The Purification and Physical Constants of Aromatic Hydrocarbons

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The physical properties of eleven aromatic hydrocarbons reported herein were obtained during a program involving the synthesis and purification of ten-gallon quantities of twenty-six aromatic hydrocarbons. The properties and methods of synthesis of the other members of the series will be reported in subsequent publications.

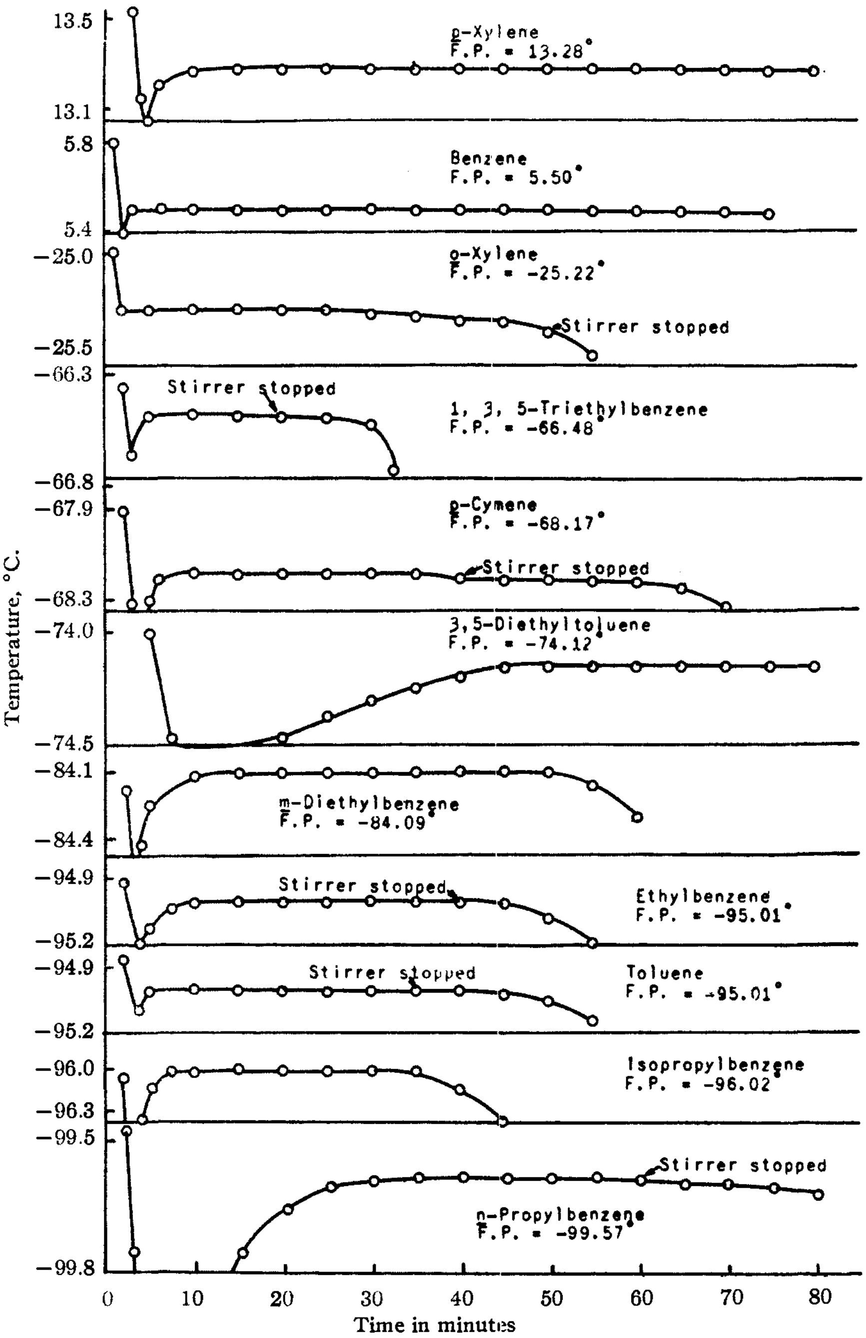

Fig. 1.—Freezing curves of aromatic hydrocarbons.

Three of the materials reported below were synthesized by literature methods while the rest were commercial products subjected to careful purification. The physical constants as well as methods of purification or synthesis are presented in Table I. The freezing curves are illustrated in Fig. 1.

The time-temperature freezing curves were determined with a platinum resistance thermometer and a G-2 Mueller bridge with accessory equipment and by methods described by Rossini and co-workers[1] except that the highest observed temperature in each case was selected as the freezing point. The boiling points were determined by the use of a platinum resistance thermometer in an apparatus modified from that described by Quiggle, Tongberg and Fenske.[2] The system was pressurized with dry air from a surge tank and held constant by adjusting a continuous bleed. The densities were determined with a 20-ml. pycnometer described by Robertson[3] and the indices of refraction were measured with a 4-place Abbé refractometer. It is estimated that the magnitude of the uncertainties for the freezing point is 0.02°, for the boiling point 0.1°, for density 0.0003 and index of refraction 0.0004, while the precision of the measurements for freezing point is ±0.003°, for boiling point ±0.04°, for density ±0.00004 and index of refraction ±0.0002. Both the re-

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(1) A. R. Glasgow, A. J. Stoiff and F. D. Rossini, *J. Res. Nat. Bur. of Standards*, **35**, 355 (1945).

(2) D. Quiggle, C. O. Tongberg and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(3) G. R. Robertson, *ibid.*, **11**, 464 (1939).

