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Some Disubstituted α-Methylstyrenes and their Polymerization Characteristics and a Comparative Study of the Refractive Indexes of Substituted Styrenes and α-Methylstyrenes[1]

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2,3-Dichloro-, 3-chloro-4-methyl- and 3,5-dichloro-α-methylstyrene have been synthesized and are reported here for the first time. 3-Methyl-4-chloro-, 3,4-dichloro- and 3,4-dimethyl-α-methylstyrene have also been synthesized by methods differing from those previously described. It has been observed that nuclear substituted α-methylstyrenes without ortho substituents usually have refractive indexes which are from 0.0080 to 0.0110 unit lower than the corresponding substituted styrenes. If an ortho substituent is present, the corresponding difference is 0.0274 to 0.0352 unit. This is believed to be due to the decreased probability of the existence of those resonance isomers of the various α-methylstyrenes which have quinoid structures.

During the course of extensive polymerization studies we have had occasion to prepare a number of disubstituted α-methylstyrenes with nuclear chloro and methyl substituents. These have included 2,3-dichloro-, 3,5-dichloro- and 3-chloro-4-methyl-α-methylstyrene which are described here for the first time, and 3,4-dichloro-,[2,3] 3,4-dimethyl-[4a] and 3-methyl-4-chloro-α-methylstyrene[4a,b] which we have prepared by different or improved methods from those previously reported.

The 2,3-dichloro- and 3,5-dichloro-α-methylstyrenes were synthesized from the corresponding toluenes.[5] The toluenes were first converted to the corresponding benzoic acids by side chain chlorination at high temperatures in the presence of light followed by hydrolysis to the benzoic acid. This proved to be an excellent method for obtaining the benzoic acids, yields usually running about 90%. The acids were then esterified and treated with methylmagnesium bromide in the conventional manner to form the dimethylarylcarbinols which were dehydrated to the corresponding α-methylstyrenes.

3-Chloro-4-methyl-α-methylstyrene was similarly prepared from 3-chloro-4-methylbenzoic acid obtained by oxidation of 3-chlorocymene[6] with nitric acid in acetic acid solution. 3-Methyl-4-chloro-α-methylstyrene, first prepared from *o*-chlorotoluene and propylene chlorohydrin,[4a,b] was obtained by treating 3-methyl-4-chloroacetophenone[7] with methylmagnesium bromide followed by dehydration.

The preparation of 3,4-dichloro-α-methylstyrene from both 3,4-dichloroacetophenone and 3,4-dichlorobenzoic acid has been described previously.[2,3] We have found that excellent yields of one of these starting materials, 3,4-dichloroacetophenone, can be obtained by acetylating *o*-dichlorobenzene with acetic anhydride using excess *o*-dichlorobenzene as solvent instead of carbon disulfide.

We have observed some interesting relationships of the refractive indexes of various styrenes and α-methylstyrenes. The refractive indexes of the dichlorostyrenes vary over a range of 0.0116 refractive index unit.[8] The indexes of the known dichloro-α-methylstyrenes (the 2,6-isomer is unknown) vary over a much wider range of 0.0280 unit, and those with 2-substituents are all very much lower than those of the other isomers. Furthermore, if there is no ortho substituent, the refractive index of a styrene or substituted styrene is always greater than that of the corresponding α-methylstyrene by 0.0080 to 0.0110 unit. But, if an ortho substituent is present, the corresponding difference is much larger, 0.0274 to 0.0352 unit.

These refractive index relationships are shown in Table I for the known styrenes and α-methylstyrenes. The refractive indexes were either measured in our laboratories or taken from the literature. All values were corrected to 25° by using a temperature coefficient of −0.0006 unit per centigrade degree where necessary.

TABLE I

COMPARISON OF REFRACTIVE INDEXES OF STYRENES AND α-METHYLSTYRENES

Substituent	(n^{25}_D styrene) − (n^{25}_D α-methylstyrene) (× 10^4)
None	80
o-Chloro	294[3,11]
m-Chloro	94[3,11]
p-Chloro	85[3,11]
o-Methyl	274[13,12]
p-Methyl	94[4a,10]
2,3-Dichloro	302[8]
2,4-Dichloro	352[3,8]
2,5-Dichloro	306[2,8]
3,4-Dichloro	100[3,8]
3,5-Dichloro	110[8]
3,4-Dimethyl	94[4a,9]

Since refraction is one manifestation of absorption, these data are related to the observations reported by Murray and Gallaway[14] and Hirschberg[15] that the ultraviolet and infrared absorption spectra of vinylbenzenes are altered by the entry of an alkyl substituent in the α-position, and are further altered by an ortho substituent in an α-alkylvinylbenzene although the ortho substituent in the styrene itself has little effect. These two changes can be clearly seen in the refractive indexes. In other words, (1) an α-methyl group and, to a

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society during the Fall Meeting held at Chicago, Ill., September, 1950.

