[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

# High Pressure Thermal Reactions of Propyl- and Isopropylbenzene, *p*-Cymene and *s*-Butylbenzene. Isomerization of Alkyl Groups[1]

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The behavior of alkyl benzenes at elevated pressures and temperatures was investigated in a flow-type apparatus using a stainless steel reaction tube lined with copper and filled with copper pellets. Isopropylbenzene, *p*-cymene and *s*-butylbenzene were passed through the reaction tube at temperatures ranging from 479 to 528° under a pressure of 816 atmospheres and at an hourly liquid space velocity of 1.00 to 1.46. The liquid products of the reaction contained alkyl benzenes having part of the original alkyl groups cleaved, isomers of the original alkyl benzenes, and higher boiling material which contained diarylalkanes. Isopropylbenzene and *p*-cymene yielded substantial amounts of *n*-propylbenzene and *p*-*n*-propyltoluene while *s*-butylbenzene formed some *n*-butylbenzene. A free radical mechanism was formulated to explain the various products identified.

The behavior of alkyl benzenes at elevated pressures and temperatures has heretofore not been investigated. It was decided to carry out the investigation in a flow-type system since it is possible to control the temperature, contact time and to readily remove the primary reaction products. The flow-type apparatus used in the present study has been described previously.[3] The stainless steel reaction tube was lined with copper and filled with copper pellets. Care was taken to eliminate any contact between the stainless steel and the hydrocarbons since at elevated pressures and temperatures, stainless steel may assume catalytic properties.[4]

**Isopropylbenzene.**—Isopropylbenzene was passed through the reaction tube at 479, 501 and 528° under a pressure of 816 atmospheres (12,000 p.s.i.) and at an hourly liquid space velocity of 1.00 to 1.46. The extent of reaction under the above described conditions amounted to 23% at 479° and to 76% at 528°. The liquid products resulting from these reactions were composed of benzene, toluene, ethylbenzene, *n*-propylbenzene and some higher boiling hydrocarbons containing most probably two or more benzene rings per molecule. At 479°, 56 mole per cent. of the reacted isopropylbenzene isomerized to *n*-propylbenzene. As the temperature of the reaction was increased, the yield of *n*-propylbenzene decreased, and it amounted to only 17% at 528°. The yield of benzene, toluene and ethylbenzene increased with the temperature of the reaction (Table I, Fig. 1). The reaction of isopropylbenzene was also accompanied by the formation of gaseous compounds, the amount of which increased with the temperature of the reaction. The amount of gases produced per mole of isopropylbenzene reacted was 0.2 mole at 480°, 0.4 mole at 500° and 0.5 mole at 528°. The gases consisted mainly of methane with smaller amounts of ethane and propane (Fig. 2).

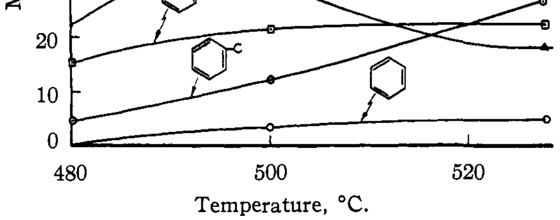

Fig. 1.—Effect of temperature upon the thermal reaction of isopropylbenzene at 816 atmospheres of pressure: ▮, conversion of cumene, mole %; O, benzene, mole % based on cumene reacted; ⊙, toluene, mole % based on cumene reacted; ⊡, ethylbenzene, mole % based on cumene reacted; ▲, propylbenzene, mole % based on cumene reacted.

