one ($k_H/k_D = 1.5$)[20] and the iodination of phenol ($k_H/k_D = 4$).[25] These results are consistent with the two-step mechanism, with step 2 at least partially rate-controlling (*i.e.*, v_{-1} comparable to or greater than v_2). Alternatively, these results can be accommodated by the one-step mechanism, 19, with C–H bond stretching having made measurable progress in the transition state. However, the two-step mechanism more reasonably accounts for both types of observations, *i.e.*, examples in which no isotope effect was found and those in which there was an isotope effect.

Perhaps the best evidence in favor of the two-step mechanism is the excellent work of Zollinger.[23] It was found that the rate of diazonium salt coupling with the unhindered 1-naphthol-4-sulfonic acid was essentially the same for the 2-deutero as for the unlabeled compound. However, the isotope effect for the coupling of the hindered 1-deutero-2-naphthol-6,8-disulfonic acid with various diazonium salts was considerable. The k_H/k_D ratio varied from 4.8 to 6.5, depending on the structure of the diazonium salt. The results were interpreted in terms of the two-step mechanism, with varying contributions of the second step to the rate-controlling processes. Base catalysis (by amines) was observed for the hindered naphthol but not for the unhindered naphthol. In addition, the catalytic effect of the base decreased as its size was increased. Zollinger's results are completely consistent with the two-step mechanism and would be difficult indeed to rationalize in terms of the one-step mechanism.

The aromatic decarbonylation is in many respects quite similar to the reaction studied by Zollinger. That is, the experimental findings show that the substitution proceeds *via* an intermediate (specifically $BH^{\oplus *}$, equation 2). Also, by a suitable change in the medium and in substrate structure, the rate-controlling step can be changed from one in which the intermediate is formed to one in which it is decomposed. Moreover, the situation has been achieved in which these two steps are *both* rate-controlling steps of comparable magnitude.

The two-step mechanism then rationally accounts for all the results cited in this section, taken separately and as a whole. The one-step mechanism can be fitted only to some of the facts. It therefore is likely that most aromatic electrophilic substitution reactions, if not all, proceed *via* an intermediate.

Acknowledgment.—The authors wish to thank the National Science Foundation for financial assistance in this study.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. Reactions of α-Ethylstyrene and *cis*- and *trans*-α,β-Dimethylstyrene with Stannic Chloride[1]

BY C. G. OVERBERGER, ELI M. PEARCE[2] AND D. TANNER[2]

RECEIVED OCTOBER 24, 1957

Reaction of α-ethylstyrene with stannic chloride at 0° for 1 hour gives a mixture of dimer (78%) and trimers (16%). The dimer was characterized as 3,5-diphenyl-5-methyl-2-heptene. After 24-hour contact with catalyst the cyclic dimer, 1,3-diethyl-1-methyl-3-phenylhydrindane, (46%) was isolated. A suggestion is made for the lack of polymer formation on the basis of steric factors. *cis*-α,β-Dimethylstyrene, after contact with stannic chloride for 24 hours, gave a mixture of dimers (31%) from which 3,5-diphenyl-5-methyl-2-heptene was characterized. *trans*-α,β-Dimethylstyrene did not react under these conditions.

α-Methylstyrene homopolymerized very rapidly with cationic catalysts[3] and has been copolymerized with a variety of substituted styrenes,[4] including *p*-chlorostyrene.[5] Values obtained for the monomer reactivity ratios for the system α-methylstyrene, *p*-chlorostyrene and stannic chloride as catalyst were indicative of the enhanced reactivity of α-methylstyrene under these conditions, which can be understood on the basis of polar and resonance effects. The electron-donating effect of the methyl group attached directly to the double bond increases the reactivity of the monomer toward a carbonium ion. In addition, the carbonium ion formed from α-methylstyrene has increased resonance stabilization due to hyperconjugation effects when compared with styrene.

When the methyl group in the α-position was lengthened by a methylene unit the following anomalous observations were made: (a) homopolymerization with stannic chloride as catalyst did not occur; (b) copolymerization with *p*-chlorostyrene gave different copolymer composition curves with scattering considerably beyond experimental error. From these data, it would seem that the reactivity of α-ethylstyrene was much less than that of *p*-chlorostyrene, a somewhat unexpected result not easily explained by steric factors alone. The present research was initiated to explain the above phenomena.

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[1] This is the 8th in a series of papers in the general field of ionic-catalyzed polymerization. For the previous paper in this series, see C. G. Overberger, G. F. Endres and Avito Monaci, THIS JOURNAL, **78**, 1969 (1956).

[2] This paper comprises portions of theses presented by D. Tanner and Eli M. Pearce in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] A. B. Hersberger, J. C. Reid and R. G. Heiligmann, *Ind. Eng. Chem.*, **37**, 1073 (1945); D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

[4] C. G. Overberger, *et al.*, THIS JOURNAL, **74**, 4848 (1952).

