

## SYNTHESIS OF *p*-ALKYLSTYRENES

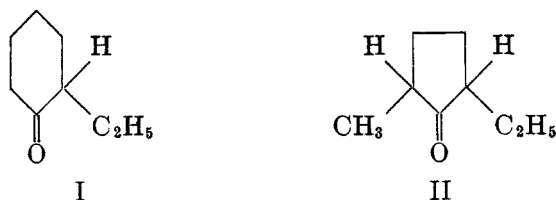
M. SULZBACHER AND E. BERGMANN

Received November 26, 1947

Recently, a number of nuclear-substituted styrenes have been synthesized and their polymerization investigated (1-7). It might, therefore, be useful to report on the synthesis of a number of *p*-alkylstyrenes which has been carried out in order to obtain oil-soluble polystyrenes. Polystyrene itself is insoluble in mineral oils (*e.g.* hydraulic oils), but the introduction of alkyl groups in the *p*-position increases the oil solubility gradually with increasing length of the alkyl chain. The polymers of *p*-heptyl- and *p*-(2-ethylhexyl)styrene are easily soluble in mineral oils.

For the synthesis of the *p*-alkylstyrenes the corresponding *p*-alkylacetophenones were reduced with aluminum isopropoxide, and the (*p*-alkylphenyl)-methylcarbinols formed dehydrated with potassium hydrogen sulfate *in vacuo*, according to the method of Brooks (3). *p*-Methyl-, *p*-ethyl-, *p*-butyl-, *p*-heptyl- and *p*-(2-ethylhexyl)-styrene were thus prepared.

For the synthesis of heptylbenzene (from which *p*-heptylacetophenone was obtained in the usual way), Clemmensen's method of reduction was applied successfully to heptanoylbenzene. (2-Ethylhexyl)benzene could not be prepared equally well through (2-ethylhexanoyl)benzene. In the synthesis of the latter ketone a noteworthy side-reaction was observed, *viz.* the formation of a ketone  $C_8H_{16}O$  by intramolecular dehydrohalogenation. Formally, this ketone could be 2-ethylcyclohexanone (I) or 2-ethyl-5-methylcyclopentanone (II).



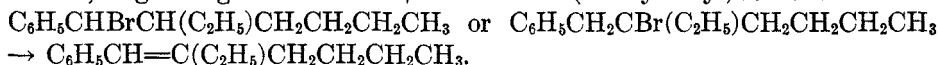
Although no conclusive evidence is offered for either of the two formulas, formula (II) is preferred, as the steric encumbrance of the carbonyl group may explain its resistance to semicarbazone formation and its slackness in the reaction with phenylmagnesium bromide.

This is undoubtedly an unexpected reaction, although the acylation of paraffinic chains by acyl chlorides in the presence of aluminum chloride has been observed before (8).

(2-Ethylhexyl)benzene was, therefore, prepared from 2-ethylhexanol and benzene with aluminum chloride.

In the study of the synthetic methods available in this series, an attempt was also made to prepare  $\beta$ -(*p*-heptylphenyl)ethyl chloride by interaction of  $\beta$ -chloroethyl *p*-toluenesulfonate (9) and the magnesium derivative of *p*-heptylbromo-

benzene. The latter substance proved available by condensation of heptanoyl chloride and bromobenzene and Clemmensen reduction of the *p*-heptanoyl-bromobenzene so obtained. Its Grignard derivative, however, gave very unsatisfactory yields of the desired  $\beta$ -phenylethyl chloride derivative. In the 2-ethylhexyl series the Friedel-Crafts reaction of 2-ethylhexanoyl chloride with bromobenzene proved unsatisfactory, as partial debromination and formation of resins took place (10). The peculiar reactivity of the 2-ethylhexyl group expresses itself also in the following fact: Bromination of (2-ethylhexyl)benzene in carbon tetrachloride solution at low temperature gave a product which decomposed with evolution of hydrogen bromide when distilled *in vacuo*. The compound formed was an unsaturated hydrocarbon, probably 1-phenyl-2-ethylhexene, originating from an  $\alpha$ - or  $\beta$ -brominated (2-ethylhexyl)benzene:



#### EXPERIMENTAL

*p*-Methyl-, *p*-ethyl-, and *p*-butyl-acetophenone were prepared from the alkylbenzenes and acetic anhydride in the presence of aluminum chloride (11, 12). The yields were above 85% of theory; *p*-ethylacetophenone boiled at 130°/23 mm. (13), the butyl compound at 167°/33 mm. (12c, 14) [lit. (13a) 100–103°/3 mm.; (14a) 140–141°/21 mm.].

*Heptanoic acid*. The catalytic oxidation of heptanal described by Weizmann (15) is preferably carried out using pure oxygen; the reaction is exothermic and raises the temperature from 20° to 65°. After 8 hours, 3.7% of the initial heptanal was recovered; heptanoic acid was obtained in 94.5% yields (or 98.2%, taking into account the recovered aldehyde); b. p. 106–110°/9 mm.

*Heptanoyl chloride*. The slow addition of 851 g. (7.2 moles) of freshly distilled thionyl chloride to 845 g. (6.5 moles) of heptanoic acid, followed by heating at 50° for 8 hours and at 100° for one hour, and then distilling, gave 840 g. (87.0%) of heptanoyl chloride; b. p. 91–93°/35 mm.

The small excess of thionyl chloride was recovered by distillation at ordinary pressure and the residue purified by vacuum distillation; b. p. 91–93°/35 mm.; yield, 840 g. (87.0%).

*Heptanoylbenzene*. A suspension of 750 g. (5.6 moles) of powdered anhydrous aluminum chloride in 4 liters of dry benzene was well stirred and cooled in ice-water. Eight hundred thirty-two grams (5.6 moles) of *n*-heptanoyl chloride was added slowly during several hours, at less than 10°. The mixture was allowed to stand for twelve hours at room temperature, gently refluxed during three hours, and decomposed with ice and concentrated hydrochloric acid; b. p. 138–139°/14 mm.; yield, 905 g. (85.0%). The substance solidified at about 10°.

*Anal.* Calc'd for  $\text{C}_{13}\text{H}_{18}\text{O}$ : C, 82.1; H, 9.5.

Found: C, 82.5; H, 9.1.

*Heptylbenzene*. Heptanoylbenzene (190 g.; 1 mole) was reduced with amalgamated zinc wool (400 g.) and hydrochloric acid (400 cc. of concentrated acid and 300 cc. of water), more concentrated acid being added from time to time to the boiling mixture, until all the metal had disappeared. The oily layer and the ethereal extract of the water layer were subjected to fractional distillation; b. p. 110°/11 mm.; yield, 124 g. (70.5%). Nineteen grams of unchanged heptanoylbenzene was recovered.

*Anal.* Calc'd for  $\text{C}_{13}\text{H}_{20}$ : C, 88.6; H, 11.4; mol. wt., 176.

Found: C, 88.3; H, 11.2; mol. wt., 179.

*p*-Heptylacetophenone. To a well-agitated solution of 176 g. (1 mole) of heptylbenzene in 450 cc. of carbon disulfide, 300 g. (2.24 moles) of powdered aluminum chloride was added slowly. The mixture was heated to the boiling point, and 91.8 g. (0.9 mole) of acetic an-

hydride was added within one hour. After a further hour, the reaction product was treated with ice and concentrated hydrochloric acid and extracted with benzene. After washing with water, dilute sodium hydroxide solution and again water, and drying, the solution was distilled; b.p. 165–175°/10 mm. [lit. (14a) b.p. 176–179°/13 mm.]; yield, 98 g. (45.0%). It is assumed by analogy that acetylation takes place in the *p*-position to the heptyl group.

