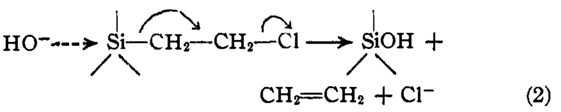
nated. The atomic electron shells remain complete throughout the change. A similar process obviously does not occur with alpha C–Cl bonds.

It should be emphasized that the reaction of a beta C–Cl bond with dilute alkali is not an ordinary hydrolysis, but is a 1:2 elimination reaction, similar in type to dehydrohalogenation, but involving a tetracovalent silicon atom instead of a combined hydrogen atom. It was shown above that small amounts of alkali accelerate β-eliminations involving silicon. β-Eliminations from alkyl halides which are favored by alkali take place by the following mechanism (E_2 elimination).[6]

$$Y\text{---}\!\!\rightarrow H\text{—}CR_2\text{—}CR_2\text{—}Cl \longrightarrow YH + CR_2{=}CR_2 + Cl^- \qquad (1)$$

In these reactions a nucleophilic (electron donor) reagent Y, such as hydroxyl ion, attacks the proton (a combined hydrogen atom) resulting in the electron transfers indicated by the curved arrows. The hydrogen atom and the electron-attracting chlorine atom are bound to adjacent carbon atoms in the original molecule. The atomic electron shells remain complete throughout the change.

The reaction of a beta C–Cl bond in a silicon compound with alkali can be formulated similarly.



$$HO^-\text{---}\!\!\rightarrow Si\text{—}CH_2\text{—}CH_2\text{—}Cl \longrightarrow SiOH + CH_2{=}CH_2 + Cl^- \qquad (2)$$

The only difference between the reactions is that in (2) the base attacks tetracovalent silicon instead of a combined hydrogen atom. In (2), just as in (1), the atomic electron shells remain complete throughout the change. Two bonds are broken, but each fission assists the other, the two together constituting a single synchronized process. It should be noted that the basic reagent might attack: (a) silicon attached to carbon, or (b) one of the two hydrogens attached to alpha carbon. Actually, the attack is exclusively on silicon, thus illustrating again the action of silicon as an electron sink.[5] As shown by the failure of primary alkyl halides to undergo dehydrohalogenation with dilute alkali, silicon attached to carbon takes part in β-eliminations far more readily than does hydrogen attached to carbon. A detailed discussion of the electronic interaction in a C–Si bond which is responsible for the behavior of silicon as an electron sink will be presented in a later paper.

Summary

1. β-Chloroethyltrichlorosilane and β-chloro-*n*-propyltrichlorosilane with aqueous alkali give ethylene and propylene, respectively. The extremely rapid reaction of beta C–Cl bonds with dilute alkali is not a hydrolysis, but a β-elimination, similar in type to the dehydrohalogenation of alkyl halides. It involves tetracovalent silicon instead of a combined hydrogen atom.

2. Reaction of β-chloroethyltrichlorosilane with methylmagnesium bromide gave ethylene and tetramethylsilane; ethylmagnesium bromide gave ethylene and tetraethylsilane.

STATE COLLEGE, PA. RECEIVED NOVEMBER 12, 1945

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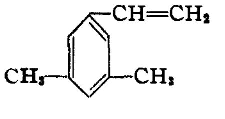
[6] Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657–659 (1941); Skell and Hauser, THIS JOURNAL, **67**, 1661 (1945).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

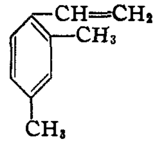
The Preparation and Polymerization of Four Isomeric Dimethylstyrenes[1,2]

BY C. S. MARVEL, J. H. SAUNDERS AND C. G. OVERBERGER

In order to investigate the effect of alkyl groups as substituents in styrene on its polymerization and on the properties of the polymer and copolymers this study of dimethylstyrenes has been made. This paper reports the synthesis of four of the isomeric dimethylstyrenes (I, II, III, IV) and gives a brief summary of the properties of their polymers. Copolymerization data will be reported in a later paper.



I



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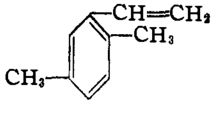
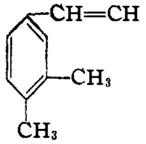


III



IV

3,5-Dimethylstyrene, 2,4-dimethylstyrene and 2,5-dimethylstyrene have been prepared previously by procedures other than those reported in this communication, but their characterization has been incomplete.

