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 frac-

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

tion 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.

RIVERSIDE, ILLINOIS

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

BY C. G. OVERBERGER, CHARLES FRAZIER,[2] JEROME MANDELMAN[2,3] AND HARRY F. SMITH[2]

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 pre-

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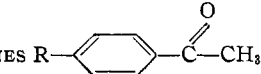
(2) Portions of theses by Charles Frazier, Jerome Mandelman and Harry F. Smith, submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.

(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).
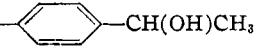
pared by conventional Friedel–Crafts procedures, then reduced with aluminum isopropoxide to give the p-n-alkylphenylmethylcarbinols, which were then dehydrated. The n-alkylbenzenes were prepared by known procedures.

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,

(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).

TABLE I

p-ALKYL SUBSTITUTED ACETOPHENONES R—⟨◯⟩—C(=O)—CH₃

R group	B.p., °C. (mm.)	$n^T D$	d^{25}_4	M.p., °C.	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-C₂H₅[a]	86 (3)	1.5273 (25)	....	....	95.7	C₁₀H₁₂O	...	...	...	...
n-C₄H₉[b]	101.5–102 (1.5)	1.5168 (25)	0.9567	....	91.3	C₁₂H₁₆O	81.77[k]	81.61	9.15	9.25
n-C₆H₁₃[c]	120 (1)	1.5096 (25)	.9415	....	90.6	C₁₄H₂₀O	82.30[k]	82.54	9.87	9.99
n-C₈H₁₇[d]	149–150 (1)	1.5044 (25)	.9260	....	94.8	C₁₆H₂₄O	82.70[k]	85.52	10.41	10.34
n-C₉H₁₉[e]	159–162 (2–3)	1.5039 (25.5)	....	....	56.6	C₁₇H₂₆O	...	...	...	...
n-C₁₀H₂₁[f]	166–168 (1.5)	....	....	37–37.5	94[b]	C₁₈H₂₈O	83.02[k]	82.97	10.84	11.02
n-C₁₂H₂₅	....	....	....	47.0–48.0	69.7[g]	C₂₀H₃₂O	83.27[l]	83.06	11.18	10.91
n-C₁₄H₂₉	....	....	....	54.3–55.4	75.0[h]	C₂₂H₃₆O	83.48[l]	83.44	11.46	11.72
n-C₁₆H₃₃	....	....	....	61.0–61.8	59.3[i]	C₂₄H₄₀O	83.65[l]	83.51	11.70	11.61
n-C₁₈H₃₇	....	....	....	65.9–66.4	61.7[j]	C₂₆H₄₄O	83.90[l]	83.63	11.90	11.89

[a] A. Klages and G. Lickroth, Ber., 32, 1549 (1899), reported b.p. 236°, n¹⁶D 1.533; ref. 8, b.p. 116–117° (13 mm.), n²⁵D 1.5275, (98%); ref. 5d, b.p. 130° (23 mm.), (>85%). [b] C. Weygand, L. Mensdorf and F. Strobelt, ibid., 68, 1825 (1935), reported b.p. 140–141° (14 mm.), (78%) and proved structure by oxidation to terephthalic acid and conversion to dimethyl ester; A. Zaki and H. A. Fahim, J. Chem. Soc., 307 (1942), reported b.p. 268–270° (766 mm.), (55%); ref. 5d, b.p. 167° (33 mm.), (78.5%). [c] Zaki and Fahim, b.p. 128° (12 mm.), (50%); Weygand, Mensdorf and Strobelt, b.p. 171–172° (18 mm.), (72%), proved structure by oxidation. [d] I. J. Rinkes, Rec. trav. chim., 64, 272 (1945), reported b.p. 192–194° (12 mm.), no yield given. Zaki and Fahim, b.p. 165–168° (4 mm.), (61%); Weygand, et al., b.p. 184–188° (13 mm.), (45%) proved structure by oxidation. [e] Weygand, et al., reported 165° (3 mm.), 80%; K. Ziegler, F. Dersch and H. Wollthan, Ann., 511, 13 (1934), reported 190° (10 mm.) (no yield given). [f] Recrystallized from methanol. [g] Yield reported on m.p. 46.8–48.8°, recrystallized from absolute ethanol. [h] Yield reported on m.p. 54.0–56.2°, recrystallized from ethyl ether; analytical sample from 1:1 ethyl ether–methanol. [i] Recrystallized from 1:2 ethyl ether–methanol. [j] Yield reported on m.p. 58.6–64.2° recrystallized from 1:1 ethyl ether–methanol, analytical sample from petroleum ether (b.p. 28–36°). [k] Analyses by Drs. Weiler and Strauss, Oxford, England, and Dr. K. Ritter, Zurich, Switzerland. [l] Analyses by Microanalytical Laboratories of American Cyanamid Company, Stamford, Conn.