*Anal.* Calc'd for  $C_{15}H_{22}O$ : C, 82.5; H, 10.1.

Found: C, 82.7; H, 10.1.

A higher-boiling fraction (198–204°/10 mm.) was obtained, probably a diacetylheptylbenzene. A small quantity of acetophenone was also present in the head fractions, due to a degrading action of aluminum chloride on *p*-heptylacetophenone.

(2-Ethylhexyl)benzene. (a) When 65 g. (0.5 mole) of 2-ethylhexanol, 67 g. (0.5 mole) of powdered aluminum chloride and 312 g. (4 moles) of benzene were mixed at room temperature, no appreciable reaction took place. The mixture was refluxed for six hours, decomposed with ice and concentrated hydrochloric acid, and the organic layer dried and freed from the excess benzene. (2-Ethylhexyl)benzene boiled at 129–131°/15 mm.; yield, 47.2 g. (50.0%, calculated on the 2-ethylhexanol used). A higher-boiling fraction, amounting to 10 g., was also obtained, boiling under the same pressure at 145–210°, and consisting of di- and possibly tri-octylbenzenes. Hardly any resinous residue remained in the distillation flask. Almost the total balance of unchanged 2-ethylhexanol was recovered as head fraction in the distillation.

*Anal.* Calc'd for  $C_{14}H_{22}$ : C, 88.3; H, 11.7.

Found: C, 88.0; H, 11.5.

(b) When the quantity of aluminum chloride was doubled, the reaction began at room temperature, and the octyl alcohol had to be added slowly, the temperature being kept below 10°. The reaction was again completed by refluxing for six hours. Treatment as above showed a slight reduction in the yield of (2-ethylhexyl)benzene (40 g. instead of 47.2 g.), an increase in the fraction consisting of di- and tri-octylbenzenes (14 g. instead of 10 g.) and in the formation of a substantial amount (20 g.) of resinous residue with a corresponding loss of recoverable 2-ethylhexanol.

(c) The reaction between benzene and 2-ethylhexyl bromide gave poor results; the yield of (2-ethylhexyl)benzene was 10%, that of the di- and tri-octylbenzene fraction 20%.

*p*-(2-Ethylhexyl)acetophenone was prepared from the foregoing hydrocarbon (175 g.) and acetic anhydride (75.2 g.) in carbon disulfide (400 cc.) and in the presence of aluminum chloride (275 g.) in the manner described for *p*-heptylacetophenone. Fractional distillation of the reaction product gave 32 g. of acetophenone, b.p. 92–94°/18 mm., and 85 g. (40%) of the desired ketone, b.p. 189°/17 mm.

*Anal.* Calc'd for  $C_{16}H_{24}O$ : C, 82.8; H, 10.3.

Found: C, 83.1; H, 10.1.

It should be borne in mind that both in the condensation of 2-ethylhexanol with benzene and in that of (2-ethylhexyl)benzene with acetic anhydride, the aluminum chloride may cause isomerization of the aliphatic chain. This aspect of the synthesis described here, has not been investigated.

(*p*-Alkylphenyl)methylcarbinols. The reduction of the *p*-alkylacetophenones (1 mole) was carried out with one mole of aluminum isopropoxide in 800 cc. of isopropyl alcohol with continuous removal of the acetone formed and occasional replacement of the part of the liquid which had distilled off. When no more acetone could be detected in the distillate, the reaction mixture was either directly treated with 20% aqueous potassium hydroxide or freed from excess solvent *in vacuo* and poured into ice-cold dilute hydrochloric acid. Extraction with ether, neutralization, drying of the extract, and distillation gave the desired carbinols (Table I).

*p*-Alkylstyrenes. Using the method of Brooks (3), the (*p*-alkylphenyl)methylcarbinols were heated under 100 mm. pressure with 1% by weight of potassium hydrogen sulfate and a nearly equal amount of hydroquinone in a Claisen flask. The distillate was dissolved in ether, dried, and fractionated (Table II).