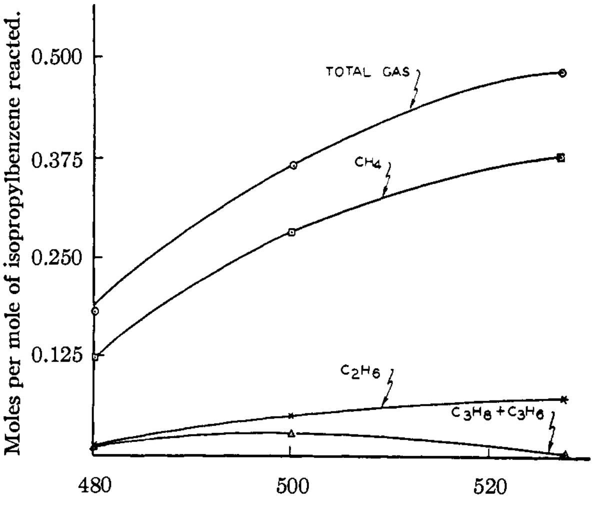

Fig. 2.—Effect of temperature upon the gases produced in the thermal reaction of isopropylbenzene.

An experiment conducted at 475°, 1.05 liquid hourly space velocity and 205 atmospheres (3000 p.s.i.) resulted in only 2% reaction of isopropylbenzene as compared with 23% reaction obtained under the same condition but at 816 atmospheres. The low conversion was probably caused by the lower contact time.

***p*-Cymene.**—The reaction was made in the flow-type high pressure apparatus at 476 and at 500° under 816 atmospheres of pressure with respective hourly liquid space velocity of 2.3 and 1.9. At 500° about 52% of the *p*-cymene which was passed through the reaction tube underwent conversion to form about 2 mole per cent. of toluene, 17% *p*-xylene, 15% *p*-ethyltoluene and 28% of *p*-*n*-propyltoluene. About 3% of the reacted *p*-cymene was converted to *p*-ethylisopropylbenzene, which indicates that methylation of the *p*-cymene occurred during the reaction. The higher boiling hydrocarbons distilled over a wide range, and according to the index of refraction and the boiling point they corre-

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[1] Presented before the Petroleum Division of the American Chemical Society at the Atlantic City Meeting, September 14–19, 1952.

[2] Deceased, November 29, 1952.

[3] V. N. Ipatieff, G. S. Monroe and L. E. Fischer, *Ind. Eng. Chem.*, **40**, 2054 (1948).

[4] V. N. Ipatieff, H. Pines and E. E. Meisinger, THIS JOURNAL, **71**, 2685 (1949).

TABLE I

THERMAL REACTION OF ISOPROPYLBENZENE AT 816 ATMOSPHERES

| Experiment | 1 | 2 | 3 |
|---|---|---|---|
| Temperature, °C. | 479 | 501 | 528 |
| Hourly liquid space velocity | 1.00 | 1.35 | 1.46 |
| Isopropylbenzene charged, g. | 195 | 177 | 314 |
| Recovered product | | | |
| Liquid, g. | 190 | 171 | 296 |
| Gaseous, l. | 1.5 | 5.4 | 21.8 |
| Isopropylbenzene reacted, % | 22.6 | 45.8 | 76.0 |
| Yield based on isopropylbenzene reacted, mole % | | | |
| Benzene | ... | 3.3 | 5.1 |
| Toluene | 5.1 | 12.2 | 26.5 |
| Ethylbenzene | 15.4 | 21.7 | 22.8 |
| *n*-Propylbenzene | 55.9 | 31.5 | 17.8 |
| Higher boiling product, g. | 10.3 | 26.9 | 74.8 |
| Analysis of gases, mole % | | | |
| Hydrogen | 10.4 | 2.8 | 0.6 |
| Methane | 70.0 | 76.3 | 77.8 |
| Ethane | 9.2 | 13.2 | 15.0 |
| Propylene | 5.4 | 0.5 | 0.5 |
| Propane | 5.4 | 6.5 | 5.0 |
| Butanes | 1.3 | 0.6 | 1.0 |
| Moles of gases produced per mole of isopropylbenzene reacted | | | |
| Hydrogen | 0.019 | 0.010 | 0.003 |
| Methane | .128 | .284 | .379 |
| Ethane | .017 | .050 | .073 |
| Propylene | .007 | .002 | ... |
| Propane | .010 | .024 | .002 |