TABLE II

p-ALKYLPHENYLMETHYLCARBINOLS R—⟨◯⟩—CH(OH)CH₃

R group	B.p., °C. (mm.)	M.p., °C.	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-C₂H₅[a]	67–68 (1)	....	63.4	C₁₀H₁₄O	....	...	...	...
n-C₄H₉[b]	86–87 (1)	....	83.3	C₁₂H₁₈O	80.85[j]	81.10	10.17	10.15
n-C₆H₁₃[c]	119–120 (2)	....	86.0	C₁₄H₂₂O	81.50[d]	81.27	10.75	10.93
n-C₈H₁₇	137–138 (1)	25–26	91.5	C₁₆H₂₆O	81.99[i]	81.78	11.18	11.23
n-C₉H₁₉	151–153 (2)	....	70.3	C₁₇H₂₈O	82.20	82.46	11.36	11.45
n-C₁₀H₂₁	153 (1)	39–40	61.5	C₁₈H₃₀O	82.38[i]	82.48	11.52	11.81
n-C₁₂H₂₆[d]	....	49.0–49.6	82.2[e]	C₂₀H₃₄O	82.69	82.57	11.80	11.65
n-C₁₄H₃₀	....	56.6–57.0	78.7[f]	C₂₂H₃₈O	82.95	83.28	12.02	11.87
n-C₁₆H₃₃	....	62.9–63.4	81.0[g]	C₂₄H₄₂O	83.17	83.33	12.22	12.12
n-C₁₈H₃₇	....	68.0–68.4	93.0[h]	C₂₆H₄₆O	83.35	83.32	12.38	12.25

[a] n²⁵D 1.5169; ref. 5d, b.p. 120° (14 mm.), 87.3%; ref. 8, b.p. 89–90 (2.5 mm.), n²⁵D 1.670, 82%, by pressure reduction with copper chromite. A. Klages, Ber., 36, 1632 (1903), reported b.p. 120° (19 mm.), (80%), by sodium–alcohol reduction. [b] n²⁵D 1.5091, d²⁵₄ 0.9435; ref. 5d reported b.p. 149–153° (30 mm.), (80%). [c] n²⁵D 1.5030, d²⁵₄ 0.9282. [d] Hydroxyl value determined by method described in H. K. Dean, "Utilization of Fats," Chemical Publishing Co., New York, N. Y., 1938, p. 58. Calcd., 193.5; found, 189.7. Yield reported on m.p. 48.0–50.0°, recrystallized from ethanol, analytical sample from petroleum ether (b.p. 28–38°). [e] Yield reported on m.p. 57.0–57.5°, recrystallized from petroleum ether (b.p. 28–38°). [f] Yield reported on m.p. 62.8–63.3°, recrystallized from petroleum ether (b.p. 28–38°). [g] Yield reported on m.p. 67.4–67.9°, recrystallized from petroleum ether. [h] Analyses by Drs. Weiler and Strauss, Oxford, England, and Dr. K. Ritter, Zurich, Switzerland. [i] Analyses by Microanalytical Laboratory of the American Cyanamid Company at Stamford, Conn.

they are included in Table I. Since para isomers have been obtained for the lower alkyl series, it is reasonable to assume, due to steric factors, that para alkylation is very dominant with the larger alkyl groups.

Since the alkylphenyl ketones and alkylbenzenes are well characterized in the literature, any description of these compounds has been omitted for brevity. In all cases, physical constants were carefully checked with reliable literature values.

B. Polymerization. I. Preparation.—The polymers were prepared in bulk in sealed tubes either catalyzed by benzoyl peroxide or ultraviolet light. Since polymers of approximately similar intrinsic viscosities were desired, it was necessary to study

empirically the reaction variables. The polymers were purified by conventional methods (Table IV). The intrinsic viscosities were carried out in toluene in an Ubbelohde viscometer. Transition temperatures (Table IV) were measured by the refractometric method developed by Wiley.[11] Three sample determinations are reported in Fig. 1. The transition temperatures of the polymers are plotted against the size of the alkyl group (Fig. 2).