*4-Heptanoylbromobenzene.* At 0°, 58 g. of heptanoyl chloride was added slowly to a well-agitated suspension of 106 g. of powdered aluminum chloride in 350 cc. of carbon disulfide and 46 cc. of bromobenzene. The mixture was then kept for twelve hours at room temperature, refluxed for two hours and decomposed with ice and concentrated hydrochloric acid. Fractionation under 30 mm. pressure gave: (a) at 145–150°, 19 g. of heptanoylbenzene (corresponding to 25% of the chloride employed); (b) at 225–230°, 42 g. of 4-heptanoylbromobenzene (corresponding to 39% of the acid chloride employed).

The second fraction crystallized and was triturated with petroleum ether; from isopropyl alcohol shiny leaflets, m.p. 81°.

TABLE I  
(*p*-ALKYLPHENYL)METHYLCARBINOLS  $RC_6H_4CHOHCH_3$

R =	% YIELD, FROM $RC_6H_4COCH_3$	B. P. °C/MM.	CALC'D C	CALC'D H	FOUND C	FOUND H
Methyl <sup>a</sup>	70.0	120/19				
Ethyl <sup>a</sup>	87.3	120/14				
Butyl	88.0	149–153/30	80.9	10.2	81.4	10.1
Heptyl	69.1	180–182/15	81.8	11.0	82.2	10.9
2-Ethylhexyl	64.4	170–174/18	82.1	11.0	83.0	11.0 <sup>b</sup>

<sup>a</sup> Described without physical constants by Gauthier and Gauthier (16).

<sup>b</sup> The product contained a small amount of (*p*-ethylhexyl)styrene.

TABLE II  
*p*-ALKYLSTYRENES,  $RC_6H_4CH=CH_2$

R =	% YIELD FROM $RC_6H_4CHOHCH_3$	B. P. °C/MM.	CALC'D C	CALC'D H	FOUND C	FOUND H
Methyl <sup>a</sup>	71.8	63/15	91.5	8.5	91.3	8.3
Ethyl <sup>b</sup>	72.0	86/20	90.9	9.1	90.5	9.0
Butyl	70.0	116–118/15	90.0	10.0	89.7	10.2
Heptyl	69.3	155–156/12	89.1	10.9	88.9	10.9
2-Ethylhexyl	30.0	138–141/7	88.9	11.1	88.7	11.3

<sup>a</sup> Shorugin and Shorugina (17a) b.p. 51°/10 mm. Gauthier and Gauthier (16) b.p. 166–167°/724 mm. Cf. Palmer (17b) and Matui (17c).

<sup>b</sup> Gauthier and Gauthier (16) b.p. 86°/20 mm. Matui (18a) b.p. 175–177°. Cf. (18b).

*4-Heptylbromobenzene.* The reduction of 40 g. of the foregoing ketone was carried out with 60 g. of amalgamated zinc wool, 50 cc. of toluene, 35 cc. of water and 90 cc. of concentrated hydrochloric acid. 4-Heptylbromobenzene boiled at 154–157°/10 mm.; 187–190°/35 mm.; yield, 30 g. (80%).

*Anal.* Calc'd for  $C_{13}H_{19}Br$ : C, 61.2; H, 7.5.

Found: C, 61.3; H, 7.4.

*β-(4-Heptylphenyl)ethyl chloride.* When 37 g. of 4-heptylbromobenzene was added to an ethereal suspension of 3.4 g. of magnesium, which had been activated with a few drops of methyl iodide, the reaction proceeded steadily; it was completed by boiling for two hours. Thirty-two grams of *β*-chloroethyl *p*-toluenesulfonate was then added. After twelve hours' standing, the solid cake was refluxed for six hours and decomposed with ice and dilute sulfuric acid. Fractionation gave two volatile products and a not inconsiderable quantity of resin: (a) b.p. 109°/10 mm.; heptylbenzene; yield, 10 g.; (b) b.p. 168°/10 mm.; *β*-(4-heptylphenyl)ethyl chloride; yield, 10 g. (30%).

