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The Application of the Chloromethylation Reaction to the Syntheses of Certain Polymethylbenzenes

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In connection with work to be reported later concerning the kinetics of catalytic hydrogenation it became necessary to prepare in quantity and in high state of purity several polymethylbenzenes. A survey of the literature[1] reveals that although the syntheses of these compounds have been reported many times, the methods employed are, in most cases, not entirely satisfactory. Consequently, it was deemed desirable to adapt other reactions, if possible, to the preparations of these compounds. The reaction which appeared to be the most generally applicable was the chloromethylation reaction followed by replacement of chlorine with hydrogen.

Experimental

Starting Materials.—Eastman Kodak Co. grade *p*-xylene and Mallinckrodt AR toluene were distilled through an eight-foot helix-packed column and only that portion which distilled with constant boiling point within the reading error of the thermometer (±0.05°) was used. Commercial *o*-xylene from the Oronite Chemical Company was purified by azeotropic fractional distillation with methoxyethanol.[2] The product thus purified had the same constant boiling point as that of a sample purified by the method of Clarke and Taylor.[3] Eastman Kodak Co. grade *m*-xylene was fractionated through the same column but the sample used had a boiling range of 0.2°. Eastman grade mesitylene was sulfonated, the sulfonic acid was recrystallized twice from chloroform and hydrolyzed with boiling 20% hydrochloric acid. The product was then distilled through the same column with constant boiling point. Du Pont tetrahydrofuran was fractionated yielding about 90% of a fraction having a boiling range of 0.1°.

The Chloromethylation Reaction.—For the preparation of pseudocumene and hemimellitene the xylenes were used as starting materials. Three methods were investigated for the introduction of the chloromethyl group. The method of Fuson and co-workers[4] was found to give a larger proportion of dichloromethylated product than was desired. The method of Vavon and Bolle[5] was found to proceed much too slowly to be useful. The method of von Braun and Nelles,[1c] on the other hand, by suitable modifications can be made to give very satisfactory yields of the desired products with a minimum of difficulty. The modifications in the original method are (1) the length of the duration of the reaction, (2) the addition of from 100 to 200 ml. of benzene to the product of the reaction per mole of chloromethyl compound prepared which, after being dried with anhydrous potassium carbonate, is removed by distillation to eliminate traces of water which often cause polymerization, and (3) the use of either formalin or paraformaldehyde. The details of these reactions are given in Table I.

TABLE I

REACTION TIMES AND YIELDS OBTAINED BY THE METHOD OF VON BRAUN AND NELLES[1c]

Starting hydrocarbon	Duration of reacn., hr.	Yields, % Mono-substd. product	Di-substd. product	Di-phenyl-methanes	Un-changed hydro-carbon
o-Xylene	9–10	80–85	6–7	2–3	5–10
m-Xylene	6–7	70–75	18–22	2–3	4–7
p-Xylene	11–12	75–80	4–5	2–3	10–12
o-Xylene[a]	18–20	38–40	56–57	2–3	0
m-Xylene[a]	16–18	23–27	68–72	2–3	0
p-Xylene[a]	20–22	38–40	56–57	2–3	0
Hemimellitene	3–4	78–82	8–12	5–6	5–6
Pseudocumene	6–7	88–90	4–5	3–4	0
Mesitylene	3–4	63–67	16–20	5–6	3–4

[a] By use of the procedure for introducing two groups.

For the preparation of durene, isodurene and prehnitene the starting materials were the three xylenes, hemimellitene, pseudocumene and mesitylene. The xylenes were used by introducing two chloromethyl groups by the method of von Braun and Nelles.[1c] The details of these reactions are given in Table I. Retreatment of the reclaimed monochloromethyl derivatives considerably increases the yields of dichloromethylated substances which are obtainable. The trimethylbenzenes were also treated by the method of von Braun and Nelles.[1c] The results of these reactions are given in Table I. The procedures used here were the same as those used for the xylenes with the exception that with mesitylene and hemimellitene a molar ratio of formaldehyde to hydrocarbon of 1.1 was used instead of the customary 1.3. It should be pointed out that in the case of mesitylene the method of Vavon and Bolle[5] gives superior yields of the monochloromethyl derivative (80 to 82%) to that of von Braun and Nelles.[1c]

For the preparation of pentamethylbenzene mesitylene was dichloromethylated by the von Braun and Nelles[1c] procedure for dichloromethylating the xylenes. However, the second addition of formaldehyde and subsequent heating is unnecessary here. The yield of bis-(chloromethyl)-mesitylene, 80 to 85%, can be increased if desired by retreating the isolated monosubstituted compound. For purposes discussed later toluene was also chloromethylated by the von Braun and Nelles[1c] procedure. The yield after 7 hours was 76% chloromethyltoluene, 7% unchanged toluene, and 3% bis-(chloromethyl)-toluene.