II. Discussion of Transition Temperatures.—Previous studies by Rehberg and Fisher[4] and Wiley and Brauer[11a] have been made of the brittle points

(11) (a) R. H. Wiley and G. M. Brauer, J. Polymer Sci., 3, 455, 647, 704 (1948); (b) R. H. Wiley, G. M. Brauer and A. R. Bennett, ibid., 5, 609 (1950).

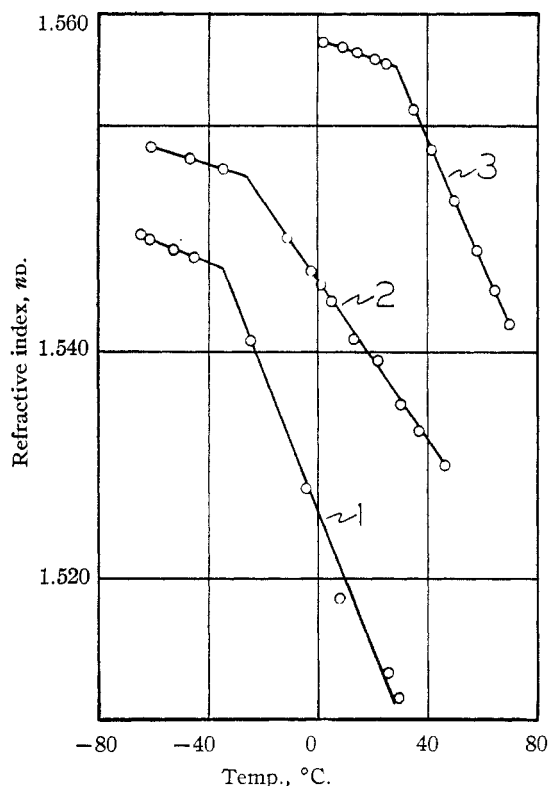Fig. 1.—Refractive index vs. temperature data for polymers of p-n-alkylstyrenes: 1, p-n-C$_{14}$; 2, p-n-C$_6$; 3, p-n-C$_2$.
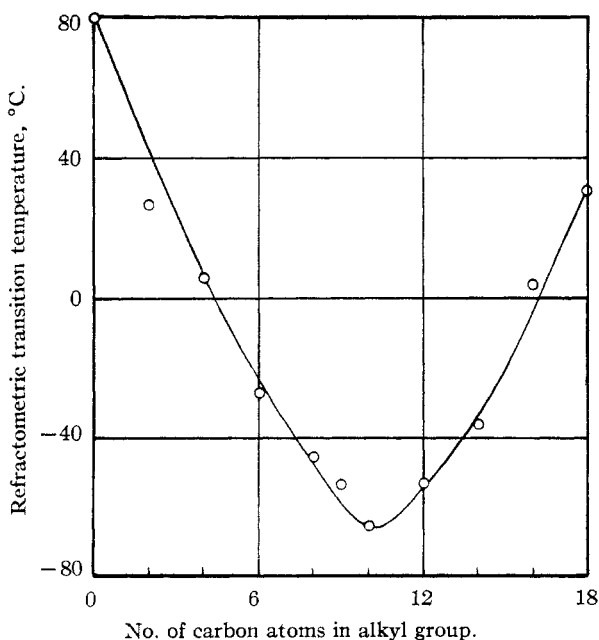

Fig. 2.—Relationship between the second order transition temperatures and the size of the straight chain alkyl group for poly-p-n-alkylstyrenes.

and second-order transition temperatures, respectively, for polymers obtained from n-alkyl esters of acrylic and methacrylic acids. These studies indicate that as the alkyl side chain increased in length there was an initial decrease in the brittle point and transition temperature of the polymer to

a minimum followed by an increase. In the acrylate series, a minimum in the brittle points was found at C$_8$; a similar minimum was found in the brittle points for the methacrylate series at C$_{12}$. Wiley and Brauer, although unable to obtain a minimum for the acrylate series, report a very low value for the transition temperature of the polymer of n-octyl acrylate.