*Anal.* Calc'd for  $C_{15}H_{23}Cl$ : C, 75.6; H, 9.4; Cl, 15.0; mol. wt. 238.

Found: C, 75.4; H, 9.8; Cl, 14.6; mol. wt. 216.

*2-Ethylhexanoylchloride.* 2-Ethylhexanoic acid (13) (120 g.) was refluxed with thionyl chloride (200 cc.) for six hours after the spontaneous reaction had subsided; b.p. 114–116°/75 mm.; 101°/40 mm.; yield, quantitative.

*Anal.* Calc'd for  $C_8H_{15}ClO$ : C, 59.3; H, 9.3.

Found: C, 59.0; H, 9.1.

*(2-Ethylhexanoyl)benzene.* The mixture of 109 g. of 2-ethylhexanoyl chloride, 100 g. of aluminum chloride and 700 cc. of benzene, prepared at 0°, was kept at room temperature for two days, refluxed for two hours and decomposed with ice and concentrated hydrochloric acid. Fractional distillation gave (a) 41 g. of b.p. 149–150°/35 mm.; (b) 18 g. of b.p. 184–185°/45 mm. Fraction (a) had the formula  $C_8H_{16}O$  and the structure (I) or (II). It did not form a semicarbazone, but reacted with phenylmagnesium bromide.

*Anal.* Calc'd for  $C_8H_{16}O$ : C, 76.2; H, 11.1.

Found: C, 76.3; H, 11.3.

Fraction (b) was the desired ketone; yield, 13%.

*Anal.* Calc'd for  $C_{14}H_{20}O$ : C, 82.4; H, 9.8.

Found: C, 82.6; H, 9.6.

When 21 g. of 2-ethylhexanoyl chloride reacted with 24 g. of bromobenzene in 150 cc. of carbon disulfide and in the presence of 37 g. of aluminum chloride, a considerable amount of resin formed. Fractional distillation gave 4 g. of the ketone  $C_8H_{16}O$  (b.p. 149–150°/35 mm.), 4 g. of (2-ethylhexanoyl)benzene (b.p. 174–175°/35 mm.) and 3 g. (8%) of *p*-(2-ethylhexanoyl)bromobenzene (b.p. 210°/45 mm.).

*1-Phenyl-2-methyl-5-ethylcyclopentanol.* The interaction of 30 g. of the ketone  $C_8H_{16}O$  and phenylmagnesium bromide (from 9 g. of magnesium and 56.3 g. of bromobenzene) was achieved by refluxing for two hours. Decomposition gave 16 g. of unchanged ketone (b.p. 149–150°/35 mm.; 53%) and 18 g. of the carbinol, b.p. 235–240°/50 mm. (yield, 37%).

*Anal.* Calc'd for  $C_{14}H_{20}O$ : C, 82.4; H, 10.0.

Found: C, 82.1; H, 9.9.

*Bromination of (2-ethylhexyl)benzene.* To a solution of 38 g. of (2-ethylhexyl)benzene in 100 cc. of carbon tetrachloride, 11 cc. of bromine was slowly added at a temperature not exceeding 5°. The reaction was rather violent. After twelve hours at room temperature, the reaction product was washed with sodium carbonate solution, dried with calcium chloride and distilled, first at ordinary pressure (carbon tetrachloride), then *in vacuo*. Practically all the product boiled under 20 mm. pressure at 135–140°, continuously giving off HBr. A small amount of a bromo compound, boiling at 212–214°/20 mm. was also obtained, but on redistillation it decomposed, too, into hydrogen bromide and the product boiling at 135–140°. The latter was treated with solid potassium hydroxide, filtered and redistilled; yield, 34 g. It was an unsaturated hydrocarbon, presumed to be 1-phenyl-2-ethylhexene-(1).