TABLE II

THERMAL REACTION OF *p*-CYMENE AT 816 ATMOSPHERES

| Experiment | 4 | 5 |
|---|---|---|
| Temperature, °C. | 476 | 500 |
| Hourly liquid space velocity | 2.3 | 1.9 |
| *p*-Cymene charged, g. | 496 | 400 |
| Recovered product | | |
| Liquid, g. | 479 | 382 |
| Gas, l. | 2.5 | 14.6 |
| *p*-Cymene reacted, % | 9.2 | 51.5 |
| Yield based on *p*-cymene reacted, mole % | | |
| Toluene | | 1.6 |
| Ethylbenzene | | 0.5 |
| *p*-Xylene | 1.9 | 17.6 |
| Isopropylbenzene | | 0.5 |
| *n*-Propylbenzene | | 0.1 |
| *p*-Ethyltoluene | | 15.1 |
| *n*-Propyltoluene | 51.3 | 27.8 |
| *p*-Ethylisopropylbenzene | | 2.8 |
| Unidentified liquid boiling higher then *n*-propyltoluene, g. | 20.0 | 67.9 |
| Analysis of gaseous product, mole % | | |
| Hydrogen | | 2.1 |
| Methane | | 66.7 |
| Ethane | | 12.7 |
| Propane | | 14.1 |
| *n*-Butane | | 1.9 |
| Isobutane | | 0.9 |
| Olefins | | 0.9 |

sponded to diarylalkanes; a small amount of product was formed having an index of refraction of about 1.60, which presumably consisted of triarylalkanes. The structure of the high boiling compounds was not determined. Gaseous compounds formed at 500° amounted to 0.43 mole per mole of *p*-cymene reacted. The gases consisted primarily of methane and of smaller amounts of ethane and propane. At 476° only 9.2% of the *p*-cymene reacted.

The experimental results are summarized in Table II.

***s*-Butylbenzene.**—This hydrocarbon seems to be more reactive than isopropylbenzene since at 480° and 816 atmospheres of pressure, 52% of the *s*-butylbenzene passed through the heated tube reacted. The main constituents of the liquid product resulting from this reaction were in descending amounts: isopropylbenzene, ethylbenzene, toluene and *n*-propylbenzene. Only 3.4% of the reacted *s*-butylbenzene was converted to *n*-butenyl- and *n*-butylbenzene; the latter mixture was identified, after selective hydrogenation, by means of infrared spectra and solid derivatives. Small amounts of amylbenzenes were also produced. According to the physical constants, the higher boiling hydrocarbons, as in the cases of isopropylbenzene and *p*-cymene, consisted most probably of diarylalkanes.

The summary of the experimental results is given in Table III.

TABLE III

THERMAL REACTION OF *s*-BUTYLBENZENE AT 816 ATMOSPHERES

| Experiment | 6 |
|---|---|
| Temperature, °C. | 479 |
| Hourly liquid space velocity | 1.62 |
| *s*-Butylbenzene charged, g. | 279 |
| Recovered product | |
| Liquid, g. | 258 |
| Gaseous, l. | 17 |
| *s*-Butylbenzene reacted, % | 52.2 |
| Yield based on *s*-butylbenzene reacted, mole % | |
| Benzene | 0.2 |
| Toluene | 9.7 |
| Ethylbenzene | 19.5 |
| Isopropylbenzene | 22.0 |
| *n*-Propylbenzene | 4.8 |
| *n*-Butylbenzene | 3.4[a] |
| Naphthalene | 1.3 |
| Unidentified, boiling below 220°, g. | 10.6 |
| Unidentified, boiling above 220°, g. | 33.2 |
| Analysis of gaseous product, mole % | |
| Hydrogen | 0.9 |
| Methane | 74.7 |
| Ethane | 14.8 |
| Propane | 4.4 |
| *n*-Butane | 2.8 |
| Olefins | 1.5 |

