derivatives.

Bulk copolymerization of styrene with p-1-propenylstyrene resulted in crosslinked, hard polymers.

Solution copolymerization of styrene and p-1-propenylstyrene under controlled conditions resulted in a white, solid polymer which on molding yielded a crosslinked, brittle resin.

In view of their slower speed of polymerization, p-allyl- and p-1-propenylstyrene could be used in solution for the preparation of linear, branched polymers, as suggested by Dreyfuss and Notley.⁷

EXPERIMENTAL

p-Bromoallylbenzene (II)

This was conveniently prepared by the reaction of allyl bromide with p-bromophenylmagnesium bromide (I) according to the method of Quelet.²

Yields ranged from 51 to 96%; b.p. 85° (5.4 mm.), b.p. 95–96° (12 mm.); $d_4^{20} = 1.269$; $n_D^{20} = 1.520$.

p-Allylphenylmagnesium Bromide (III)

The Grignard compound of p-bromoallylbenzene was made essentially by the method described by Quelet.² Varying amounts of bromine and iodine were added to the reaction mixture to catalyze the reaction. However, once the reaction had started, the mixture had to be externally cooled until the reaction had subsided. A dark red ethereal solution of the Grignard compound (III) resulted, which was used for the next step.

p-Allyl- β -Phenethyl Alcohol (IV)

The ethereal solution of *p*-allylphenylmagnesium bromide (III), prepared from 930 g. of p-bromoallylbenzene (II), was placed in a 5-l. three-necked flask equipped with stirrer, reflux condenser, and a dropping funnel with a cooling mantle. The flask was immersed in an ice-salt freezing mixture. A solution of 560 ml. of ethylene oxide in 850 ml. of anhydrous ether was slowly added through the dropping funnel which was surrounded by Dry The addition of the ethylene oxide solution was regulated at such a Ice. rate that gentle refluxing occurred. After addition of all of the ethylene oxide solution, which resulted in the formation of a hard, yellowish-white mass, the mixture was heated under reflux for $\frac{3}{4}$ hr. It was then decomposed in ice water. The yellow ether layer was decanted and dried over anhydrous sodium sulfate. After the solution was filtered, the solvent was removed. The residual liquid was distilled in vacuo in the presence of pyrogallol as inhibitor. Rejecting the forerun, we found that the product distilled at 109–116° (1–1.6 mm.) as a colorless liquid; $n_{\rm D}^{20} = 1.5374$. The yield of the carbinol (IV) was 27-30%.

ANAL.: Calc. for C11H14O: C 81.48%, H 8.64%. Found: C 81.36%, H 8.72%.

About one third of the crude product polymerized in the distillation flask as a reddish resin. The resin formation is probably due to the partial dehydration of the alcohol (IV), followed by vinyl polymerization. The water formation towards the end of the distillation could actually be observed. The resin formation can be reduced by removal of the solvent *in vacuo*, as well as by distilling the product at low pressure in the presence of pyrogallol or hydroquinone as inhibitors.

p-1-Propenylstyrene (p-Propenylvinylbenzene) (V)

The dehydration of p-allyl- β -phenethyl alcohol (IV) was carried out in a column consisting of a quartz tube insulated by an asbestos fiber pack. Heating was effected by means of Nichrome wire wound around the column and connected to a variable transformer. The tube was filled with 180 cc. of activated alumina (Aluminum Ore Co., 8–14 mesh), held in place by means of a wire gauze and a metal spring. The receiving flask was

immersed in a Dry Ice-alcohol bath and was connected to a vacuum outlet. The carbinol (IV) (151 g.), containing pyrogallol as inhibitor, was passed slowly through a dropping funnel at the top of the column while a vacuum of 20–25 mm was applied. The temperature of the column was maintained at 300°. The resulting yellow liquid was separated from the water formed during the dehydration. It was washed with dilute sodium hydroxide and water to remove any adhering inhibitor. Afterwards the product was dried over anhydrous calcium chloride and then distilled *in vacuo*. Rejecting the forerun, we found that the product distilled at 75° (1.75 mm.) as a colorless liquid, possessing a characteristic odor. Yields ranged from 47–61%. $n_D^{20} = 1.5835$; $d_4^{20} = 0.9335$; M_R (Calcd.), 51.82; M_R (Found), 51.58.

ANAL.: Calc. for C11H12: C 91.66%; H 8.33%. Found: C 91.78%; H 8.46%.

Rearrangement of Allylbenzene (VI) to 1-Propenylbenzene (VII)

Allylbenzene (VII) was prepared from phenylmagnesium bromide and allyl bromide. The pure product distilled at 60-61° at 27 mm. (52-53° at 17 mm.). $n_D^{20} = 1.5135$ (literature value: $n_D^{20} = 1.5143$).