[2] Mowry, Huber and Ringwald, THIS JOURNAL, **69**, 851 (1947).

[3] Bachman and Finholt, *ibid.*, **70**, 622 (1948).

[4a] Bachman and Hellman, *ibid.*, **70**, 1772 (1948).

[4b] Stempel and Sobel, *ibid.*, **72**, 4314 (1950).

[5] Marvel, *et al.*, *ibid.*, **68**, 861 (1946).

[6] Lubs and Young, *Ind. Eng. Chem.*, **11**, 1130 (1919).

[7] Allen, THIS JOURNAL, **49**, 1846 (1927).

[8] Michalek and Clark, *Chem. Eng. News*, **22**, 1559 (1944).

[9] Sturrock and Lawe, U. S. Patent 2,420,689 (May 20, 1947).

[10] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[11] Brooks, *ibid.*, **66**, 1295 (1944).

[12] V. Auwers, *Ann.*, **413**, 295 (1917).

[13] Sabatier and Murat, *Compt. rend.*, **156**, 185 (1927).

[14] Murray and Gallaway, THIS JOURNAL, **70**, 3867 (1948).

[15] Hirschberg, *ibid.*, **71**, 3241 (1949).

greater extent, (2) an α-methyl group plus an ortho substituent both decrease the probability of the existence of those resonance isomers of substituted vinylbenzenes having quinoid structures,[14,15] a condition which is reflected in the refractive indexes of these compounds as well as in their absorption spectra.

It is interesting to observe further that *all* known styrenes with nuclear halogen or alkyl substituents have been found to homopolymerize and copolymerize with butadiene in the presence of peroxides.[3,4a,5,8] However, α-methylstyrene and its nuclear substituted chloro and alkyl derivatives with no ortho substituent have been found to copolymerize by free radical mechanism with butadiene, but fail to undergo peroxide-catalyzed homopolymerization. Finally α-methylstyrenes with ortho chloro or alkyl substituents have been found to fail to homopolymerize or copolymerize under similar conditions.[3,4a] We have found that the polymerization characteristics of all of the substituted α-methylstyrenes which we have examined fit into this general pattern. Thus these substituted styrenes and α-methylstyrenes fall into the same three groups according to absorption spectra, refractive indexes and polymerization characteristics.

Acknowledgment.—We are indebted to Dr. J. E. Ablard, Mr. E. S. Pfau and Dr. G. S. Schaffel under whose direction some of the polymerization experiments were performed, and to Dr. A. J. Beber under whose direction the analyses were performed.

Experimental

3,4-Dimethyl- (b.p. 86° (8 mm.), n^{25}_D 1.5377) and 3-methyl-4-chloro-α-methylstyrene (b.p. 95–96° (19 mm.), n^{25}_D 1.5525) were prepared from *o*-xylene and *o*-chlorotoluene, respectively, by acetylation, reaction of the ketone with methylmagnesium bromide, followed by hydrolysis and dehydration.[2]

2,3-Dichloro- and 3,5-Dichloro-α-methylstyrene.—2,3-Dichloro-α-methylstyrene and its 3,5-isomer were prepared from 2,3- and 3,5-dichlorotoluenes. The dichlorotoluenes were made from *o*-toluidine by the methods summarized by Marvel.[5] The conversion of 3,5-dichlorotoluene to 3,5-dichloro-α-methylstyrene is typical. Chlorine was passed into 50 g. of 3,5-dichlorotoluene, heated to 185–190°, and irradiated with a 150-watt lamp for about 8 hours when the total weight increase was 28 g. To the product, weighing 78 g., was added dropwise with stirring 200 g. of 8% fuming sulfuric acid. No heat was evolved. After stirring for 30 hours the mixture was poured onto cracked ice and the precipitated acid was purified by dissolving in potassium hydroxide, treating the solution with activated carbon, and reprecipitating the acid with hydrochloric acid. The 3,5-dichlorobenzoic acid was then filtered off and dried. The yield was 53 g., 90%. The acid melted at 181°.

To 50 g. of 3,5-dichlorobenzoic acid was added 45 g. of thionyl chloride and the mixture was refluxed until no more hydrogen chloride was evolved. The 3,5-dichlorobenzoyl chloride, which boiled at 105–107° (5 mm.), was recovered by distillation and was then refluxed with an excess of methanol. The methyl 3,5-dichlorobenzoate boiled at 120–125° (7 mm.). The yield was 54 g., or 86%.