[5] (a) G. Smets and L. deHaes, *Bull. soc. chim. Belges*, **59**, 13 (1950); (b) C. G. Overberger, L. H. Arond and J. J. Taylor, THIS JOURNAL, **73**, 5541 (1951).

Experimental[6]

α-Ethylstyrene was prepared by the procedure of Overberger and Tanner[7] by pyrolysis of β-phenylbutyl acetate and gave a 74% yield of a water-white liquid, b.p. 85–86° (30 mm.), $n^{26.5}_D$ 1.5260 (70% yield, b.p. 31° (1.3 mm.), n^{25}_D 1.5264, from β-phenylbutyl acetate[7]).

cis- **and** *trans*-**α,β-Dimethylstyrene.** (a) **Preparation from 3-Phenyl-2-butyl Acetate.** (1) **3-Phenyl-2-butanol.**—To 75.3 g. of magnesium (3.1 g. at.) in 250 ml. of anhydrous ethyl ether was added dropwise with stirring, 440 g. (3.1 moles) of methyl iodide in 2500 ml. of anhydrous ethyl ether and refluxed for an additional hour. To the Grignard reagent was added 403 g. (3.0 moles) of freshly distilled hydratropic aldehyde in 500 ml. of anhydrous ethyl ether, and the reaction mixture was refluxed for an additional hour. A saturated aqueous ammonium chloride solution (*ca.* 450 ml.) was added, and the ethyl ether layer decanted from the white solid residue. The residue was washed twice with 250-ml. portions of ethyl ether. The ethyl ether washes were combined with the original ethyl ether layer and dried overnight with magnesium sulfate. The ethyl ether was removed by atmospheric distillation and the residue distilled *in vacuo* through a 2 × 25 cm. Vigreux column to give 379 g. (82%) of 3-phenyl-2-butanol, b.p. 92° (5 mm.), n^{26}_D 1.5160, d^{25}_4 0.9824 (no yield reported, b.p. 108° (10 mm.), n^{25}_D 1.5159 for racemate I; b.p. 105° (10 mm.), n^{25}_D 1.5167 for racemate II, by separation of racemates of the alcohol from the reaction of hydratropic aldehyde and methylmagnesium bromide).[8]

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.82; H, 9.41.

(2) **3-Phenyl-2-butyl Acetate.**—3-Phenyl-2-butanol (192.2 g., 1.28 moles) was refluxed for 24 hr. with 306 g. (3 moles) of acetic anhydride and 50 g. of sodium acetate and worked up by the procedure of Overberger and Tanner.[7] Distillation *in vacuo* gave 215.4 g. (87.6%) of the acetate, b.p. 76° (1.5 mm.), n^{24}_D 1.4885, d^{20}_4 0.9924 (no yield given, no b.p., n^{25}_D 1.4877, by treatment of *p*-toluenesulfonate, with acetic acid, acetic anhydride and potassium acetate[8b]).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.27; H, 8.37.

(3) **α,β-Dimethylstyrene.**—The acetate was pyrolyzed at 500° by the technique previously described[7] to give a 74% yield of olefinic material. Vacuum distillation through a 2 × 90 cm. column packed with $^1/_{16}$ in. Fenske helices gave a fraction corresponding to *cis*-α,β-dimethylstyrene (38%), b.p. 93–94° (30 mm.), n^{25}_D 1.5404, λ_{max} 243 mμ, log ε 4.03 (no yield reported, b.p. 93.8° (29.5 mm.), n^{25}_D 1.5402, λ_{max} 243 mμ, log ε 4.08, by refluxing methyl ethyl phenylcarbinol with sulfuric acid[8b]), an intermediate fraction (5%), b.p. 81–93° (30 mm.), n^{25}_D 1.5368, and a fraction corresponding to a mixture of *trans*-α,β-dimethylstyrene and 3-phenyl-1-butene (31%), b.p. 79–81° (30 mm.), n^{25}_D 1.5130, λ_{max} 235 mμ, log ε 3.65 (no yield given, b.p. 79° (30 mm.), n^{25}_D 1.5093, λ_{max} 235 mμ, log ε 3.3, by pyrolysis of the xanthate at 180°[8a]).