*Anal.* Calc'd for  $C_{14}H_{20}$ : C, 89.4; H, 10.6.

Found: C, 89.4; H, 10.7.

LONDON, ENGLAND

REHOVOTH, PALESTINE

#### REFERENCES

- (1) MARVEL AND CO-WORKERS, *J. Am. Chem. Soc.*, **58**, 1176 (1936); **66**, 2054 (1944); **68**, 861, 1365 (1946).
- (2) WALLING AND WOLFSTIRN, *J. Am. Chem. Soc.*, **69**, 852 (1947). STRASSBURG, GREGG, AND WALLING, *J. Am. Chem. Soc.*, **69**, 2141 (1947).
- (3) BROOKS, *J. Am. Chem. Soc.*, **66**, 1295 (1944).
- (4) MOWRY, RENOLL, AND HABER, *J. Am. Chem. Soc.*, **66**, 1105 (1944).
- (5) TONG AND KENYON, *J. Am. Chem. Soc.*, **69**, 1902 (1947).
- (6) INSKEEP AND DEENIM, *J. Am. Chem. Soc.*, **69**, 2237 (1947).

- (7) SHORUIGIN AND SHORUIGINA, *Chem. Abstr.*, **29**, 6885 (1935).
- (8) For a survey, based mainly on the work of Hopff and of Nenitzescu, see THOMAS, "Anhydrous Aluminum Chloride in Organic Chemistry", p. 744 ff.
- (9) HIGGINBOTTOM AND HILL, *J. Chem. Soc.*, 264 (1937).
- (10) See PROSSER, *Proc. Trans. Roy. Soc. Can.*, (3) **18**, Sec. III, 118 (1924); *Chem. Zentr.*, **1925** I, 1491. GROGGINS *et al.*, *Ind. Eng. Chem.*, **27**, 893 (1931). HAHN AND REID, *J. Am. Chem. Soc.*, **46**, 1645 (1924).
- (11) *Org. Syntheses*, Coll. Vol. I, 2nd Ed., 109, (1941).
- (12) See also (a) DERMER *et al.*, *J. Am. Chem. Soc.*, **63**, 2881 (1941); **64**, 464 (1942). (b) I. G. FARBEN, German Patent 646,702; *Chem. Abstr.*, **31**, 6673 (1937). (c) KURSANOV AND ZELVIN, *Chem. Abstr.*, **34**, 4062 (1940).
- (13) (a) BRUSON AND STEIN, U. S. Patent 2,004,069; *Chem. Abstr.*, **29**, 4773 (1935). (b) WAGNER-JAUREGG AND HIPPCHEM, *Ber.*, **76**, 694 (1943). (c) NORRIS AND ARTHUR, *J. Am. Chem. Soc.*, **62**, 874 (1940). (d) German Patent 637,384; *Chem. Abstr.*, **31**, 703 (1937).
- (14) (a) WEYGAND, MONSDORF, AND STROBELT, *Ber.*, **68**, 1825 (1935). (b) ZAKI AND FAHION, *J. Chem. Soc.*, 307 (1942).
- (15) WEIZMANN, British Patent, 550,134; *Chem. Abstr.*, **38**, 979 (1944).
- (16) GAUTHIER AND GAUTHIER, *Bull. soc. chim.*, (4) **53**, 323 (1933).
- (17) (a) SHORUIGIN AND SHORUIGINA, *Chem. Abstr.*, **29**, 6886 (1935). (b) Cf. PALMER, U. S. Patent 2,291,915; *Chem. Abstr.*, **37**, 2392 (1943). (c) MATUI, *Chem. Abstr.*, **35**, 4744 (1941).
- (18) (a) MATUI, *Chem. Abstr.*, **38**, 3748 (1944). (b) Cf. I. G. FARBEN, French Patent 682,569; *Chem. Abstr.*, **24**, 4523 (1930).