The methyl alcoholic mother liquors were poured into cold water and the precipitate thus obtained was filtered off and crystallized from petroleum ether (b. p., 50–60°). About 0.5 g. of product melting at 96–99° was obtained. A 0.2g. sample in 10 cc. of chloroform gave a rotation of —1.4° (Ventzke scale) in a 1dcm. tube; $[\alpha]^{25}_{\mathrm{D}} = -24.27°$. This material was not purified further, but its physical constants were very close to those of the levorotatory iodomercuri compound obtained from the corresponding bromomercuri derivative.

A solution of 5 g. of *l*-menthyl β-methoxy-α-bromomercuri-hydrocinnamate (m. p., 144–145°) was dissolved in 150 cc. of methyl alcohol and added to a solution of 2.5 g. of sodium iodide in 50 cc. of methyl alcohol. The precipitate of sodium bromide was filtered off, and the methyl alcoholic solution was diluted with water. The precipitated mercury compound was filtered off and recrystallized from petroleum ether (b. p., 50–60°); m. p., 102–103°. When mixed with a sample of the levorotatory iodomercuri isomer obtained from the acetoxymercuri compound the melting point was not depressed. A 0.2g. sample in 10 cc. of chloroform gave an observed rotation of —1.3° (Ventzke scale) in a 1dcm. tube; $[\alpha]^{25}_{\mathrm{D}} = -22.5°$.

Anal. Subs., 0.2017: HgS, 0.0731. Subs., 0.2048: AgI, 0.0743. Calcd. for $C_{20}H_{29}O_3HgI$: Hg, 31.11; I, 19.68. Found: Hg, 31.25; I, 19.60.

Summary

The addition of mercuric salts to olefins of the type RR′C=CRR′ leads to the production of optically active isomers which can be explained only by the assumption that these addition products are true organic mercury compounds and not molecular addition products.

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A STUDY OF THE METHYLATION OF XYLENE. THE PREPARATION OF DURENE, PENTAMETHYLBENZENE AND HEXAMETHYLBENZENE

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The method of Friedel and Crafts has been used many times for the methylation of benzene and its homologs, and the reaction has been investigated in some detail by a number of workers.[2]

The quantities methylated were usually small, however, and the object was not primarily to obtain efficient methylation for the production of

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[1] Abstracted from a thesis by F. J. Dobrovolny, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Friedel and Crafts, *Ann. chim. phys.*, **1**, 449 (1884). Jannasch and Fittig, *Z. Chem.*, **6**, 161 (1870). Jannasch, *Ber.*, **7**, 692 (1874); *Ann.*, **161**, 79 (1872); *Ber.*, **8**, 355 (1875); **10**, 1355 (1877); **11**, 30 (1878). Ador and Rilliet, *Ber.*, **11**, 1627 (1878); **12**, 329 (1879). Jacobsen, *Ber.*, **9**, 256 (1876); **10**, 1009 (1877); **14**, 2624 (1881); **18**, 338 (1885). Anschütz, *Ann.*, **235**, 177 (1886). Claus, *Ber.*, **20**, 3097 (1887). Beaurepaire, *Bull. Soc. Chim.*, **50**, 677 (1888). See also Jacobsen, *Ber.*, **21**, 2824 (1888), and Beilstein, *Ann.*, **137**, 326 (1866).

the more highly methylated benzenes, but rather to study the course of the reaction. While practically all of the homologs of benzene have been methylated by the method of Friedel and Crafts, the starting materials were always pure substances. Up to the present, no one has made a study of the methylation of the mixture of xylenes occurring in refined coal-tar xylene, nor has any attempt been made to use this material as a source for the highly methylated benzenes. We desired large amounts of the tetramethylbenzenes, and particularly durene, for use in other experiments. The direct methylation of the xylenes seemed to us the most promising method for obtaining these and, accordingly, we have made a study of this reaction.

The difficulties involved in the use of the Friedel-Crafts synthesis for the production of the higher homologs of benzene are due chiefly to the fact that it is not possible to separate position isomers in this series from each other by the usual fractional distillations, and hence, while the methylation takes place readily, the reaction product on distillation gives a mixture of the xylenes, a mixture of the trimethylbenzenes and a mixture of the tetramethylbenzenes, besides pentamethylbenzene and higher-boiling products.

Of all the methylated benzenes, only three are solids at ordinary temperatures. These are durene (1,2,4,5-tetramethylbenzene), m. p. 80°, pentamethylbenzene, m. p. 52°, and hexamethylbenzene, m. p. 165°. The last two of these can easily be removed from the reaction mixture by distillation, leaving in one fraction the three tetramethylbenzenes. Of these, one (1,2,3,5-, isodurene) has never been obtained as a solid, another (1,2,3,4-, pseudodurene, prehnitene) is reported to melt at —4°, while the third, durene, has a relatively high melting point, 80°. If the methylation of xylene could be conducted in such a way as to yield a tetramethylbenzene fraction rich in durene, it should be possible to freeze it out as a solid and filter it off.