Allylbenzene (163 g.) was passed dropwise through the dehydration column as described above. The temperature was kept at 300°. The resulting light yellow liquid was dried over anhydrous calcium chloride. It was then filtered and distilled *in vacuo*. The yield of pure colorless 1-propenylbenzene (VII) was 135 g. (83%), b.p. 63-65° (15 mm.), $n_D^{20} = 1.5482$ (literature value $n_D^{20} = 1.5492$).

p-Allylstyrene (p-allylvinylbenzene) (VIII)

The ethereal solution of 612 g. of *p*-allylphenylmagnesium bromide (III) was placed in a 3-l. three-necked flask equipped with stirrer, reflux condenser, gas inlet tube, and a dropping funnel surrounded by a cooling mantle. Eighteen grams of anhydrous cobaltous chloride was added slowly, with evolution of heat, to the solution. The flask was then immersed in an ice bath and 196 ml. (296 g., d = 1.5167) of vinyl bromide was added slowly through the dropping funnel cooled by means of Dry Ice. Dry nitrogen gas was passed through the reaction flask at all times. When all of the vinyl bromide solution had been added, the mixture was stirred overnight at room temperature. It was then refluxed for $\frac{3}{4}$ hr. The reaction mixture was decomposed in ice water, the dark green ether layer drawn off and dried over anhydrous sodium sulfate. A small amount of pyrogallol was added and the solvent removed. The residual liquid was vacuum The fraction distilling at 86-87° at 6-7 mm. pressure was distilled. collected and redistilled. The product distilled at 74° at 5.5 mm. as a colorless liquid, possessing a characteristic odor. $n_{\rm D}^{20} = 1.5375, d_4^{20} =$ 0.914. The yields ranged from 6 to 15%. $M_{\rm R}$ (Calc.), 48.47; $M_{\rm R}$ (Found), 49.24; exaltation, 0.77.

ANAL.: Calc. for C11H12: C 91.66%; H 8.33%. Found: C 91.31%; H 8.48%.

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p-Bromoisopropanolbenzene (IX)

This compound was prepared from *p*-bromophenylmagnesium bromide and acetone according to the method of Ziegler and Tiemann.⁵ The yield of the product was 37.5%, b.p. 108° (3 mm.), $n_{\rm D}^{20} = 1.5620$, $d_4^{20} = 1.356$, $M_{\rm R}$ (Calc.), 50.56; $M_{\rm R}$ (Found), 51.66. These results indicated that a certain amount of dicarbinol had formed owing to the presence of some dimagnesium compound in the Grignard solution.

p-Bromoisopropenylbenzene (X)

303 g. of *p*-bromoisopropanolbenzene (IX) was passed slowly through a dehydration column filled with 180 cc. of activated alumina. The setup used was the same as that described above. The temperature was kept at 300° and the pressure at 25 mm. The resulting yellow liquid was dried over anhydrous CaCl₂. The product distilled at 110–111° (6.5 mm.) as a colorless liquid; $n_{20}^{20} = 1.580$; $d_4^{20} = 1.320$; $M_{\rm R}$ (Calc.), 49.22; $M_{\rm R}$ (Found) 49.91; unsaturation, 112.4%. The yield was 55%.

ANAL.: Calc. for C₉H₉Br: C 54.82%, H 4.57%. Found: C 56.46%, H 4.90%.

The analytical results indicate that a certain amount of diisopropenylbenzene was present in the product.

Attempts to prepare the corresponding Grignard compound of p-bromoisopropenylbenzene by conventional methods were unsuccessful.

p-Bromostyrene

Method I

In a 5-l. three-necked flask equipped with stirrer, reflux condenser, and a dropping funnel surrounded by a cooling mantle was placed a solution of 1550 g. of *p*-bromophenylmagnesium bromide (I) in 1330 ml. ether and 720 ml. benzene. A solution of 400 ml. of ethylene oxide in 500 ml. cold, dry ether was added slowly to the Grignard solution, forming a yellowish-white precipitate. Afterwards the mixture was refluxed for $\frac{3}{4}$ hr. It was then decomposed in ice water, the organic layer drawn off and dried over anhydrous sodium sulfate. After removal of the solvents, the residual liquid was fractionated. *p*-Bromo- β -phenethyl alcohol (XI), a colorless liquid, distilled at 130–140° at 7–8 mm. pressure. The yield was 20%.