3,5-Dimethylstyrene (I)

This monomer was prepared by the following series of reactions.

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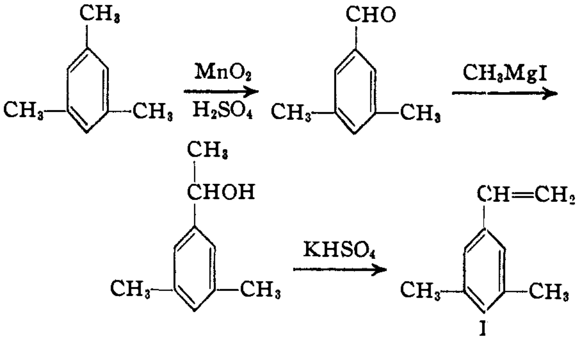
[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] This is the twenty-second communication on vinyl polymers. For the twenty-first, see Marvel, Overberger, Allen, Johnston, Saunders and Young, THIS JOURNAL, **68**, 861 (1946).



I

3,5-Dimethylbenzaldehyde.—This was prepared by the oxidation of mesitylene according to the method of Weiler[3] who characterized the aldehyde only by its boiling point. The oxidation was carried out at 65° for ten hours. From 500 g. (4.16 moles) of mesitylene there was obtained 67–112 g. (33–48% based on mesitylene used) of 3,5-dimethylbenzaldehyde, b. p. 77–78° (3.5 mm.), n^{20}_{D} 1.5385. The recovery of mesitylene was 200–375 g. (40–75%).

Anal.[4] Calcd. for $C_9H_{10}O$: C, 80.55; H, 7.52. Found: C, 80.48; H, 7.50.

The semicarbazone was prepared according to the usual method,[5] m. p. 200.5–201°. Law and Perkin[6] have reported a melting point of 201–202° for this semicarbazone but have not further characterized it.

Anal. Calcd. for $C_{10}H_{13}N_3O$: C, 62.78; H, 6.86. Found: C, 62.74; H, 6.70.

3,5-Dimethylphenylmethylcarbinol.—The 3,5-dimethylbenzaldehyde was treated with methylmagnesium iodide in the usual manner to obtain this carbinol. From 380 g. (2.83 moles) of 3,5-dimethylbenzaldehyde there was obtained 338.5 g. (80%) of 3,5-dimethylphenylmethylcarbinol, b. p. 94–96° (4 mm.); n^{20}_{D} 1.5210, d^{25}_{25} 0.986.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.41. Found: C, 79.61; H, 9.29.

3,5-Dimethylstyrene.—The dehydration of 3,5-dimethylphenylmethylcarbinol was effected according to the general procedure of Marvel and Shertz,[7] except that 0.1 g. *p*-*t*-butylcatechol was added to the carbinol and to the fused potassium acid sulfate as an inhibitor. From 338 g. (2.25 moles) of 3,5-dimethylphenylmethylcarbinol there was obtained 159.5 g. (87% based on carbinol dehydrated) of 3,5-dimethylstyrene, b. p. 57–58° (4 mm.), n^{20}_{D} 1.5382, d^{25}_{25} 0.897. The yield of recovered carbinol was 130 g. (38.4%).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.51; H, 9.19.

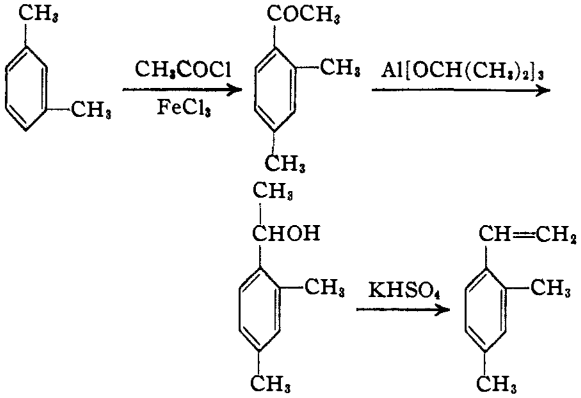
The preparation of 3,5-dimethylstyrene by dehydrogenation of the corresponding substituted ethylbenzene has been reported in an American Patent[8] but no description of the compound is included in this report.

To further characterize the styrene, its dibromide was prepared in the following manner. To 2 cc. of 3,5-dimethylstyrene in a 300-cc. Erlenmeyer flask was added a dilute solution of bromine in glacial acetic acid until the bromine was no longer absorbed. The solution was heated gently to remove excess bromine and cooled. Water was added to precipitate the dibromide. After repeated recrystallizations from 95% alcohol, the pure 3,5-dimethylstyrene dibromide was obtained, m. p. 89.5°.