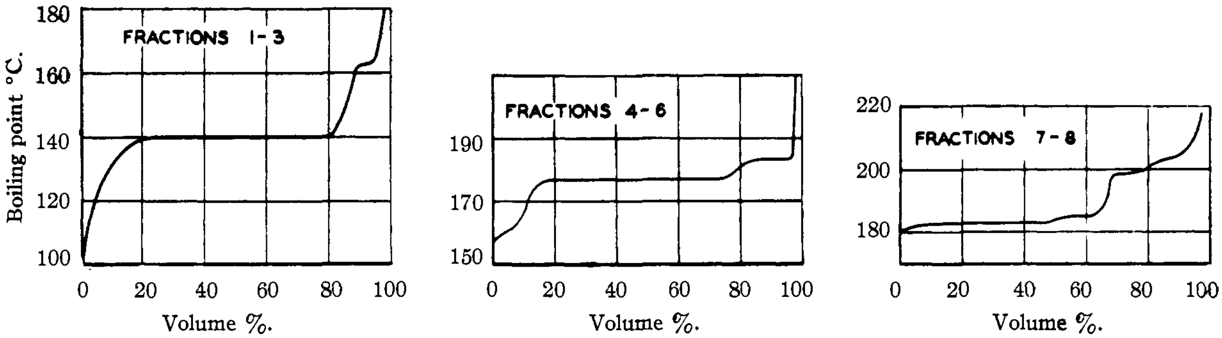
[a] About 50% of it was butenylbenzene.

## Discussion of Results

The thermal reaction of alkyl benzenes in the presence of copper pellets is non-catalytic, it is, therefore, plausible to assume that the reaction proceeds *via* a free radical mechanism. This mechanism permits the explanation of the formation of the various products from alkyl benzenes.

The following equations will illustrate some of the steps which may be involved in the formation of the various compounds.

$$\underset{\text{(I)}}{C_6H_5CH(CH_3)_2} \longrightarrow \underset{\text{(II)}}{C_6H_5\dot{C}HCH_3} + \underset{\text{(III)}}{CH_3\cdot}$$



Graph—1. Graph—2. Graph—3.

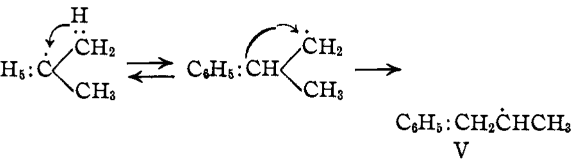
Fig. 3.—Redistillation of liquid fractions from experiment no. 5.

$$\mathrm{I} + \mathrm{II} \longrightarrow C_6H_5\dot{C}(CH_3)_2 + \underset{(\mathrm{IV})}{C_6H_5CH_2CH_3}$$

$$\mathrm{I} + \mathrm{III} \longrightarrow \mathrm{IV} + CH_4$$

The formation of diarylalkanes may be explained by the condensation of two arylalkyl free radicals formed in the reaction. It is also possible for the arylalkyl free radicals to react with a methyl free radical to form methane and alkenylaromatic hydrocarbons. The latter may then react with free radicals to form eventually higher boiling hydrocarbons.

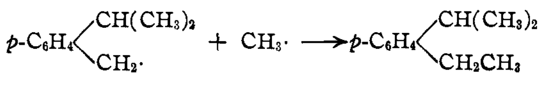
It is most likely that the hydrogen atom is removed from the tertiary carbon atom of the isopropyl group. The isomerization of isopropylbenzene to *n*-propylbenzene may occur by the steps



$$C_6H_5{:}\dot{C}\langle^{CH_2}_{CH_3} \rightleftarrows C_6H_5{:}CH\langle^{\dot{C}H_2}_{CH_3} \longrightarrow \underset{\mathrm{V}}{C_6H_5{:}CH_2\dot{C}HCH_3}$$

$$\mathrm{V} + \mathrm{I} \longrightarrow C_6H_5CH_2CH_2CH_3 + \mathrm{IV}$$

In the case of the thermal reaction of *p*-cymene, the presence of *p*-ethylisopropylbenzene was detected. This compound may have been produced by the condensation of a methyl free radical with a *p*-isopropylbenzyl free radical.