The mixture containing 3-phenyl-1-butene, 14 g., was placed in a steel bomb with 15 g. of potassium hydroxide in 38 ml. of absolute ethanol and heated with shaking for 48 hr. at 150°.[9] The cooled reaction mixture was extracted three times with 100 ml. of ether, the ether washed with water until neutral to litmus and dried overnight with magnesium sulfate. The ether was removed *in vacuo* and the residue vacuum distilled through a 0.5 × 6 in. Vigreux column giving a 7 g. (50%) mixture of *cis*- and *trans*-α,β-dimethylstyrene, b.p. 82–83° (30 mm.), n^{24}_D 1.5438, λ_{max} 243 mμ, log ε 4.01 (76% yield, b.p. 107–109° (21 mm.), λ_{max} 244 mμ, log ε 3.94, by dehydration of methylethylphenylcarbinol with acetic anhydride[10]).

(b) **Preparation from Methylethylphenylcarbinol.**—Methylethylphenylcarbinol was refluxed with 4 *N* sulfuric acid and the reaction mixture worked up as previously described by Cram.[8] Distillation in vacuum gave a fraction b.p. 77–92° (30 mm.) (80%). Repeated fractionation through a 2 × 90 cm. column packed with $^1/_{16}$ in. Fenske helices gave the following fractions: *cis*, b.p. 92° (30 mm.), n^{26}_D 1.5408, λ_{max} 243 mμ, log ε 4.09 (no yield given, b.p. 93° (30 mm.), n^{25}_D 1.5393, λ_{max} 243 mμ, log ε 4.08[8]); b.p. 80–92°, n^{26}_D 1.5360; *trans* and *cis* mixture (85:15), b.p. 86–89° (45 mm.), n^{26}_D 1.5230, λ_{max} 235 mμ, log ε 3.92 (for pure *trans*, no yield given, b.p. 77° (29.5 mm.), n^{25}_D 1.5192, λ_{max} 235 mμ, log ε 3.91[8]). This material was subsequently used in all experiments where *cis*- and *trans*-α,β-dimethylstyrene were used.

Reaction of α-Ethylstyrene with Stannic Chloride for One Hour.—The procedure was identical to that of Endres and Overberger[11] for the polymerization of styrene with stannic chloride. The charge consisted of 31.1 g. of α-ethylstyrene, 0.9 g. of stannic chloride, 50 ml. of nitrobenzene and 42 ml. of carbon tetrachloride. After 1 hr. at 0°, the mixture was stirred vigorously with 150 ml. of water. The organic and aqueous layers were separated, the aqueous layer washed twice with 25 ml. of carbon tetrachloride, and the washes added to the organic layer. The organic layer was dried with Drierite overnight, and the nitrobenzene and carbon tetrachloride removed in vacuum. The residue was distilled *in vacuo* to give 24.7 g. (78%) of unsaturated dimer, b.p. 133–135° (1.2 mm.), n^{25}_D 1.5634, d^{20}_4 0.9884, λ_{max} 242 mμ, log ε 3.74, λ_{max} 272 mμ, log ε 3.05; and 5.0 g. (16%) of trimers, b.p. 219° (1.5 mm.), λ_{max} 243, log ε 3.39, λ_{max} 273, log ε 3.04. The infrared spectrum of the dimer exhibited a band at 840 cm.$^{-1}$ due to C–H out of plane deformation.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 91.04; H, 8.80; mol. wt., 245. Calcd. for $C_{30}H_{36}$: C, 90.85; H, 9.15; mol. wt., 396. Found: C, 90.88; H, 9.02; mol. wt., 355.

Structure Proof of 3,5-Diphenyl-5-methyl-2-heptene (I). (a) **Reduction.**—To 250 mg. of reduced platinum oxide in 20 ml. of glacial acetic acid in a semi-micro hydrogenation apparatus was added 2.53 g. of the unsaturated dimer in 30 ml. of glacial acetic acid. The hydrogen uptake was 236 ml. (100% calculated for one aliphatic double bond). The reaction mixture was added to 75 ml. of water and extracted three times with 100 ml. of ethyl ether. The ether was washed with a 10% sodium bicarbonate solution until the evolution of carbon dioxide ceased, and then washed with water until neutral to litmus. The washes were combined and extracted with 100 ml. of ethyl ether which was then washed with 50 ml. of water and combined with the main ethyl ether extract. The ethyl ether was dried over magnesium sulfate and the residue distilled at 124–125° (0.7 mm.) to give 1.94 g. (77%) of the saturated hydrocarbon, 3,5-diphenyl-5-methylheptane, $n^{25.5}_D$ 1.5442, d^{20}_4 0.9665. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.43; H, 10.00.