Anal. Calcd. for $C_{10}H_{12}Br_2$: C, 41.19; H, 4.14. Found: C, 41.19; H, 4.19.

2,4-Dimethylstyrene (II)

This compound was prepared according to the scheme



2,4-Dimethylacetophenone.—This compound was prepared according to the procedure of Perkin and Stone.[9] From 475 g. (4.47 moles) of *m*-xylene there was obtained 490 g. (73.6%) of 2,4-dimethylacetophenone, b. p. 92–94° (5 mm.), n^{20}_{D} 1.5340. Klages[10] has reported a boiling point of 108° (12 mm.) for the 2,4-dimethylacetophenone prepared in a similar manner.

2,4-Dimethylphenylmethylcarbinol.—The reduction of 2,4-dimethylacetophenone with aluminum isopropoxide was done according to the procedure of Marvel and Overberger,[11] for the reduction of *p*-cyanoacetophenone. From 690 g. (4.68 moles) of 2,4-dimethylacetophenone there was obtained 517 g. (74%) of 2,4-dimethylphenylmethylcarbinol, b. p. 96° (4 mm.), n^{20}_{D} 1.5265, d^{25}_{25} 0.986.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.41. Found: C, 79.73; H, 9.51.

Klages[10] has prepared this carbinol by reduction of 2,4-dimethylacetophenone by means of sodium and alcohol. He reported a boiling point of 118° (12 mm.), d^{18}_{4} 0.9863 and further characterized the carbinol with the formation of a crystalline phenylurethan.

2,4-Dimethylstyrene.—Dehydration of the carbinol was accomplished by the method used for the 3,5-isomer. From 517 g. (3.44 moles) of 2,4-dimethylphenylmethylcarbinol there was obtained 252 g. (71% based on the carbinol dehydrated) of 2,4-dimethylstyrene, b. p. 90° (25 mm.), n^{20}_{D} 1.5423, d^{25}_{25} 0.907. The recovery of carbinol was 114 g. (22%).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.49; H, 9.00.

Klages and Keil[12] have prepared 2,4-dimethylstyrene by the dehydrohalogenation of 2,4-dimethyl-α-chloroethylbenzene with pyridine. They reported a boiling point of 79–80° (12 mm.), $d^{21.4}_{4}$ 0.9022, n^{20}_{D} 1.5214. No temperature was recorded with the index of refraction. They further characterized the 2,4-dimethylstyrene by reduction to 2,4-dimethylethylbenzene with sodium and alcohol. Harispe[13] has prepared 2,4-dimethylstyrene from β-(2,4-dimethylphenyl)-ethyl alcohol. He reported a boiling point of 81–85° (14 mm.), n^{20}_{D} 1.539, d^{20}_{4} 0.905.

In order to confirm the position of the methyl groups in our 2,4-dimethylstyrene, oxidation to 2,4-dimethylbenzoic acid was accomplished. One gram of 2,4-dimethylstyrene and 15 cc. of 5% potassium permanganate solution were placed in a 50-cc. Erlenmeyer flask. The flask and its contents were shaken for five minutes in a water-bath at 18°, and allowed to stand at room temperature for an hour. The mixture was made alkaline to litmus by the addition

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(3) Weiler, *Ber.*, **33**, 464 (1900).

(4) All microanalyses reported in this manuscript were done by Mr. H. S. Clark, Illinois State Geological Survey.

(5) "Systematic Identification of Organic Compounds," Shriner and Fuson, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 142.

(6) Law and Perkin, *Chem. Zentr.*, **76**, I, 359 (1905).

(7) Marvel and Shertz, This Journal, **65**, 2054 (1943).

(8) U. S. Patent 1,541,175, June 9, 1925; see *Chem. Zentr.*, **96**, II, 1805 (1925).

(9) Perkin and Stone, *J. Chem. Soc.*, **127**, 2275 (1925).

(10) Klages, *Ber.*, **35**, 2245 (1902).

(11) Marvel and Overberger, This Journal, **67**, 2250 (1945).

(12) Klages and Keil, *Ber.*, **36**, 1632 (1903).