$$p\text{-}C_6H_4\langle^{CH(CH_3)_2}_{CH_2\cdot} + CH_3\cdot \longrightarrow p\text{-}C_6H_4\langle^{CH(CH_3)_2}_{CH_2CH_3}$$

The latter was probably formed from the interreaction of *p*-cymene with a free radical produced from the thermal decomposition of *p*-cymene.

The alkenyl benzenes were most likely formed by the loss of a hydrogen atom from phenylalkyl free radicals.

The formation of ethane is likely due to the condensation of two methyl free radicals.

In the thermal reactions of the arylalkanes the carbon atoms attached to the aromatic ring split off less readily than the other carbon atoms in the alkyl group. This is based on the reaction of *p*-cymene in which the amounts of monoalkylbenzenes formed are small in comparison to *p*-xylene, *p*-ethyltoluene and *p*-*n*-propyltoluene.

**Apparatus and Procedure.**—The experiments were made in a previously described[8] high pressure flow-type apparatus. The copper lined reaction tube with 5/8″ diameter bore was 34″ long. The upper 15″ was fitted with a spiral type copper preheater; the lower 9″ was occupied by a close fitting solid copper bar, and the 10″ in between was packed with 50 ml. of 1/8 × 1/8″ copper punchings. A thermocouple was placed in the center of the packing bed. The outer walls of the thermocouple well were copper covered. The aromatic hydrocarbons were pumped from a graduated glass cylinder through the reaction tube. A prerun of sufficient length of time, to replace the liquid in the apparatus, was allowed before product was collected for examination. The liquid product was collected in a calibrated receiver and the exit gases were passed through a Dry Ice cooled trap and into a gas collecting bottle.

The liquid product obtained from the reaction was fractionated on a column of about 10–12 theoretical plates. The various fractions were then refractionated on a Piros-Glover spinning band column of about 50–60 plate efficiency. Narrow boiling fractions were collected and each fraction was submitted to an infrared spectral analysis. From the analysis and amount of each fraction present, the composition of the product was determined.

The composition of the gaseous hydrocarbons was determined by means of a mass spectrograph.

Sharp boiling plateaus of the various alkyl benzenes given in Table I were obtained. The composition of the various fractions was determined by means of infrared analysis.

***n*-Propylbenzene** was found in the fraction which distilled at 159°, $n^{20}_{D}$ 1.4922. It was acetylated according to the method described previously[5] and the semicarbazone derived from it melted at 181.0–181.5°. It did not depress the melting point of the semicarbazone obtained from a known sample of acetylated *n*-propylbenzene.

*Anal.* Calcd. for $C_{12}H_{13}N_3O$: N, 19.18. Found: N, 19.08.

**Naphthalene** was separated from a fraction boiling at 62–80° (0.9 mm.), $n^{20}_{D}$ 1.5810; after crystallization from ethanol, it melted at 80°.

***p*-Diphenylbenzene** was found in the fraction which distilled at 190–210° (0.9 mm.); crystallized from ethanol, it melted at 203–205°. Authentic *p*-diphenylbenzene melted at 206–207°. The mixed melting point of the two samples was 203–205°.

*Anal.* Calcd. for $C_{18}H_{14}$: C, 93.91; H, 6.09. Found: C, 93.81; H, 6.35.