(b) **Ozonolysis.** (1) **Procedure.**—The procedure was similar to that previously described.[7] About three times the theoretical quantity of a 3% ozone–oxygen mixture was passed through a solution of 2 g. of the dimer dissolved in 50 ml. of ethyl acetate. The mixture was then added to 10 g. of zinc dust in 50 ml. of water and shaken vigorously for 20 minutes. To the water layer was added 3.64 g. of methone dissolved in 25 ml. of 50% ethanol. The white precipitate was filtered and recrystallized twice from 50% ethanol to give 2.1 g. (48%) of acetaldehyde dimedone, m.p. 138–140°, mixed m.p. with an authentic sample 140–142° (139°).[12] The ethyl acetate layer was dried over magnesium sulfate and the residual colorless liquid was dissolved in 20 ml. of 95% ethanol and allowed to react with 2,4-dinitrophenylhydrazine reagent by the procedure of Shriner and Fuson.[13] A mixture consisting chiefly of a yellow-orange 2,4-dinitrophenylhydrazone, m.p. 85–86°, and a small amount of a red 2,4-dinitrophenylhydrazone, m.p. 110–112°, was obtained which could be separated and isolated after about 15 recrystallizations from 95% ethanol.

(c) **Preparation of 1,3-Diphenyl-3-methylpentan-1-one 2,4-Dinitrophenylhydrazone.** (1) **Preparation of Ethyl 1-Cyano-3-methyl-3-phenyl Valerate.**—To 4.9 g. (0.2 g. atm.) of magnesium previously treated with 25 g. (0.2 mole) of ethyl bromide in 400 ml. of anhydrous ethyl ether at 0° was

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[6] All melting points are corrected. Analyses by Dr. Schwarzkopf, New York, N. Y., and Dr. K. Ritter, Basel, Switzerland.

[7] C. G. Overberger and D. Tanner, THIS JOURNAL, **77**, 369 (1955).

[8] (a) D. J. Cram, *ibid.*, **71**, 3883 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952).

[9] A. Klages, *Ber.*, **39**, 2587 (1906).

[10] Y. Hirschberg, THIS JOURNAL, **71**, 3241 (1949).

[11] G. F. Endres and C. G. Overberger, *ibid.*, **77**, 2201 (1955).

[12] W. M. D. Bryant, *ibid.*, **60**, 2815 (1938).

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Ed., John Wiley and Sons, New York, N. Y., 1948, p. 171.

added 43.4 g. (0.2 mole) of ethyl 1-cyano-2-methylcinnamate[14] in 100 ml. of anhydrous ether. After the final addition the mixture was refluxed for 1 hr., cooled, and the Grignard complex destroyed with a saturated ammonium chloride solution. The ethyl ether was decanted, the residue washed with additional ethyl ether, and combined with the decanted solution. The ether was removed by atmospheric distillation and the residue distilled *in vacuo* to give 39 g. (80%) of ethyl 1-cyano-3-methyl-3-phenylvalerate, b.p. 135° (0.6 mm.), $n^{24}\mathrm{D}$ 1.5096, d^{20}_4 1.060.

Anal. Calcd. for $C_{15}H_{19}O_2N$: C, 73.40; H, 7.80; N, 5.71. Found: C, 73.56; H, 7.72; N, 6.00.

The infrared spectrum showed nitrile absorption at 2240 cm.$^{-1}$ and ester carbonyl absorption at 1740 cm.$^{-1}$. There was no $\lambda_{\max}$ in the ultraviolet spectrum.

(2) **Preparation of 2-Methyl-2-phenylvaleric Acid.**—To 39.0 g. (0.16 mole) of ethyl 1-cyano-3-methyl-3-phenylvalerate in 144 ml. of ethylene glycol monomethyl ether was added 80 g. of potassium hydroxide in 40 ml. of water. The mixture was refluxed for 8 hr., cooled, added to 144 ml. of concentrated hydrochloric acid, and extracted 5 times with 200-ml. portions of ethyl ether. The ether extract was washed 4 times with 200-ml. portions of 10% sodium hydroxide and the hydroxide washes acidified with concentrated hydrochloric acid. The acidified mixture was extracted 3 times with 200-ml. portions of ethyl ether, the ether evaporated, and the residue refluxed for 6 hr. with 150 ml. of 10% hydrochloric acid. The reaction mixture was then extracted 3 times with 100-ml. portions of ethyl ether, the ether layer washed with 10% aqueous sodium bicarbonate, and then with water until neutral to litmus. The ether layer was dried over Drierite. Distillation of the residue gave 16.4 g. (54%) of 2-methyl-2-phenylvaleric acid, b.p. 122° (0.8 mm.), $n^{27}\mathrm{D}$ 1.5172, d^{20}_4 1.037.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; neut. equiv., 192. Found: C, 74.99; H, 8.31; neut. equiv., 194.