TABLE I

PHYSICAL CONSTANTS

Aromatic hydrocarbon	F. p., °C.	B. p., 760 mm., °C.	Density, g./ml. at 20°C.	$n^{20}D$
Benzene[a]	+ 5.50	80.08	0.8789	1.5011
Toluene[a]	−95.01	110.58	.8670	1.4967
Ethylbenzene[a]	−95.01	136.25	.8671	1.4958
n-Propylbenzene[c]	−99.57	159.31	.8618	1.4919
Isopropylbenzene[a]	−96.02	152.42	.8619	1.4912
o-Xylene[b]	−25.22	144.41	.8798	1.5052
p-Xylene[b]	+13.28	138.36	.8608	1.4958
m-Diethylbenzene[a]	−84.09	181.62	.8641	1.4955
p-Cymene[a]	−68.17	177.23	.8567	1.4908
1,3,5-Triethylbenzene[d]	−66.48	215.92	.8621	1.4958
3,5-Diethyltoluene[e]	−74.12	200.70	.8631	1.4969

[a] Commercial product purified by distillation through 100 theoretical plate columns. [b] Purified by low-temperature fractional crystallization as well as distillation. [c] Synthesized according to H. Gilman and W. E. Catlin in Gilman, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, Coll. Vol. I, 2nd ed., p. 471, and purified by distillation. [d] Prepared according to W. B. Dillingham and E. E. Reid, THIS JOURNAL, **60**, 2606 (1938), except that ethylbenzene was used instead of benzene. It was also purified by distillation. [e] Prepared by the ethylation of toluene according to J. F. Norris and D. Rubinstein, THIS JOURNAL, **61**, 1163 (1939), except that the ethylation was run at room temperature. Ethyl bromide was used in both ethylations.

fractometer and the method of density determination were checked by the use of National Bureau of Standards sample of toluene, No. 211a.

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Improved Preparation of Creatinine Zinc Chloride

BY WM. A. PEABODY

The preferred process for making creatinine zinc chloride has been the fusion method of Edgar and Hinegardner.[1] Its advantage, the adequacy of technical creatine as a raw material, is offset by relatively poor yield, the need for recrystallization, and occasional difficulty in controlling the fusion (particularly with larger batches.) Inspection of their recrystallization procedure led to the conclusion that the synthesis should result satisfactorily by simple metathesis between creatinine hydrochloride and zinc acetate in water. Preliminary trials proved this to be the case; primary yields were high, and quality under properly controlled conditions was equal to that of the recrystallized product of the fusion method.

Procedure.—Combine in the proportions 500 g. of dry creatinine hydrochloride and 367 g. of C. P. zinc acetate dihydrate, dissolved separately in approximately 310 cc. and 750 cc. of hot distilled water in 2 and 1.5 liter beakers, respectively. Since final concentrations are near saturation, make small water additions as needed to replace evaporation losses until solutions are complete. Stir the hydrochloride solution while pouring the acetate solution into it fairly rapidly, followed by a little wash water. Cool promptly in tap water, then chill to about 0°. Filter by suction, wash with one or two small portions of 70–80% methanol or ethanol, then with 99.5% methanol until acetic odor is faint or absent, and dry; yield, 545–560 g. of white product (90–92.5%). A second crop of about 13 g., obtained by chilling the filtrate after addition of 1–1.5 volumes of methanol, requires recrystallization from acetic acid[1] to reach analytical purity.

The creatinine hydrochloride need not be white, but should not be more than slightly yellow or greenish-yellow. When the hydrochloride is available, the present method is a great saver of time and materials. If one must begin with technical creatine, the choice between the two methods may be a matter of personal preference. Conversion of creatine[1,2] to a good grade of creatinine hydrochloride is not particularly difficult, but does take some time and effort. With experience, one presumably should be able to omit final crystallization of the hydrochloride if its concentrated solution is sufficiently pure and its concentration determined with moderate accuracy. The use of concentrated reactant solutions eliminates the need of alcohol at the precipitation stage, which, together with acetic acid formation, minimizes co-precipitation of any excess reactant or dissolved impurities.

The author is indebted to Mrs. Ruth H. Powell, Miss Alice Parson and Mr. W. J. Martin for a number of the analyses.

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[1] Edgar and Hinegardner, "Organic Syntheses," Coll. Vol. I, 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 173, 172.

[2] Hunter, "Creatine and Creatinine," Longmans, Green and Co., Ltd., London, 1928, pp. 54–55.

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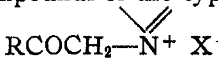
Some Quaternary Ammonium Salts of Heterocyclic Bases. II[1,2]

BY JONATHAN L. HARTWELL AND SYLVIA R. L. KORNBERG

The biological results obtained by our collaborators[3] on compounds of the type represented by the formula  $RCOCH_2—N^+ X^-$, where the nitrogen atom is the hetero atom in an aromatic base of the type of pyridine and its homologs or benzologs,[4] warranted the preparation of other series of related quaternary ammonium salts. For this purpose, two series were prepared, in which R was α-naphthyl and β-naphthyl, respectively. These compounds were formed by the addition of the appropriate naphthacyl bromide to the base, except in the case of the 1-(α-naphthacyl)-3-picolinium and 1-(α-naphthacyl)-3-methylisoquinolinium halides where difficulty was encountered in obtaining the bromides pure. In these two instances, iodides were then prepared by both the ionic reaction of the bromides with potassium

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[1] Paper XIII in the series entitled "Chemical Treatment of Tumors." Paper XII in this series: Hartwell and Kornberg, THIS JOURNAL, **68**, 868 (1946).

[2] Material contained in this paper was presented, in part, at the meeting of the American Association for Cancer Research at Atlantic City, N. J., March 11, 1946. Abstract in *Cancer Research*, **6**, in press (1946).

[3] Peters, Hartwell, Dalton and Shear; Dalton and Peters, *ibid.*, **6**, in press (1946).

[4] Hartwell and Kornberg, ref. 1.