***p*-Cymene, Experiment 5.**—The liquid product was first distilled on a 26-inch high modified Podbielniak type column of about 10–12 plate efficiency. The material boiling above 205° was distilled on a column of about 5–7 plate efficiency. Fractions 1–3 boiling at 81–160°, 4–6 boiling at 160–177° and 7–8 boiling at 177–205° were redistilled on a spinning band column of 50–60 plate efficiency. The distillation curves are given in Fig. 3.

Fraction, b.p. 139.5°, $n^{20}_{D}$ 1.4945, consisted, according to the infrared spectral analysis, of 90–95% *p*-xylene, 2–4% *m*-xylene and 3–5% ethylbenzene.

Fractions, b.p. 162–163°, $n^{20}_{D}$ 1.4945, contained 95% *p*-ethyltoluene, 1–3% *n*-propylbenzene and 1% isopropylbenzene.

Fraction, b.p. 177° consisted of *p*-cymene.

Fraction, b.p. 183°, contained pure *p*-*n*-propyltoluene according to the infrared spectra.

Semicarbazone of the acetylated sample melted, after

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(5) H. Pines, A. Weizmann and V. N. Ipatieff, THIS JOURNAL, **70**, 3859 (1948).

crystallization from dilute ethanol, at 161–162°. It was identical, according to the melting and mixed melting point, with the semicarbazone prepared from a known sample of *p*-*n*-propyltoluene.

*Anal.* Calcd. for $C_{13}H_{18}N_3O$: N, 18.02. Found: N, 17.87.

Since the fraction boiling at 189–216° showed the presence of unsaturation by the permanganate test[6] it was selectively hydrogenated to the saturated aromatic hydrocarbons in the presence of copper chromite catalyst. The hydrogenation which was made at 120° under 100 atmospheres of initial hydrogen pressure indicated the presence of 0.3 double bonds per mole of hydrocarbons charged. The main fraction of the hydrogenated product distilled at 189–190°, $n^{20}D$ 1.4936, and contained 9% *p*-*n*-propyltoluene and 80% *p*-ethylisopropylbenzene.

The presence of unsaturated hydrocarbons in the product of experiment 6 boiling at 169–220° made it difficult to obtain a reliable infrared analysis; it was therefore selectively hydrogenated by the procedure described above. A fraction of the hydrogenated product boiling at 183°, $n^{20}D$ 1.4910, contained, according to infrared analysis, about 90–95% *n*-butylbenzene.

The sample was acetylated and the following derivatives were prepared: 2,4-dinitrophenylhydrazone melting at 160°.

*Anal.* Calcd. for $C_{18}H_{20}N_4O_4$: N, 15.73. Found: N, 15.54.

Semicarbazone melting at 180°.

*Anal.* Calcd. for $C_{13}H_{19}N_3O$: N, 18.02. Found: N, 17.71.

Both derivatives have the same melting and mixed melting point as those prepared from a known sample of *n*-butylbenzene.

The fractions boiling at 80–215° (0.3 mm.), $n^{20}D$ 1.5695–1.5792, contained polynuclear and polyarylated hydrocarbons. The higher boiling product was crystalline.

**Acknowledgment.**—The authors wish to thank Edmond Baclawski for the infrared spectral analyses and Joseph Grutka for the mass spectrographic analyses.

RIVERSIDE, ILLINOIS

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[6] V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **70**, 1658 (1948).

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# The Preparation and Polymerization of *p*-Alkylstyrenes.[1] Effect of Structure on the Transition Temperatures of the Polymers

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The preparation and polymerization of eight new *p*-*n*-alkylstyrenes is reported. New *p*-*n*-alkylphenylmethylcarbinols and *p*-*n*-alkylacetophenones, intermediates in the synthesis of the styrenes are also reported. Transition temperatures of the amorphous polymers have been determined and their values correlated with the size of the alkyl group. The results are in accord with the previously suggested theory concerning the effect of alkyl side chains on the transition temperatures of amorphous polymers.