(3) **1,3-Diphenyl-3-methylpentan-1-one 2,4-Dinitrophenylhydrazone (III).**—Anhydrous cadmium chloride, 8.8 g., was added to a cold solution of phenylmagnesium bromide previously prepared from 1.95 g. (0.08 g. at.) of magnesium, 8.85 ml. (0.084 mole) of bromobenzene and 50 ml. of dry ethyl ether according to the procedure of Hoehn and Moffett.[15] The crude acid chloride was prepared from 6 g. (0.03 mole) of 2-methyl-2-phenylvaleric acid with 10 ml. of thionyl chloride. Excess thionyl chloride was removed by distillation *in vacuo*, and 10 ml. of a 1:1 ethyl ether–benzene solution was added and removed twice, under vacuum. The acid chloride was dissolved in 100 ml. of anhydrous benzene, the solution heated to reflux, and the diphenylcadmium solution added dropwise. The mixture was refluxed for an additional half-hour, cooled, and decomposed by the addition of 100 ml. of 10% hydrochloric acid. The organic and aqueous layers were separated, the aqueous layer washed with ethyl ether, and the ethyl ether wash combined with the organic layer. The combined benzene-ether layer was washed with dilute hydrochloric acid and then with water, and the benzene and ether removed by distillation. Distillation of the residue *in vacuo* gave 7.2 g. of a crude ketonic fraction, b.p. 140–160° (0.8 mm.), which could not be purified by further distillations. Chromatography on 100 g. of neutral alumina of 3.9 g. of the crude ketonic fraction with petroleum ether (b.p. 39–51°) as the eluent, and subsequent reaction of the fractions with 2,4-dinitrophenylhydrazone reagent,[13] gave a 5.2 g. mixture of a yellow-orange 2,4-dinitrophenylhydrazone (III), and a small quantity of a red 2,4-dinitrophenylhydrazone. The over-all yield, based on acid, was approximately 70% of the 2,4-dinitrophenylhydrazone. After about 15 recrystallizations from 95% ethanol, a pure sample of 2,4-dinitrophenylhydrazone III, m.p. 85–86°, mixed m.p. with yellow-orange derivative from ozonolysis, m.p. 85–86°, melted at 85–86°, was obtained.

Anal. Calcd. for $C_{24}H_{24}N_4O_4$: C, 66.49; H, 5.59; N, 12.96. Found: C, 66.56; H, 5.76; N, 12.77.

The red 2,4-dinitrophenylhydrazone IV, m.p. 110–112°, mixed m.p. with red derivative from ozonolysis, m.p. 110–112°, melted at 110–112°, obtained from the final mother liquor analyzed correctly for the monohydrate.

Anal. Calcd. for $C_{24}H_{24}N_4O_4H_2O$: C, 61.76; H, 5.82; N, 12.44. Found: C, 61.68; H, 5.75; N, 12.05.

Reduction of Trimer.—The α-ethylstyrene trimer, 0.6374 g., with 100 mg. of reduced platinum oxide in 30 ml. of glacial acetic acid as previously described adsorbed 15 ml. (40% based on one aliphatic double bond) of hydrogen.

Reaction of α-Ethylstyrene with Stannic Chloride for 24 Hours.—The procedure was the same as described above except that the contact time with catalyst was 24 hr. From the reaction mixture was isolated a dimeric fraction, b.p. 104–106° (0.3 mm.). Ozonolysis of the dimeric fraction, followed by chromatography of 1.8 g. of the ethyl acetate residue on 100 g. of basic alumina, with petroleum ether (b.p. 39–51°) as the eluent, gave 0.82 g. (46%) of 1,3-diethyl-1-methyl-3-phenylhydrindane, $n^{22}\mathrm{D}$ 1.5642; $\lambda_{\max}$ 259 mμ, log ϵ 2.92, $\lambda_{\max}$ 265 mμ, log ϵ 3.04, $\lambda_{\max}$ 272, log 3.00. A detailed structure proof was not attempted.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.08; H, 9.05.

Reaction of *cis*-α,β-Dimethylstyrene with Stannic Chloride for 24 Hours.—The procedure was the same as that previously described. The charge consisted of 18.8 g. of *cis*-α,β-dimethylstyrene, 0.54 g. of stannic chloride, 30.0 ml. of nitrobenzene and 25.2 ml. of carbon tetrachloride and was kept at 0° for 24 hr. A 5.7-g. (30.3%) yield of dimeric material, b.p. 127.5° (0.5 mm.), $n^{25}\mathrm{D}$ 1.5670, was obtained.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15; mol. wt., 264. Found: C, 91.17; H, 9.03; mol. wt., 264.

The dimeric fraction, 0.5294 g., was hydrogenated as previously described with 100 mg. of reduced platinum oxide in 30 ml. of glacial acetic acid. The hydrogen uptake was 22.5 ml. (45% based on one aliphatic double bond).