The dehydration of p-bromo- β -phenethyl alcohol (XI) was carried out in the dehydration column described above over activated alumina. The temperature was maintained at 300°, and a vacuum of 40 mm. was applied. A 236-g. portion of (XI) containing a small amount of pyrogallol as inhibitor was passed slowly through the dropping funnel at the head of the column. The resulting yellow liquid was washed with dilute sodium hydroxide and water to remove any remaining inhibitor. The product was extracted with ether and dried over anhydrous calcium chloride. After the solvent was removed, the residual liquid was vacuum distilled. p-Bromostyrene (XII) distilled at 68° (4.8-4.9 mm.). The yield was 90 g. (42%).

Method II

A 1000-ml. portion of the etheral solution of p-bromophenylmagnesium bromide (I), containing 430 g. of the Grignard compound, was placed in a 3-1. three-necked flask equipped with stirrer, reflux condenser, dropping funnel with a cooling mantle, and a gas inlet tube. Dry nitrogen gas was passed through the flask at all times. Anhydrous cobaltous chloride (18.2 g.) was added in small amounts, forming a dark solution with some heat evolution. Afterwards 385 ml. of vinyl bromide was added slowly through a dropping funnel surrounded by Dry Ice. During the addition of the vinyl bromide, the reaction flask was immersed in an ice bath. The mixture was stirred overnight and was then refluxed for 1/2 hr. The green solution was decomposed in ice water, the ether layer separated and dried over anhydrous calcium chloride. After removal of the solvent, the product (XII) distilled at 71° at 4.5 mm. as a colorless liquid, $n_{\rm D}^{18} = 1.599$ (lit. $n_{\rm D}^{18} = 1.599$). The yield was 12.5 g. (4.2%). Unsaturation was 100.8% by the bromide-bromate method; 100.2% by the mercuric acetate method.

p-Chloroallylbenzene (XIV)

A solution of 101 g. of allyl bromide in 200 ml. of anhydrous ether was gradually added, with gentle refluxing, to a solution of 180 g. of *p*-chlorophenylmagnesium bromide (XIII) in 800 ml. ether and 150 benzene. Afterwards the mixture was refluxed for one hour. It was then decomposed in ice water, the organic layer drawn off and dried over anhydrous sodium sulfate. After removal of the solvents, the residual liquid was fractionated, yielding 100 g. (66% yield) of *p*-chloroallylbenzene. The pure product distilled at 52° (0.8 mm.); $n_{\rm D}^{20} = 1.5325$; $d_4^{20} = 1.055$; $M_{\rm R}$ (Calc.), 44.84; $M_{\rm R}$ (Found), 44.56.

ANAL.: Calc. for C₉H₉Br: C 70.82%; H 5.88%. Found: C 70.90%; H 5.80%.

Bulk Polymerization and Copolymerization of p-1-Propenylstyrene

In a preliminary series of polymerizations catalyzed by 0.5% benzoyl peroxide, it was established that *p*-divinylbenzene polymerized faster than *p*-1-propenylstyrene which, in turn, polymerized more quickly than *p*-allylstyrene. The bulk polymerizations were carried out in test tubes which were heated to 60° . For the following series of experiments only *p*-1-propenylstyrene was used as a crosslinking agent because it reacts considerably faster than *p*-allylstyrene.

Three samples were placed in screw-cap vials as follows: (1) 3 g. styrene; (2) 2.7 g. styrene + 0.3 g. p-1-propenylstyrene + 0.5% benzoyl peroxide; (3) 3 g. p-1-propenylstyrene + 0.5% benzoyl peroxide. The samples were placed in an oven at 60° C. for 24 hr. While Sample 1 polymerized fairly rapidly, Samples 2 and 3 polymerized only very slowly at this temperature. After the samples were transferred to an oven at 75°, the polymerization proceeded rapidly with both. They were allowed to remain at this temperature for 24 hr. and afterwards baked at 110° for 48 hr. to hard, glasslike solids. Samples 2 and 3 were insoluble in common organic solvents and were infusible on a hot plate at 180° . Hence *p*-1-propenyl styrene shows definite crosslinking properties.

Solution Polymerization

A solution of 45 g. styrene, 5 g. p-1-propenylstyrene, and 0.25 g. benzoyl peroxide in 100 ml. benzene was refluxed for 6 hr. The progress of the polymerization was followed periodically by taking an aliquot and precipitating it in an excess of ethyl alcohol. The formation of the polymer reached 57% after 6 hrs. heating. Additional amounts of benzoyl peroxide were added to bring the catalyst concentration up to 4%. After 1 hr. of refluxing, a viscous liquid resulted which was precipitated in an excess of alcohol. The white precipitate was washed with alcohol, dried, and powdered. The white copolymer was molded at 180° for 15 min. at 1000 psi to a light-yellow, transparent, brittle resin whose insolubility and infusibility showed it to be crosslinked.