In contrast to this minimum, polymers from 2-alkylbutadienes[1] appeared to show no significant minimum in their transition temperatures between polybutadiene and poly-2-n-heptyl-1,3-butadiene. This may be interpreted to indicate that the double bonds available in the polybutadienes do not appreciably contribute to the weak forces holding the chains together and the steric screening effect of the n-alkyl groups is therefore not important. As previously noted, there is an increase in the transition temperature for the 2-n-decyl-1,3-butadiene polymer. Difficulties in the interpretation of these results are discussed in reference 1.

It was of interest to observe the effect of a phenyl group on the transition temperatures of such polymers. From the transition temperatures observed (Table IV), it can be seen that the minimum occurs at C$_{10}$. The minimum is similar to that observed in the acrylate series. Furthermore, the general order observed in the acrylate series is obeyed. *This is an indication that the phenyl group has about the same order of magnitude as the carbonyl group or the (-O-CO) group in regard to dipole effects which are responsible for the attractive forces between chains in these amorphous polymers.*

The results again indicate the applicability of the theory proposed earlier to explain the order of the transition temperatures in the acrylate series.[1]

The effect of the molecular weight of ethyl acrylate polymers on the second-order transition point has been discussed by Wiley, et al.[11a] As noted, differences in intrinsic viscosity between 0.5 and 2.0 result in a change of only 4° in the transition temperature of polyethylacrylate. With the exception of the polymer from p-n-dodecylstyrene, the intrinsic viscosities reported here are all between 1.00 and 2.00, with the majority having values between 1.0 and 1.4. Therefore any error introduced in the comparison of the transition temperatures due to differences in the molecular weight of these polymers should be very small.
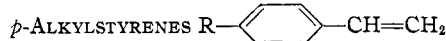
Experimental

p-Alkylacetophenones.—The acid chlorides from butyric hexanoic, octanoic and decanoic acids were prepared by the procedure of Helferich and Schaefer[12] and were purified by distillation through a Vigreux column. The remainder of the acid chlorides were prepared according to the procedure of Mikeska and collaborators[13] except that higher reaction temperatures were employed. The products were purified by distillation through a 10-in., helices-packed column.

The alkylphenyl ketones were prepared by a modification of the procedure of Sulzbacher and Bergmann[5d] except for stearophenone which was prepared by the method of reference 13. The alkylphenyl ketones were purified by fractional distillation through the columns indicated above or

(12) B. Helferich and W. Schaefer, "Organic Syntheses," Coll. Vol. I, sec. edition, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 147.

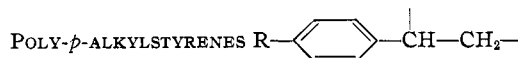(13) L. A. Mikeska, C. F. Smith and E. Lieber, J. Org. Chem., **2**, 500 (1938).

TABLE III

p-ALKYLSTYRENES R—⟨benzene⟩—CH=CH₂

R group	B.p., °C. (mm.)	n^{25}D	d^{25}_4	Yield, %[c]	Formula	Composition, % Carbon Calcd.	Found	Hydrogen Calcd.	Found
n-C₂H₅[a]	73 (10)	1.5349	....	82.5[d]	C₁₀H₁₂	....	...	...	...
n-C₄H₉[b]	64 (1)	1.5233	0.9768	79.1[d]	C₁₂H₁₆	89.93[k]	89.66	10.07	9.96
n-C₆H₁₃	89–90 (1)	1.5156	.8742	75.5[d]	C₁₄H₂₀	89.29[k],	89.37	10.71	10.60
n-C₈H₁₇	113–114 (1)	1.5100	.8714	78.4[d]	C₁₆H₂₄	88.82[k]	88.66	11.18	11.51
n-C₉H₁₉	140–145 (2.3–2.5)	1.5055	.8802	51.6 (41.2)[e,f]	C₁₇H₂₆	88.62[l]	88.63	11.38	11.47
n-C₁₀H₂₁	139–143 (1)	1.5045	.8706	85.5[d]	C₁₈H₂₈	88.45[k]	88.32	11.55	11.68
n-C₁₂H₂₅	158–163 (1.2–1.4)	1.5011	.8831	55.4 (49.5)[g]	C₂₀H₃₂	88.16[l]	97.79	11.84	11.88
n-C₁₄H₂₉	192–196 (2.2)	M.p. 26.0–27.0	....	92.0 (35.6)[h]	C₂₂H₃₆	87.92[l]	97.69	12.08	12.00
n-C₁₆H₃₃	....	M.p. 30.8–31.4	....	32.6 (16.3)[i]	C₂₄H₄₀	87.73[i]	87.90	12.27	12.41
n-C₁₈H₃₇	....	M.p. 38.3–39.0	....	66.4 (53.6)[j]	C₂₆H₄₄	87.56[l]	87.32	12.44	12.29