(13) Harispe, *Ann. Chim.*, (11) **6**, 326 (1936).

of 0.5 g. sodium hydroxide and filtered. The filtrate was extracted with 10 cc. of ether, and the extract discarded. The aqueous layer was acidified with sulfuric acid. The solid which was formed on acidification was removed by filtration and recrystallized from alcohol and water. The 2,4-dimethylbenzoic acid thus obtained melted at 124.5–125°. Perkin and Stone[9] reported a melting point of 126° for 2,4-dimethylbenzoic acid.

2,5-Dimethylstyrene (III)

This monomer was prepared according to the scheme used for the preparation of 2,4-dimethylstyrene except that *p*-xylene was used instead of *m*-xylene. Klages and Keil[12] have prepared 2,5-dimethylstyrene by a different procedure and have reported physical constants for 2,5-dimethylstyrene in its dibromide which differ slightly from the constants reported in this paper.

2,5-Dimethylacetophenone.—The procedure was that of Perkin and Stone.[9] From 600 g. (5.66 moles) of *p*-xylene there was obtained 571 g. (68.3%) of 2,5-dimethylacetophenone, b. p. 93–94° (8 mm.), $n^{20}\mathrm{D}$ 1.5291. Von Auwers[14] who prepared this compound by a similar procedure reported $n^{20}\mathrm{D}$ 1.5294, d^{20}_{4} 0.995.

2,5-Dimethylphenylmethylcarbinol.—The procedure was that used for the 2,4-isomer. From 570 g. (3.85 moles) of 2,5-dimethylacetophenone there was obtained 415 g. (71.9%) of 2,5-dimethylphenylmethylcarbinol, b. p. 93–94° (4 mm.), $n^{20}\mathrm{D}$ 1.5270, d^{25}_{25} 0.987.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.41. Found: C, 80.40; H, 9.65.

Klages and Keil[12] prepared this compound by the reduction of 2,5-dimethylacetophenone with sodium and alcohol. They reported a boiling point of 114° (12 mm.), d^{16}_{4} 0.9747.

2,5-Dimethylstyrene.—The procedure was that used for the 3,5-isomer. From 346 g. (2.3 moles) of 2,5-dimethylphenylmethylcarbinol there was obtained 230.5 g (88.4%), (based on carbinol dehydrated) of 2,5-dimethylstyrene, b. p. 82–83° (23 mm.), $n^{20}\mathrm{D}$ 1.5395, d^{25}_{25} 0.902. The recovery of carbinol was 50 g. (14.5%).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.53; H, 9.13.

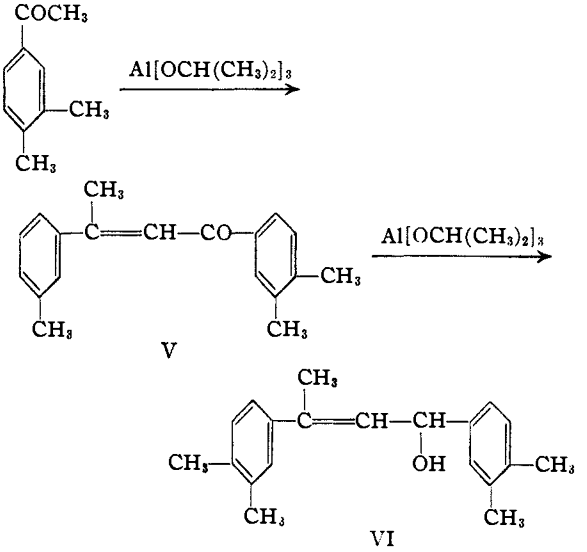
Klages and Keil[12] prepared 2,5-dimethylstyrene by the dehydrohalogenation of 3,4-dimethyl-α-chloroethylbenzene which they had obtained from 3,4-dimethylphenylmethylcarbinol. They reported a boiling point of 69° (10 mm.), $d^{17.5}_{4}$ 0.9072, $n^{17.5}\mathrm{D}$ 1.5236.

The dibromide of 2,5-dimethylstyrene was prepared in a similar manner to that described for 3,5-dimethylstyrene. The white crystalline solid melted at 62–62.5°. Klages and Keil[12] reported a melting point of 55°.

Anal. Calcd. for $C_{10}H_{12}Br_2$: C, 41.19; H, 4.14. Found: C, 41.03; H, 3.94.