Replacement of Chlorine by Hydrogen.—Of all of the reactions tried for this purpose the most satisfactory involves treatment of the halide with lithium hydride and lithium aluminum hydride in tetrahydrofuran solution by the method of Johnson, Blizzard and Carhart.[6] The yields are quantitative except for negligible mechanical losses. The reaction of the halide with sodium acetate in acetic acid, followed by alkaline hydrolysis in aqueous alcohol and catalytic hydrogenation of the resulting carbinol using copper chromite as a catalyst also gives essentially quantitative yields. However, the use of high pressure hydrogenation apparatus seriously limits the size of the batches which can

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[1] (a) For pseudocumene see R. W. Maxwell and Roger Adams, THIS JOURNAL, **52**, 2962 (1930); L. I. Smith and A. P. Lund, *ibid.*, **52**, 4147 (1930); E. R. Ebersole, *Natl. Advisory Comm. Aeronaut., Tech. Note* No. 1020, 9 pp. (1946), *C. A.*, **41**, 4113a (1947). (b) For hemimellitene see L. I. Smith and L. J. Spillane, THIS JOURNAL, **62**, 2639 (1940); J. M. Lamberti, T. W. Reynolds and H. H. Chanan, *Natl. Advisory Comm. Aeronaut, Tech. Note* No. 1163, 8 pp. (1946), *C. A.*, **41**, 2009g (1947). (c) For durene see L. I. Smith, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 248; J. von Braun and J. Nelles, *Ber.*, **67**, 1094 (1934). (d) For isodurene see L. I. Smith, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 361; W. J. Hickinbottom and C. R. Porter, *J. Inst. Petroleum*, **35**, 630 (1949). (e) For prehnitene see L. I. Smith, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 370; S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, THIS JOURNAL, **71**, 1364 (1949). (f) For pentamethylbenzene see L. I. Smith, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 250; W. J. Hickinbottom and C. R. Porter, *J. Inst. Petroleum*, **35**, 630 (1949).

[2] A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 141 (1946).

[3] H. T. Clarke and E. R. Taylor, THIS JOURNAL, **45**, 830 (1923).

[4] R. C. Fuson and co-workers, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., p. 65, note 5.

[5] G. Vavon and J. Bolle, *Compt. rend.*, **204**, 1826 (1937).

[6] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

be prepared conveniently. Hydrolysis of the Grignard reagents of the halides gives 60 to 65% yields of the hydrocarbons in the case of the monochloromethyl compounds. With the dichloromethylated compounds, however, the method is a failure. The results of the reductions of the chloromethyl compounds by the method of Johnson, Blizzard and Carhart are given in Table II.

TABLE II

PRODUCTS OBTAINED BY REPLACEMENT OF CHLORINE BY HYDROGEN

Compound reduced	Yield of hydrocarbon mixt. %	Ratios of isomers in hydrocarbon mixtures
Chloromethyltoluene	97	0.54 *p*-xylene; 0.43 *o*-xylene; 0.03 *m*-xylene
Chloromethyl-*o*-xylene	97	0.28 hemimellitene; 0.72 pseudocumene
Chloromethyl-*m*-xylene	98	0.89 pseudocumene; 0.11 hemimellitene; very small but unmeasured amount of mesitylene
Chloromethyl-*p*-xylene	97	1.00 pseudocumene
Chloromethylpseudocumene	96	0.80 durene; 0.02 isourene; 0.18 prehnitene
Chloromethylhemimellitene	97	0.95 prehnitene; 0.05 isodurene
Chloromethylmesitylene	97	1.00 isodurene
Bis-(chloromethyl)-*o*-xylene	94[a]	0.53 durene; 0.19 isodurene; 0.28 prehnitene
Bis-(chloromethyl)-*m*-xylene	94[a]	0.72 to 0.73 durene; <0.01 isodurene; 0.27 prehnitene
Bis-(chloromethyl)-*p*-xylene	94[a]	0.83 durene; 0.09 isodurene; 0.08 prehnitene
Bis-(chloromethyl)-pseudocumene	93[a]	1.00 pentamethylbenzene
Bis-(chloromethyl)-hemimellitene	92[a]	1.00 pentamethylbenzene
Bis-(chloromethyl)-mesitylene	92[a]	1.00 pentamethylbenzene

[a] Corrected for residue, calculated as polymethyldiphenylmethanes formed during the chloromethylation in the amounts indicated in Table I, column 5.