[a] D. Gauthier and P. Gauthier, Bull. soc. chim., 53, 323 (1933), reported b.p. 80° (20 mm.), (80%); Klages, ref. a, Table II, b.p. 86° (20 mm.), n^{15}D 1.5377, no yield given, prepared by treatment of α-chloroethylbenzene with pyridine. Ref. 8, b.p. 68° (16 mm.), n^{25}D 1.5350 (83%) by high temperature alumina dehydration. R. H. Dreisbach and R. A. Martin, Ind. Eng. Chem., 41, 2875 (1949), reported b.p. 192.3° (760 mm.), n^{25}D 1.53484, on purified commercial material; ref. 5d, b.p. 86° (20 mm.), (72%). [b] Ref. 5d, b.p. 116–118° (15 mm.), (70%). [c] Yield of C₂, C₄, C₆, C₈ and C₁₀ based on recovered carbinol; yield of C₉, C₁₂, C₁₄, C₁₆ and C₁₈ based on monomer plus polymer; yield in parentheses only based on monomer. [d] Charge of carbinol 25 g., 1 g. fused KHSO₄, 0.259 g. of hydroquinone, dropwise procedure, reaction temperatures 170–240° at 7 mm., see ref. 5c. [e] Charge of carbinol 8–15 g., 1 g. of fused KHSO₄, 0.19 g. of t-butylcatechol. Dodecylstyrene prepared by dropwise procedure, but C₉, C₁₄, C₁₆ and C₁₈ styrenes prepared by allowing portions of carbinol (2–3 ml.) to react at 25–50 mm. and distilling by reducing the pressure to less than 5 mm. [f] Main reaction temperature, 220–250°. [g] 220–250°. [h] 260–275°. [i] 220–253°. [j] 250–277°. [k] Analyses by Drs. Weiler and Strauss, Oxford, England, Dr. K. Ritter, Zurich, Switzerland. [l] Analyses by Microanalytical Laboratory of the American Cyanamid Company, Stamford, Conn.

TABLE IV

POLY-p-ALKYLSTYRENES R—⟨benzene⟩—CH—CH₂—

R group	[η][h]	Transition temp., °C.	Formula	Composition, % Carbon Calcd.	Found	Hydrogen Calcd.	Found
n-C₂H₅[a]	2.02	27	(C₁₀H₁₂)ₓ	90.85	91.10	9.15	9.02
n-C₄H₉[a]	1.28	6	(C₁₂H₁₆)ₓ	89.94[j]	89.81	10.06	9.94
n-C₆H₁₃[a]	1.57	-27	(C₁₄H₂₀)ₓ	89.29[j]	89.15	10.71	10.57
n-C₈H₁₇[a]	1.11	-45	(C₁₆H₂₄)ₓ	88.82	89.22	11.18	10.90
n-C₉H₁₉[b,c]	1.25	-53	(C₁₇H₂₆)ₓ	88.62[k]	87.96	11.38	11.18
n-C₁₀H₂₁[a]	0.90	-65	(C₁₈H₂₈)ₓ	88.45[j]	88.74	11.55	11.36
n-C₁₂H₂₆[b,d]	0.46	-52	(C₂₀H₃₂)ₓ	88.16[k]	87.50	11.84	11.84
n-C₁₄H₃₀[b,e]	1.30	-36	(C₂₂H₃₆)ₓ	87.92[k]	88.11	12.08	12.22
n-C₁₆H₃₃[b,f]	1.33	4.5	(C₂₄H₄₀)ₓ	87.73[k]	87.70	12.27	12.18
n-C₁₈H₃₇[b,g]	1.44	32[i]	(C₂₆H₄₄)ₓ	87.56[k]	87.47	12.29	12.39