Ozonolysis and chromatography of 1.9 g. of the dimeric fraction as previously described gave 0.9 g. (47%) of dimeric material, $n^{23}\mathrm{D}$ 1.5676, and 0.35 g. of a crude ketonic fraction. The infrared spectrum of the dimeric material was similar but not identical to that of 1,3-diethyl-1-methyl-3-phenylhydrindane. The ultraviolet spectrum exhibited the following absorption peaks: $\lambda_{\max}$ 244 mμ, log ϵ 3.44, $\lambda_{\max}$ 265 mμ, log ϵ 3.06, $\lambda_{\max}$ 272 mμ, log ϵ 2.96. Another ozonolysis of the ozonized hydrocarbon fraction gave similar spectral results. The ketonic fraction was treated with 2,4-dinitrophenylhydrazine reagent and the hydrazones recrystallized as previously described to yield 1,3-diphenyl-3-methylpentan-1-one 2,4-dinitrophenylhydrazone, m.p. 85–86°, mixed m.p. 85–86°, and the hydrate, m.p. 110–112°, mixed m.p. 110–112°.

When the aqueous ozonolysis layer was treated with methone reagent and the derivative recrystallized as previously described, 0.5 g. of acetaldehyde dimedone, m.p. 138–140°, was obtained. A mixed m.p. with an authentic sample, m.p. 142°, melted at 140–142° (139°).[12]

Reaction of *trans*-α,β-Dimethylstyrene with Stannic Chloride for 24 Hours.—The procedure was identical to that previously described. The charge consisted of 6.7 g. of *trans*-α,β-dimethylstyrene, 0.18 g. of stannic chloride, 16.2 g. of nitrobenzene and 13.2 g. of carbon tetrachloride maintained at 0° for 24 hr. Distillation gave 14 g. of material, b.p. 65° (4 mm.), $n^{25}\mathrm{D}$ 1.5410, which appeared to be a mixture of α,β-dimethylstyrene and nitrobenzene. No dimeric material was isolated.

Attempted Copolymerizations. (a) With *p*-Chlorostyrene.—Copolymerizations of α-ethylstyrene and *cis*- and *trans*-α,β-dimethylstyrene, with *p*-chlorostyrene and stannic chloride as catalyst were attempted by the procedure previously described.[5b] No copolymers were isolated with *cis*- and *trans*-α,β-dimethylstyrene. α-Ethylstyrene, in three separate runs, gave three different copolymer composition curves with scattering beyond experimental error (Table I).

(b) With Chloroprene.—Copolymerization of *cis*- and *trans*-α,β-dimethylstyrene with freshly distilled chloroprene and stannic chloride as catalyst were attempted by the procedure previously described.[5b] No copolymers were isolated.

Results and Discussion

The results of the present investigation indicate that α-ethylstyrene formed dimers and trimers with stannic chloride under conditions in which α-methylstyrene polymerized.[3] The following is suggested as a plausible mechanism (equation 1)

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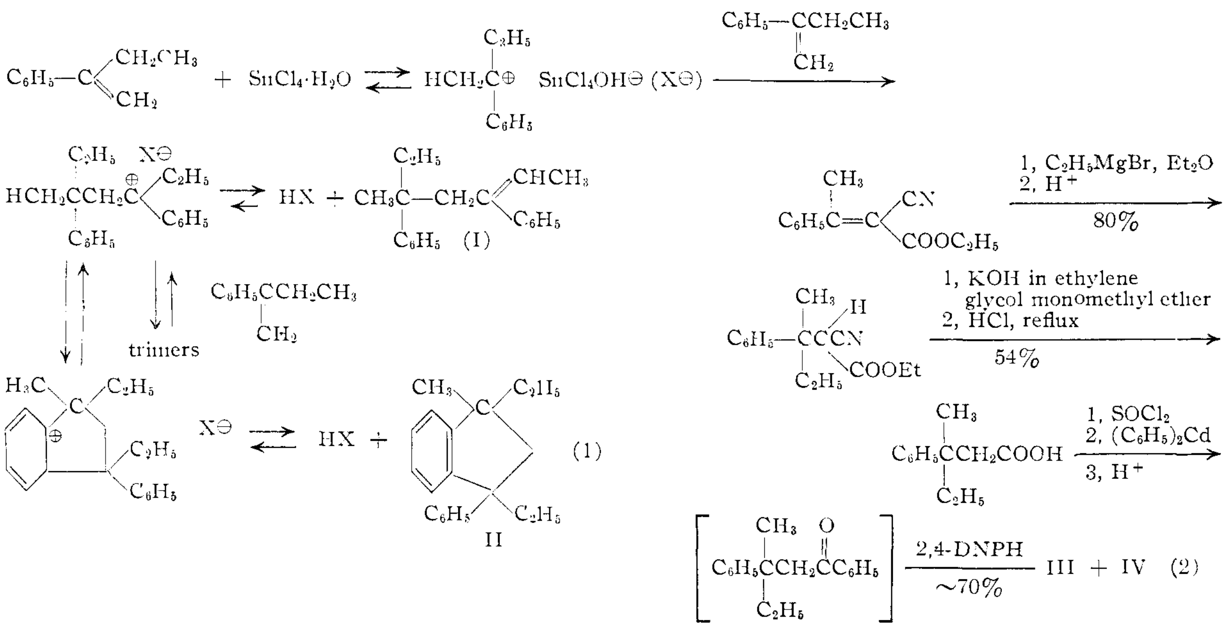
[14] A. C. Cope, C. M. Hoffman, C. Wykoff and E. Hardenbergh, This Journal, **63**, 3452 (1941).