Analysis of the Hydrocarbon Mixtures.—In all of the preceding reductions except five the resulting hydrocarbons were mixtures of isomers. These mixtures were separated, where possible, by careful fractional distillations in helix-packed columns having from 50 to 120 theoretical plates. The freezing points of the resulting fractions together with examination of the distillation curves were used to determine the relative amounts of the various isomers present in the original mixtures.

To illustrate, chloromethyl-*o*-xylene gives a mixture of pseudocumene and hemimellitene. A representative distillation curve for this mixture is given in Fig. 1. Simple inspection of this curve indicates the relative proportion of the two isomers. However, bis-(chloromethyl)-*o*-xylene gives a mixture of durene, isodurene and prehnitene. Distillation separates the prehnitene (b.p. 205.0°) from the durene–isodurene mixture (b.p.'s 196.8 and 197.9°, respectively), but freezing point determinations were necessary in order to analyze the durene–isodurene fractions. A representative distillation curve with freezing points of the durene–isodurene fractions is shown in Fig. 2, curve 1.

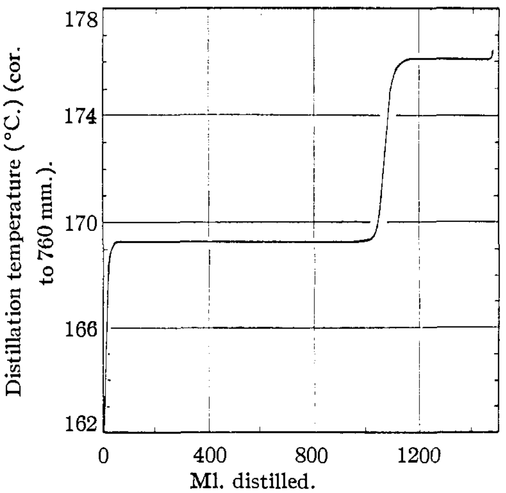

FIG. 1.—Distillation curve for pseudocumene–hemimellitene mixture from chloromethyl-*o*-xylene.

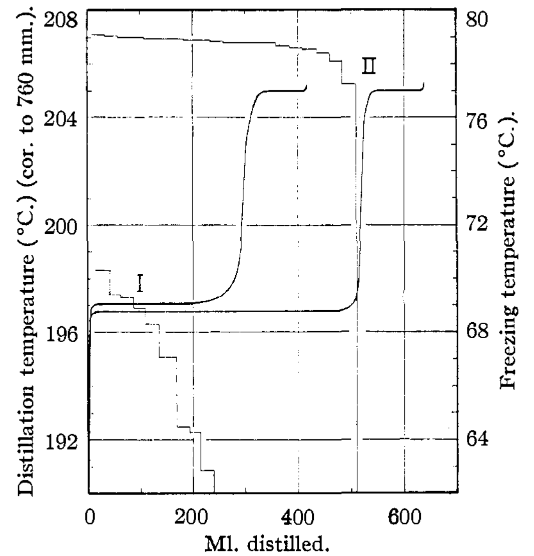

Fig. 2.—Distillation and freezing point curves for durene–isodurene–prehnitene mixtures: I, from bis-(chloromethyl)-*o*-xylene; II, from chloromethylpseudocumene.

Figure 2, curve 2 gives the same information for the mixture of hydrocarbons obtained from chloromethylpseudocumene. The freezing point–composition diagram of Smith and MacDougall[7] was used for the analyses of the durene–isodurene fractions. In the same way the data of Nakatsuchi[8] was used for analysis of the *p*-xylene–*m*-xylene fractions which were separated from *o*-xylene by the distillation of the hydrocarbon mixture obtained from chloromethyltoluene.

Figure 3 shows distillation curves for the hydrocarbons obtained from hemimellitene and mesitylene. These are prehnitene plus a small amount of isodurene in the former case, and pure isodurene in the latter. The results of the calculations of the percentages of the various isomers formed by the various reactions are given in Table II.

Discussion

By the methods described, isomerically pure pseudocumene is obtained from pure *p*-xylene. If mixed xylene is used as a starting material the resulting pseudocumene can be separated from the small amount of hemimellitene also obtained by careful fractional distillation. For the preparation of hemimellitene the use of a xylene rich in the ortho isomer is necessary, pure *o*-xylene yielding 22 to 24% hemimellitene. Although this yield is somewhat lower than those reported by Smith and Spillane[1b] and by Lamberti, Reynolds and Chanan,[1b] the procedure is much more satisfactory, particularly if technical *o*-xylene such as that available from the Oronite Chemical Company is used.