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Synopsis

Two new higher homologues of p-divinylbenzene, p-allylstyrene (p-allylvinylbenzene) and p-1-propenylstyrene (p-1-propenylvinylbenzene) were synthesized and characterized. Intermediates for the synthesis of difunctional aromatic vinylogs, p-chloroallylbenzene was prepared for the first time and p-bromostyrene was made by methods different from those reported previously for this material. The usefulness of anhydrous cobaltous chloride for the activation of vinyl bromide in the reaction with aromatic Grignard compounds was demonstrated in the synthesis of *p*-allyl- and *p*-bromostyrene. Rearrangement of the allyl to the 1-propenyl group on treatment with activated alumina at 300° was shown in the synthesis of p-1-propenylstyrene and 1-propenylbenzene. Peroxide-initiated bulk polymerization of p-divinylbenzene, p-1-propenylstyrene, and pallylstyrene established the following order of reactivity: vinyl > 1-propenyl > allyl. Preliminary polymerization of 1-propenylstyrene and copolymerization with styrene in bulk and in solution showed the former to be an efficient though slower crosslinking agent than p-divinylbenzene. Molding of solid copolymers of styrene and p-1-propenylstyrene was carried out, resulting in the formation of thermosetting clear and brittle resins.

Résumé

Deux homologues nouveux du p-divinylbenzène, le p-allylstyrène (p-allylvinylbenzène) et le p-1-propénylstyrène (p-1-propényl vinylbenzène) ont été synthétisés et caractérisés. Le p-chloro-allylbenzène a été préparé pour la première fois et le p-bromostyrène a été synthétisé par des méthodes différentes de celles décrites précédemment pour cette substance. Ces dérivés sont utilisés comme intermédiaires dans la synthèse de vinylogues aromatiques bifonctionnels. L'utilité du chlorure cobalteux anhydre pour l'activation du bromure de vinyle dans la réaction avec les composés de Grignard aromatiques a été démontrée dans la synthèse du p-allyle et du p-bromostyrène. Le réarrangement du groupe allyle en 1-propényle par traitement avec de l'alumine activée à 300° a été mis en évidence dans la synthèse du p-1-propénylstyrène et du 1-propénylbenzène. La polymérisation en bloc initiée par des peroxydes du p-divinylbenzène, du p-1-propénylstyrène et du p-allylstyrène a établi l'ordre de réactivité suivant vinyle > 1-propényle >allyle. La polymérisation préliminaire du 1-propénylstyrène et la copolymérisation avec le styrène en bloc et en solution ont montré que ce dérivé est un agent de pontage efficient quoique plus lent que le p-divinylbenzène. Le moulage de copolymères solides de styrène et de p-1-propénylstyrène a été réalisé et a permis l'obtention de résines thermodurcissables claires et cassantes.

Zusammenfassung

Zwei neue, höhere Homologe des p-Divinylbenzols, nämlich p-Allylstyrol (p-Allylvinylbenzol) und p-1-Propenylstyrol (p-1-Propenylvinylbenzol) wurden synthetisiert und charakterisiert. Als Vorstufe für die Synthese von bifunktionellen, aromatischen Vinylogen wurde p-Chlorallylbenzol zum ersten Mal und p-Bromstyrol unter Verwendung neuer Methoden dargestellt. Die Brauchbarkeit von wasserfreiem Kobaltchlorid zur Aktivierung von Vinylbromid bei der Reaktion mit Grignardverbindungen wurde bei des Synthese von p-Allyl- und p-Bromstyrol gezeigt. Umlagerung der Allylzur 1-Propenylgruppe bei Behandlung mit aktiviertem Aluminiumoxyd wurde bei der Synthese von p-1-Propenylstyrol und 1-Propenylbenzol nachgewiesen. Die Massepolymerisation von p-Divinylbenzol, p-1-Propenylstyrol und p-Allylstyrol unter Anregung mit Peroxyd führte zur Aufstellung folgender Reaktivitätsreihe: Vinyl > 1-Propenyl > Allyl. Vorläufige Versuche über die Polymerisation von 1-Poropenylstyrol und Copolymerisation mit Styrol in Masse und in Lösung zeigten, dass ersteres ein wirksames, wenn auch langsamer als p-Divinylbenzol wirkendes Vernetzungsmittel ist. Die Verarbeitung fester Copolymerer aus Styrol und p-1-Propenylbenzol wurde durchgeführt und ergab die Bildung wärmehärtender, klarer und spröder Harze.

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