This paper describes the preparation and polymerization of ten *p*-alkyl substituted styrenes: *p*-alkyl groups, R = $C_2H_5$, *n*-$C_4H_9$, *n*-$C_6H_{13}$, *n*-$C_8H_{17}$, *n*-$C_9H_{19}$, *n*-$C_{10}H_{21}$, *n*-$C_{12}H_{25}$, *n*-$C_{14}H_{29}$, *n*-$C_{16}H_{33}$ and *n*-$C_{18}H_{37}$. The analyses, intrinsic viscosities and transition temperatures of these polymers have been determined. In particular, the effect of the alkyl group and the phenyl group on the transition temperatures has been correlated with transition temperatures of other related amorphous polymers from 2-alkylbutadienes[1] and *n*-alkyl acrylates[4a] and methacrylates.[4b]

**A. Preparation of Monomers.**—Established procedures for preparing the alkyl styrenes were employed.[5] *p*-Acetyl-*n*-alkylbenzenes were prepared by conventional Friedel–Crafts procedures, then reduced with aluminum isopropoxide to give the *p*-*n*-alkylphenylmethylcarbinols, which were then dehydrated. The *n*-alkylbenzenes were prepared by known procedures.

*p*-Ethylstyrene and *p*-*n*-butylstyrene have previously been reported. Refractive index and density data are reported here for these styrenes (Table III). The following branched chain, *p*-alkyl substituted styrenes have previously been reported: iso-$C_3H_7$,[6] *s*-$C_4H_9$,[7] *t*-$C_4H_9$,[8] *t*-$C_5H_{11}$,[6] cyclohexyl,[8,9] *n*-$C_7H_{15}$,[5d] 2-ethylhexyl[5d] and *p*-benzyl[10] prepared by a wide variety of methods.

Some experimental difficulties were encountered in the distillation of the *p*-*n*-$C_{12}H_{25}$, *n*-$C_{14}H_{29}$, *n*-$C_{16}H_{33}$ and *n*-$C_{18}H_{37}$ styrenes. Other experimental deviations from established procedure are recorded in the experimental section. The new *p*-alkylacetophenones, *p*-alkylphenylmethyl carbinols and *p*-alkylstyrenes are described in Tables I, II and III, respectively. Some of the *p*-alkylacetophenones have previously been prepared and their structures proved by oxidation but since we are reporting refractive index and density data for the first time,

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[1] This is the fifth in a series of articles concerned with the polymerization of monomers containing alkyl groups and the relation of structure to the physical properties of the polymers. For the fourth paper in this series see C. G. Overberger, L. H. Arond, R. H. Wiley and H. R. Garrett, *J. Polymer Sci.*, **7**, 431 (1951).

[2] Portions of theses by Charles Frazier, Jerome Mandelman and Harry F. Smith, submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.

[3] Deceased, September, 1952.

[4] (a) C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1203 (1946); (b) C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1426 (1948).

[5] Since the literature for the preparation of substituted styrenes is rather voluminous, only general references are given (a) C. F. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 127. (b) W. S. Emerson, *Chem. Revs.*, **45**, 183 (1949). (c) C. G. Overberger and J. H. Saunders, "Organic Syntheses," **28**, 31 (1948). (d) M. Sulzbacher and E. Bergmann, *J. Org. Chem.*, **13**, 303 (1948).

[6] A. Klages and R. Keil, *Ber.*, **36**, 1632 (1903); W. H. Perkin *J. Chem. Soc.*, **32**, 388 (1877).

[7] E. Matsui, *J. Soc. Chem. Ind. Japan, Suppl. binding*, **44**, 284 (1941); *C. A.*, **44**, 7580 (1950).

[8] D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68**, 1105 (1946).

[9] C. S. Marvel, R. E. Allen and C. G. Overberger, *ibid.*, **68**, 1088 (1946).

[10] C. S. Marvel and D. W. Hein, *ibid.*, **70**, 1895 (1948).