The most satisfactory starting material for the preparation of prehnitene is hemimellitene. However, since it is not commercially available at pres-

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[7] L. I. Smith and F. H. MacDougall, THIS JOURNAL, **51**, 3001 (1929).

[8] A. Nakatsuchi, *J. Chem. Ind. Japan*, **29**, 29 (1926).

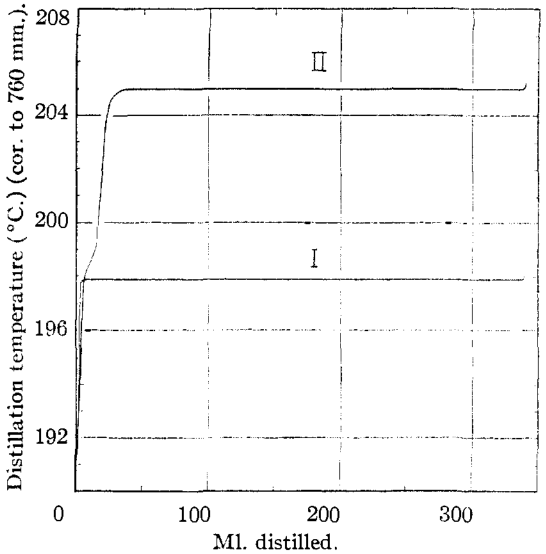

Fig. 3.—Distillation curves for: I, isodurene from chloromethylmesitylene; II, isodurene–prehnitene mixture from chloromethylhemimellitene.

ent, its use for this purpose is not usually practical. By use of the dichloromethylation procedure described with *o*- or *m*-xylene plus the method of Birch, Dean, Fidler and Lowry[1e] the yield of prehnitene obtainable from either of these xylenes is 67 to 69%. For the preparation of durene, *p*-xylene is the best starting material, although mixed xylene consisting primarily of the *p*- and *m*-isomers is satisfactory. For the preparation of isodurene the chloromethylation of mesitylene by the procedure of Vavon and Bolle[5] gives the best yields of the methods tried.

There are few reactions for which sufficient information is available to allow a check of the method of Condon[9] for the correlation of the proportions of isomers obtained in aromatic substitutions with the relative rates of these reactions. Fortunately, the work of Szmant and Dudek[10] together with the present work make such calculations possible for the chloromethylation reaction. According to these authors the relative rates of chloromethylation at 85° for benzene, toluene, *p*-xylene and mesitylene are 1, 3.1, 1.6 and 13, respectively. By the method of Condon[9] the value for the relative rate of chloromethylation of *p*-xylene compared to that of benzene as unity is 0.75 and that for mesitylene is 80. A further check of this method of calculation can be applied to the ratios of isomers formed from *o*-xylene, *m*-xylene, pseudocumene and hemimellitene. In Table III there is given a summary of the calculated and the observed ratios. Here, the agreement between experimental and calculated results is more satisfactory.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED RATIOS OF ISOMERS FORMED DURING CHLOROMETHYLATION

Starting hydrocarbon	Calcd. ratio of products	Obsd. ratio of products
o-Xylene	0.72 pseudocumene	0.72 pseudocumene
	.28 hemimellitene	.28 hemimellitene
m-Xylene	.83 pseudocumene	.89 pseudocumene
	.17 hemimellitene	.11 hemimellitene
	.0008 mesitylene	Trace mesitylene
Pseudocumene	.70 durene	.80 durene
	.28 prehnitene	.18 prehnitene
	.02 isodurene	.02 isodurene
Hemimellitene	.03 isodurene	.05 isodurene
	.97 prehnitene	.95 prehnitene

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Summary

Methods of preparation requiring only two steps are presented for the following polymethylbenzenes in the yields indicated: pseudocumene, 73 to 78% based on *p*-xylene; hemimellitene, 22 to 24% based on *o*-xylene; durene, 70 to 72% based on pseudocumene; isodurene, 78 to 80% based on mesitylene; prehnitene, 71 to 75% based on hemimellitene; durene, 50 to 55% based on *m*- or *p*-xylene; prehnitene, 19 to 20% based on *o*- or *m*-xylene; and pentamethylbenzene, 74 to 83% based on mesitylene. For the last three examples cited, the yields can be increased to 65 to 70%, 23 to 25%, and 87 to 90%, respectively, by recycling the recovered monochloromethylated hydrocarbon.

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(9) F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

(10) H. H. Szmant and J. Dudek, *ibid.*, **71**, 3763 (1949).