[15] W. M. Hoehn and R. B. Moffett, *ibid.*, **67**, 740 (1945).



(1)

(2)

After a 1-hour contact with catalyst, the dimer, 3,5-diphenyl-5-methyl-2-heptene (I) (78%) and a mixture of trimers (16%) were isolated. The olefin I adsorbed 100% of the theoretical quantity of hydrogen with reduced platinum oxide in glacial acetic acid and the product analyzed correctly for 3,5-diphenyl-5-methylheptane. Ozonolysis of the olefin I gave acetaldehyde dimethone, 1,3-diphenyl-3-methylpentan-1-one 2,4-dinitrophenylhydrazone (III) and its hydrate IV. The 2,4-dinitrophenylhydrazones were prepared independently as shown in equation 2, and no depression of melting points were observed. A previously reported synthesis of 1,3-diphenyl-3-methylpentan-1-one by the reaction of ethylmagnesium bromide on dypnone was not satisfactory for preparative purposes.[16] The infrared and ultraviolet spectra of olefin I were consistent with the proposed structure.

Table I

Copolymerization of α-Ethylstyrene (M_2) with p-Chlorostyrene (M_1)

M_2 in monomer mixture[a]	Reaction time, hr.	Conversion, %	Cl, %	m_2 in copolymer
0.195	0.3	9	20.37	0.213
.302	.3	6	20.43	.210
.399	.4	6	20.54	.206
.493	1.0	5	20.57	.206
.592	1.3	6	15.67	.399
.732	34.0	6	13.13	.498
.802	23.6	5	18.54	.285
.504	0.7	5	20.32	.214
.305	.7	8	20.54	.205
.160	.1	8	19.88	.233
.246	.3	7	18.96	.268
.346	.4	5	17.81	.314
.443	.5	6	18.62	.282
.541	1.0	6	19.28	.255
.648	2.3	7	17.74	.316
.745	14.3	5	19.67	.240
.845	96.0	5	17.76	.317

[a] Corrected for conversions above 6% using the formula $M_2 = M_2' + \frac{M_2' - m_2}{2} \times$ conversion, where M_2 and M_2' are the corrected and uncorrected values, respectively, for the concentration of M_2 in the monomer mixture.

Reduction of the trimer fraction showed the presence of an olefin (40%) probably similar in structure to I, with the remaining 60% of trimer probably related to II. The ultraviolet spectrum of the trimer mixture supported these conclusions.

After α-ethylstyrene was in contact with stannic chloride for 24 hr., 1,3-diethyl-1-methyl-3-phenylhydrindane (II) (46%) was isolated. The evidence for the structure of II was based primarily on the fact that olefin I was an intermediate in its formation and its structure was not proven rigorously. The ultraviolet spectra contained three maxima at 259, 265 and 272 mμ, consistent with the proposed structure.[17]

These results were in agreement with those suggested by Dainton and Tomlinson[18] for the termination process involved in the polymerization of α-methylstyrene with stannic chloride where kinetic termination gave a postulated terminal olefin which subsequently gave a substituted hydrindane upon rearrangement. Similar results have been obtained from styrene and α- and β-substituted styrenes, by refluxing the respective compounds with aqueous inorganic acids. Styrene, by refluxing with 53% sulfuric acid, gave an unsaturated and a saturated dimer and trimers.[19] Dimerization of a variety of ring substituted styrenes and α-methylstyrenes has been reported recently.[20] Van der Zanden and Rix have reported that α-methylstyrene dimerized faster than β-methyl-

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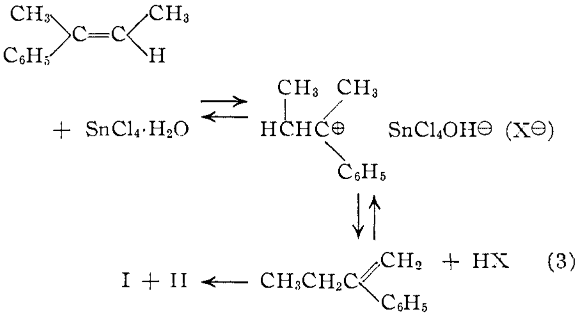
styrene[21] as do the *p*-methoxy substituted compounds.[22] The unsaturated dimer obtained from α-methylstyrene and phosphoric acid has been cyclized by treatment with stannic chloride,[23] as has been the unsaturated dimer obtained from the *p*-methoxy substituted compound.[24] Many other examples of the acid dimerization reaction are known and are reviewed by Müller.[25]