3,4-Dimethylstyrene (IV)

This monomer was prepared according to the series of reactions described for the preparation of 2,4-dimethylstyrene except that *o*-xylene was used instead of *m*-xylene. Reduction of 3,4-dimethylacetophenone with Raney nickel and hydrogen gave satisfactory yields of the carbinol. Reduction by means of aluminum isopropoxide gave a low yield of the desired carbinol and a large quantity of high boiling material. A possible explanation is indicated in the scheme below. This high-boiling product could be the result of a dypnone-type condensation with subsequent reduction of the carbonyl group. Evidence described in the experimental section favors this possibility.



3,4-Dimethylacetophenone.—The procedure was that of Perkin and Stone[9] except that the reaction was carried out at 0°. The use of a higher temperature gave a lower yield of product. From 528 g. (4.98 moles) of *o*-xylene there was obtained 276 g. (47.8% based on the xylene used) of 3,4-dimethylacetophenone, b. p. 95–97° (4 mm.), $n^{20}\mathrm{D}$ 1.5381. The recovered xylene was 112 g. (21.3%). Norris and Arthur[15] reported an index of refraction at 20° of 1.5390.

3,4-Dimethylphenylmethylcarbinol.—Procedure A: (Aluminum Isopropoxide). The method of Marvel and Overberger[11] was employed. From 380 g. (2.56 moles) of 3,4-dimethylacetophenone there was obtained 104 g. (27%) of 3,4-dimethylphenylmethylcarbinol, b. p. 91° (3 mm.), $n^{20}\mathrm{D}$ 1.5284, d^{25}_{25} 0.970.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.41. Found: C, 79.95; H, 9.28.

3,4-Dimethylphenylmethylcarbinol has been prepared by Claus[16] by reduction of 3,4-dimethylacetophenone by means of zinc and alcoholic potassium hydroxide. He reported no physical constants for this carbinol.

The yield of high-boiling material was 210 g., b. p. 164–166° (4 mm.), $n^{20}\mathrm{D}$ 1.5384. The high boiling product reacted with bromine rapidly without the evolution of hydrogen bromide and reacted slowly with sodium. When a 25-g. sample was boiled with 200 cc. of 5% sodium hydroxide solution for three hours, no hydrolysis to the original 3,4-dimethylacetophenone occurred. This indicated that compound V, the primary product of the condensation, had been transformed to VI by reduction of the ketone group to the secondary hydroxyl group. A carbon–hydrogen analysis also indicated structure VI. On the basis of this cursory evidence, compound VI was assumed to be 1,3-di-(3,4-dimethylphenyl)-2-butene-1-ol.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.65; H, 8.63. Found: C, 85.41; H, 9.03.

Procedure B (Raney Nickel).—In a 500-cc., high-pressure steel bomb was placed 138 g. (0.93 mole) of 3,4-dimethylacetophenone, and one-half tablespoon of Raney nickel catalyst. The reduction was carried out at 100°. The initial hydrogen pressure was 1800 pounds at 100°. After dropping to 650 pounds, an additional 950 pounds of hydrogen pressure was added. The Raney nickel was removed by filtration and the alcohol removed by distillation. A second experiment was conducted in an identical

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[14] v. Auwers, *Ann.*, **408**, 212 (1915).

[15] Norris and Arthur, This Journal, **62**, 874 (1940).

[16] Claus, *J. prakt. Chem.*, (2) **41**, 396 (1889).

manner and the combined residues were distilled through a helix-packed column. The product boiled at 103-104° (6 mm.), n^{20}_D 1.5274. The yield of carbinol was 241 g. (1.61 moles) or 86% of the theoretical amount.

3,4-Dimethylstyrene.—The dehydration was carried out as described for the 3,5-isomer. From 256 g. (1.71 moles) of 3,4-dimethylphenylmethylcarbinol there was obtained 137 g. (80% based on the carbinol dehydrated) of 3,4-dimethylstyrene, b. p. 94-96° (26 mm.), n^{20}_D 1.5463, d^{25}_{25} 0.909. The recovery of carbinol was 62 g. (24.2%).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.04; H, 9.23.

3,4-Dimethylbenzoic Acid.—This styrene was further characterized by oxidation in the same manner as that described for the preparation of 2,4-dimethylbenzoic acid. The 3,4-dimethylbenzoic acid thus obtained melted at 162-163°. Frey and Horowitz[17] reported a melting point of 163° for this acid.

Polymerization of Isomeric Dimethylstyrenes.—In a Pyrex test-tube was placed 1 g. of the monomer. The test-tube was suspended under an ultraviolet lamp and left there until a hard polymer had been formed (ninety-two hours). The polymer was dissolved in 50 cc. of benzene and precipitated by slowly dropping the solution into 250 cc. of methanol with methanical stirring. This process was repeated and the powder obtained was dried for five days in a vacuum desiccator. All of these polymers are soluble in benzene.