[a] Polymerized at 70° with benzoyl peroxide as a catalyst. Precipitated from benzene with methanol. [b] Polystyrenes which contained some benzene-insoluble polymer which was removed. [c] Polymerized with ultraviolet light and traces of benzoyl peroxide for 96 hr.; precipitated three times with equal volumes of a 50:50 ethyl ether–methanol mixture from benzene. [d] Polymerized with ultraviolet light for 90 hr., precipitated three times with equal volumes of methanol from petroleum ether (b.p. 28–38°) and benzene. [e] Polymerized with ultraviolet light and trace of benzoyl peroxide (144 hr.), precipitated three times with four times the volume of acetone from benzene. [f] Polymerized with ultraviolet light and trace of benzoyl peroxide (160 hr.); precipitated with two times the volume of acetone from benzene. [g] Polymerized by ultraviolet light and a trace of benzoyl peroxide (160 hr.), precipitated as in f. [h] Ubbelohde viscometer used and specific viscosity determined on polymer solutions in redistilled anhydrous toluene. [i] Not determined refractometrically, softening point in capillary tube. [j] Analyses by Drs. Weiler and Strauss, Oxford, England. [k] Analyses by Microanalytical Laboratory of the American Cyanamid Co., Stamford, Conn.

recrystallized from appropriate solvents; C₁₂, C₁₄, methanol; C₁₆, ethanol; C₁₈, ether–methanol.

The alkylbenzenes were prepared by some modification of the general Clemmensen reduction. The C₄ compound was reduced by the method of Clemmensen.[14] Evidence accumulated that small traces of olefinic materials were present. Thus weak positive tests for unsaturation were obtained with bromine in carbon tetrachloride solution and with potassium permanganate. The product was dissolved in ethanol and hydrogenated over palladium to ensure purity of the final product. The C₆ compound required more strenuous conditions than the C₄ to reduce the ketone to the hydrocarbon. The C₈ and C₁₀ ketones were reduced using the method of Schneider and Spielman.[15] In all of these latter three cases, traces of olefinic material were removed by catalytic hydrogenation. To obtain a significant

yield of alkylbenzene for the C₁₂ and higher ketones, it was necessary to solubilize the ketone in the reacting system. This problem was best solved by using a modification of the Schneider and Spielman procedure introduced by Schmidt and Shirley,[16] who increased the volume of alcohol.

The p-alkylacetophenones were prepared according to the procedure of Mowry, Renoll and Huber adapted from that of Perrier[17] and are described in Table I. Fractionation of liquids were carried out as described previously.

p-Alkylphenylmethylcarbinols.—The method used was that described in "Organic Reactions"[18] except for minor details in the use of fractionating columns to remove slowly acetone. The compounds are described in Table II.

(14) E. Clemmensen, Ber., 46, 1838 (1913).

(15) A. K. Schneider and M. A. Spielman, J. Biol. Chem., 142, 345 (1942).

(16) G. A. Schmidt and D. A. Shirley, THIS JOURNAL, 71, 3804 (1949).

(17) G. Perrier, Ber., 33, 815 (1900).

(18) A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 203.

p-Alkylstyrenes.—The dehydration of the carbinols was carried out according to the general method described in reference 5c. In all cases, the styrenes were removed by distillation from the reaction mixture. For the higher boiling styrenes, it was necessary to use pressures of 1 to 2 mm. during dehydration. *p*-Alkyl C_2, C_4, C_6, C_8, C_9, C_{10}, C_{12} and C_{14} styrenes were purified by successive distillations, *p*-C_{16} and C_{18} styrenes were recrystallized from petroleum ether (b.p. 28–36°). Monomers were stored with inhibitor, usually *p*-*t*-butylcatechol and purified by removing inhibitor with dilute sodium hydroxide followed by distillation or recrystallization before analysis and polymerization. The styrenes are described in Table III.

Preparation of Polymers.—The polymerization of the C_2, C_4, C_6, C_8 and C_{10} styrenes was carried out in the following way. In a standard test-tube were placed 2 g. of the monomer and 0.1% by weight of benzoyl peroxide. The air in the test-tube was displaced with carbon dioxide and the tube sealed. The tubes were then heated in a water-bath at 70° until no flow could be observed. The approximate time required for polymerization varied from 30 hours for *p*-ethylstyrene to 72 hours for the *n*-decylstyrene. The polymers were dissolved in benzene and the filtered solution added slowly with rapid stirring into a large excess of meth-

anol. After 5 such precipitations, the polymers were dried in a vacuum desiccator for several days.

The C_9, C_{14}, C_{16} and C_{18} alkylstyrenes were polymerized in a similar manner under nitrogen except that only 1 to 3 mg. of benzoyl peroxide was used and the monomers were exposed to ultraviolet light. The approximate temperature under the light was 70°. Precipitation of the benzene solution was carried out with different solvents (Table IV).