Fifty grams of methyl 3,5-dichlorobenzoate in ether solution was added dropwise to the methylmagnesium chloride obtained from methyl chloride and 12 g. of magnesium. The Grignard complex was decomposed with dilute hydrochloric acid and the ether layer containing the tertiary carbinol was separated and distilled. The product, a mixture of the carbinol and 3,5-dichloro-α-methylstyrene, was refluxed with fused sodium bisulfate to complete the conversion of the tertiary alcohol to the α-methylstyrene. Distillation yielded 32 g., 72% of theory, of 3,5-dichloro-α-methylstyrene, b.p. 90–91° (4 mm.), n^{25}_D 1.5635, d^{25} 1.196; molar refractivity: theoretical 49.42, experimental 50.9.

Anal. Calcd. for $C_9H_8Cl_2$: Cl, 37.91. Found: Cl, 37.69.

2,3-Dichloro-α-methylstyrene, n^{25}_D 1.5507, b.p. 103° (6 mm.), prepared in a similar fashion, had molar refractivity: theoretical 49.42, experimental 50.8.

Anal. Calcd. for $C_9H_8Cl_2$: C, 57.8; H, 4.3; Cl, 37.9. Found: C, 57.7; H, 4.3; Cl, 37.8.

3,4-Dichloro-α-methylstyrene.—To a well-stirred mixture of 447 g. of anhydrous aluminum chloride in 728 g. of *o*-dichlorobenzene was added, at such a rate as to keep the temperature at about 75°, 138 g. of acetic anhydride. After the addition was complete, the reaction mixture was stirred at about 75° for 8 hr. or until hydrogen chloride evolution had ceased. The aluminum chloride complex was destroyed with ice and the bottom layer was separated, dried with calcium chloride and distilled. The 3,4-dichloroacetophenone (I) fraction boiling at 130–135° weighed 236 g. (92.5% yield). I was converted to 3,4-dichloro-α-methylstyrene by the method previously described by Mowry.[2]

3-Chloro-4-methylbenzoic Acid.—To a solution of 100 g. of 2-chlorocymene[8] in 750 ml. of glacial acetic acid heated to 110° was added dropwise 750 ml. of concentrated nitric acid (sp. gr. 1.42) at such a rate that a steady reflux was maintained. After the addition, which required about 6 hours, the reaction mixture was allowed to reflux until no more NO_2 was evolved. This required about 12 hours. Upon cooling in an ice-bath, 3-chloro-4-methylbenzoic acid separated. The mixture was filtered, the white solid washed with cold water and dried. The yield was 51 g. (50%) of an acid melting at 194–196°[4b] and sufficiently pure for use in the next step.

Methyl 3-Chloro-4-methylbenzoic Acid.—3-Chloro-4-methylbenzoic acid was converted in 92% yield to the methyl ester by refluxing 16–20 hours in an excess of methanol containing 5% by volume of concentrated sulfuric acid. The methyl 3-chloro-4-methylbenzoate (II) boiled at 105–107° (6.5 mm.), and melted at 28°.

3-Chloro-4-methyl-α-methylstyrene.—To 184 g. of II in 500 ml. of ether was added 750 ml. of 4 *M* methylmagnesium bromide. The mixture was refluxed for half an hour and then poured onto 2 kg. of ice. The Grignard complex was decomposed by adding hydrochloric acid until two clear layers formed. The layers were separated, the lower layer washed twice with small quantities of ether and the ether washings combined with the ether layer. The ether was then distilled from the solution and the carbinol distilled under vacuum. To the distillate was added 0.5 g. of picric acid and 100 g. of anhydrous potassium bisulfate, the mixture was refluxed for 2 hours and then extracted with ether. The ether extract was dried, the ether stripped off and the product distilled under vacuum. The 3-chloro-4-methyl-α-methylstyrene distilled at 80° (3.5 mm.), n^{25}_D 1.5525. The yield was 138 g., 83%.

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.29. Found: Cl, 21.31, 21.14.

Peroxide-Catalyzed Homopolymerizations.—About 0.1 g. of benzoyl peroxide was added to 3–5 g. of each of the substituted α-methylstyrenes. After standing for an hour in a water-bath at 80–90° the sample was visually examined for evidence of polymerization and the refractive index of the material in the tube was measured. None of the substituted α-methylstyrenes appeared to polymerize under these conditions.

Copolymerizations with Butadiene.—The polymerizability of each chloro-substituted α-methylstyrene with butadiene was tested using the following recipe (parts by weight): butadiene 70, substituted α-methylstyrene 30, water 180, soap 5, potassium persulfate 0.3 and dodecyl mercaptan 0.3–0.6. The polymerizations were carried out in bottles on a rotating wheel immersed in a bath kept at a constant temperature of 50° for 12–16 hours. The latexes were coagulated with alcohol and the polymers obtained tested for chlorine. Those with no ortho substituent yielded polymers containing chlorine, whereas those containing a substituent ortho to the isopropenyl group yielded chlorine-free polymers which appeared from physical examination to be polybutadiene.

AKRON, OHIO RECEIVED JUNE 30, 1950