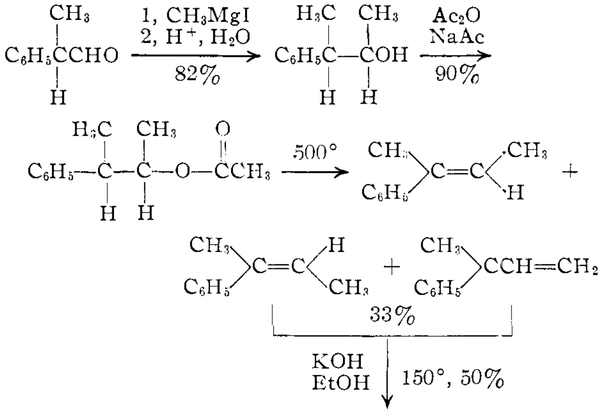
The predominant product obtained from α-methylstyrene with stannic chloride catalyst was polymer, with small quantities of dimer, trimer and other low molecular weight fractions.[18] As noted here with α-ethylstyrene, the dimerization process predominates with no apparent polymer formation. The addition of a methylene unit in the α-position is capable of creating a steric factor which makes polymerization to high polymer prohibitive. Stated another way, the added steric factor raises the activation energy of the propagation step sufficiently to approach the activation energy for the termination processes.[26] This steric factor may readily be seen from an examination of molecular models, thus more than three units of α-ethylstyrene cannot be readily joined. The lack of reproducibility in the copolymerization studies of α-ethylstyrene with *p*-chlorostyrene can be explained by the presence of varying amounts of dimeric material in the reaction mixture which would be difficult to control due to the nature of the system itself.

cis-α,β-Dimethylstyrene gave a 31% yield of dimers with stannic chloride for 24 hours at 0°, whereas the *trans* isomer did not give dimers under the same conditions. The dimer mixture was quantitatively reduced, showing the presence of 55% olefin. Ozonolysis of the mixture with separation and identification of the oxidation fragments showed that the olefin was identical to olefin I. This suggested that one of the primary reactions involved was the equilibration of *cis*-α,β-dimethylstyrene to α-ethylstyrene, with subsequent dimerization of the α-ethylstyrene (equation 3).



An explanation for the lack of reactivity of the *trans* isomer under these conditions is the good possibility that steric interaction of the vicinal methyl and phenyl groups prevents complete coplanarity in the transition state preceding the formation of the adduct carbonium ion; thus the monomer is less reactive.

cis- and *trans*-α,β-dimethylstyrene were prepared initially by the pyrolysis of 3-phenyl-2-butyl acetate, in preference to the acid dehydration of methylethylphenylcarbinol,[8] since it was desired to obtain the respective dimethylstyrenes free from α-ethylstyrene. From the acetate pyrolysis, in addition to *cis*- and *trans*-α,β-dimethylstyrene 3-phenyl-1-butene also was obtained. It is of interest that the Saytzeff elimination products predominated over the Hofmann elimination product. However, Bailey and Hewitt[27] have shown that under acidic conditions the Hofmann elimination products from the acetate pyrolysis can isomerize to the more resonance stabilized compounds. Similar results have been obtained for the pyrolysis of 3-phenyl-2-butyl xanthate.[8a] 3-Phenyl-1-butene was isomerized to a mixture of *cis*- and *trans*-α,β-dimethylstyrene by heating with ethanolic potassium hydroxide in a bomb[9] (equation 4)



cis- and *trans*-α,β-DMS (4)

Initially it was not apparent why the dehydration of methylethylphenylcarbinol with aqueous sulfuric acid gave only *cis*- and *trans*-α,β-dimethylstyrene. It now seems obvious from our previous observations that some α-ethylstyrene was probably formed but subsequently dimerized, and thus was not isolated. *cis*- and *trans*-α,β-dimethylstyrene prepared *via* the dehydration procedure was used in all experiments. The α,β-dimethylstyrene did not copolymerize with *p*-chlorostyrene or chloroprene at 0° with stannic chloride as catalyst.

Acknowledgment.—We are grateful to E. I. du Pont and Nemours and Co. for a research fellowship granted to Eli M. Pearce for the year 1955–1956 which made this research possible. We are also grateful to the Research Corporation for a grant which made a portion of this research possible.

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