Properties of Polymers.—Analyses of the purified polymers are listed in Table IV. Intrinsic viscosities (four concentrations) were determined at 20° in toluene with an Ubbelohde viscometer. The determination of the transition temperatures is outlined in the discussion.

BROOKLYN, N. Y.

Friedel–Crafts Reactions between Gaseous Benzene and Ethyl Chloride on Solid Aluminum Chloride

BY MONTE BLAU AND JOHN E. WILLARD

It has been shown that gaseous ethyl chloride and benzene at a few cm. pressure and 0 to 25° react rapidly to form ethylbenzenes when in contact with solid aluminum chloride. The rate is proportional to the pressure of each reactant and the over-all activation energy is about 4 kcal./mole. Infrared analysis, radiocarbon analysis and titration of hydrogen chloride have been used to follow the reaction. The products include ethylbenzene, the three diethylbenzenes and more complex compounds.

Introduction

It has been found earlier: (1) that exchange of chlorine between aluminum chloride and carbon tetrachloride requires the presence of a surface of solid aluminum chloride[1]; (2) that solid aluminum chloride can exchange chlorine with gaseous organic chlorides[2] and with hydrogen chloride[3] at room temperature and below; and (3) that a Friedel–Crafts reaction takes place when gaseous benzene and carbon tetrachloride are mixed over an aluminum chloride surface.[2]

The present paper gives the results of experiments on the ethylation of gaseous benzene with gaseous ethyl chloride catalyzed by aluminum chloride.

Experimental[4]

Procedure.—Aluminum chloride synthesized[1,2] *in situ* on a vacuum system from aluminum and silver chloride was sublimed onto the walls of a one-liter flask which served as the reaction vessel. Metered quantities of gaseous ethyl chloride and benzene were condensed together in a trap and then rapidly vaporized together and allowed to pass into the reaction vessel. Following the desired time of contact the products and unconsumed reactants were removed by condensing them in cold traps.

One experiment (No. IV of Table I) was carried out on a flow system in which the reaction vessel was a glass tube 3.7

(1) C. H. Wallace and J. E. Willard, THIS JOURNAL, **72**, 5275 (1950).

(2) M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951).

(3) M. Blau, W. T. Carnall and J. E. Willard, *ibid.*, **74**, 5762 (1952).

(4) Further details are given in the Ph.D. thesis of Monte Blau, University of Wisconsin (1952).

cm. in diameter and 30 cm. long with large projections, similar to those of a Vigreux column, pushed into the walls. The interior surfaces were coated with aluminum chloride as above. In order to carry out a reaction, benzene and ethyl chloride vapors were continuously bled into the reaction region through 0.05-mm. capillary tubes and pumped out through a 0.75-mm. capillary tube into a product collecting trap. The pressure was measured with a mercury-oil multiplying manometer. The amount of each reactant used was determined by weighing its reservoir before and after the experiment.

Methods of Analysis.—Three methods of analysis were used to determine the extent of the reaction $C_6H_6 + C_2H_5Cl \rightarrow C_6H_{6-x}(C_2H_5)_x + xHCl$.

In those experiments where the information desired was the gross amount of reaction, the quantity of hydrogen chloride produced was measured. This was done by condensing it in a liquid air trap, dissolving in water, adding excess potassium iodide and potassium iodate and titrating the liberated iodine with standard thiosulfate.

A quantitative measure of the fraction of the initial benzene which was converted to ethylbenzene as compared to that converted to more highly ethylated benzenes was obtained by using benzene labeled with C^{14}. The unreacted radioactive benzene and radioactive ethylated products (0.1 to 0.2 cc.) were condensed in a Dry Ice trap and diluted with measured amounts of inactive benzene, ethylbenzene and diethylbenzenes. This mixture was fractionated in a Piros–Glover micro-still operating at an efficiency of 20 theoretical plates, and small cuts of pure benzene and ethylbenzene were isolated. The residue in the still-pot was used for estimation of higher-boiling activity. A sample of each cut was oxidized to carbon dioxide, precipitated as barium carbonate and counted as an "infinitely thick" sample in a windowless proportional counter. From the relative counting rates the amounts of benzene converted to ethylbenzene and higher boiling products were calculated.

Infrared absorption analysis was used in experiments designed to identify the ethylation products more rapidly