Table I summarizes the data on these polymers.

TABLE I

Poly-dimethyl-styrene	Approximate mol. wt.[a]	Softening point, °C.	Analyses,[b] % Found C	H
3,5	17,700	148-152	90.76	9.27
2,4	9,000	178-180	90.38	9.27
2,5	18,500	171-176	90.09	9.30
3,4	15,500	163-175	90.94	9.26

[a] These approximate molecular weights were determined by viscosity measurements with the use of an equation developed by Kemp and Peters for the determination of the molecular weight of polystyrene using the *K* value for styrene (Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942)). [b] Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15.

Summary

1. The preparations of 3,5-, 2,4-, 2,5- and 3,4-dimethylstyrene are described.

2. The polymers of these monomers have been prepared and characterized.

URBANA, ILL. RECEIVED FEBRUARY 8, 1946

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[17] Frey and Horowitz, *J. prakt. Chem.*, (2) **43**, 113 (1891).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

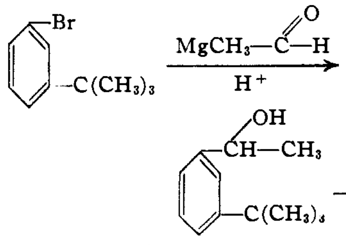
The Preparation and Polymerization of Some Alkyl Styrenes[1,2]

BY C. S. MARVEL, R. E. ALLEN AND C. G. OVERBERGER

In order to investigate the effects of large alkyl groups on the polymerization and copolymerization of styrene derivatives, a study of several branched-chain alkyl substituted styrenes has been carried out in this Laboratory. This paper reports the syntheses of *m-t*-butylstyrene, *m-s*-butylstyrene and *p*-cyclohexylstyrene and gives a brief summary of the properties of their polymers. Data on copolymerization will be reported later.

m-t-Butylstyrene

This monomer was prepared through the following series of reactions.



m-Bromo-t-butylbenzene.—This was prepared from 2-bromo-4-*t*-butylaniline by a procedure described in "Organic Syntheses" for the conversion of 3-bromo 4-aminotoluene[3] to *m*-bromotoluene. From 303 g. (1.33 moles) of 2-bromo-4-*t*-butylaniline there was obtained 160 g. (56.2%) of *m*-bromo-*t*-butylbenzene, b. p. 103-106° (17 mm.), n^{20}_D 1.5337, d^{4}_{20} 1.251.

Anal.[4] Calcd. for $C_{10}H_{13}Br$: C, 56.35; H, 6.15. Found: C, 56.88; H, 6.21.

m-t-Butylphenylmethylcarbinol.—Into a 5-liter three-necked, round-bottomed flask fitted with a stirrer, dropping funnel and condenser was placed 49.5 g. (2.04 gram atoms) of magnesium turnings covered with 50 cc. of dry ether. A solution of 434 g. (2.04 moles) of *m*-bromo-*t*-butylbenzene in 1.5 l. of dry ether was added over a period of two hours and the reaction mixture was stirred two hours longer. A solution of 110 g. (2.5 moles) of freshly distilled acetaldehyde dissolved in 1.5 liters of dry ether was added in one hour and the mixture was stirred for an additional two hours.

The reaction mixture was treated in the usual manner, to isolate the product.

After the solvent was removed, the residue was distilled through a helices-packed column. The product boiled at 130-134° (17 mm.), n^{20}_D 1.5120, d^{4}_{20} 0.9578. The yield of *m-t*-butylphenylmethylcarbinol was 200 g. (55%).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.96; H, 9.94.

m-t-Butylstyrene.—The *m-t*-butylphenylmethylcarbinol was dehydrated by two standard procedures.

Procedure A: The general method of Marvel and Brown[5] was used, except that 1 g. of *p-t*-butylcatechol was added to the reaction mixture as an inhibitor. From 377 g. (2.12 moles) of *m-t*-butylphenylmethylcarbinol there was

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] This is the twenty-third communication on vinyl polymers. For the twenty-second, see Marvel, Saunders and Overberger, THIS JOURNAL, **68**, 1085 (1946).

[3] Bigelow, Johnson and Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 133.

[4] Microanalyses by Mr. H. S. Clark, Illinois State Geological Survey.

[5] Marvel and Brown, THIS JOURNAL, **59**, 1175 (1937).