The earlier workers generally used methyl iodide as the methylating agent, either undiluted or with carbon disulfide as the solvent. In one case methyl bromide was used, and in a few cases methyl chloride. Our preliminary experiments with the reaction, using methyl iodide, showed that this substance gave a very poor yield of tetramethylbenzene fraction, none of which could be made to solidify by ordinary methods. Moreover, the products were always contaminated with iodine compounds which were very difficult to remove. For these reasons, we chose methyl chloride as the methylating agent.

Our experiments show that the methylation of ordinary xylene, using methyl chloride and aluminum chloride, takes place readily, and that the methylation may be easily controlled so that trimethylbenzenes, tetramethylbenzenes or pentamethylbenzene constitute the main product.

Moreover, the mixture of tetramethylbenzenes made in this way is rich in durene, and by cooling at least to —10° and filtering at this temperature, this substance may easily be made in quantity.

The filtrate from the durene, when warmed on the water-bath with fresh aluminum chloride, undergoes a reaction in which more durene is produced, together with small amounts of low- and high-boiling materials and, after decomposition, it may be fractionated, and the durene then frozen out again as in the original procedure. By working over these filtrates, and by methylating the lower-boiling fractions, it is possible to obtain a yield of durene as high as 35%, based on the original xylene.

Experimental Part

Reagents and Apparatus

Xylene.—This was a good, colorless, laboratory grade, having a distilling range of 135–140°, supposed to contain about 70% of *m*-xylene.

Aluminum Chloride.—The best grade of resublimed aluminum chloride that could be procured was used. The methylation is very unsatisfactory if the aluminum chloride is of an inferior grade.

Methyl Chloride.—This was generated as needed during the course of each experiment, by heating a mixture of methyl alcohol, sulfuric acid and sodium chloride. Thus, to prepare a charge of 10 equivalents of methyl chloride, 50 g. of water was added to 550 g. of concd. sulfuric acid. To this cooled acid was added 350 g. of commercial, straw-colored methyl alcohol at such a rate that the temperature did not rise above 60–70°. This mixture was poured into a round-bottomed flask, and 600 g. of sodium chloride added. The flask, fitted with a reflux condenser, was heated on a sand-bath so that a regular stream of methyl chloride was evolved through the condenser. The gas was washed with water, and then passed through concd. sulfuric acid and into the reaction flask.

Procedure

The xylene-aluminum chloride mixture is placed in a large flask on a steam-bath, which keeps the temperature at about 95° during the entire reaction. The methyl chloride, generated as described above, is passed through two wash bottles containing water, then through two bottles half filled with sulfuric acid. Three safety bottles are interposed in the train, one on each end, and one between the water and sulfuric acid bottles. The dried methyl chloride is passed into the xylene-aluminum chloride mixture through a wide tube reaching well to the bottom of the flask. The spent gases, consisting of the excess of methyl chloride and hydrogen chloride, pass through a long reflux condenser and then through a column of mercury, usually 10 cm. high. Thus, the whole apparatus is under a slight pressure. It is necessary to pass through about a 100% excess of methyl chloride in order to get a good yield of the tetramethylbenzene fraction. The absorption of the methyl chloride is much more rapid and complete if the amount of aluminum chloride is increased to about two-thirds of the weight of the xylene (compare Runs 20 and 100), but the product is very viscous and is difficult to handle in large quantities. A sample run, representing the best procedure, will be described, and other runs given in a table.

3180 g. of xylene (30 equivalents) and 900 g. of anhydrous aluminum chloride (about 6.7 equivalents) were placed in a 5-liter flask on the steam-bath. The aluminum chloride forms a thick, red, oily layer with the xylene in the bottom of the mixture.

The methyl chloride was generated in a 5-liter flask which was charged thrice, generating in all about 120 equivalents in 100 hours. Each charge consisted of 2200 g. of sulfuric acid, 200 g. of water, 1400 g. of methyl alcohol and 2400 g. of sodium chloride. The methyl chloride generator requires practically no attention until the evolution of gas slows down and the mixture is practically spent.

The rapid current of methyl chloride through the reaction mixture furnished sufficient stirring.[3] The dark layer on the bottom rose slowly and after two days it had spread throughout. At the end of the reaction (100 hours) the steam was turned off and the mixture allowed to stand overnight. It was then decomposed by slowly pouring it onto ice in five or six 2-liter beakers. Much hydrogen chloride was evolved, and when the decomposition was complete, the greenish oil was separated from the aqueous layer, dried with calcium chloride and filtered into several 2-liter flasks. The flasks were fitted with Glinsky columns, and the oil was fractionated twice. The products were colorless, highly-refractive liquids, and the fractions were cut as follows.

TABLE I

Fraction	Temp. range, °C.	Distillate Yield, g.	Distillate Substance
I and II	Up to 150	..	benzene, xylenes
III	150–180	570	trimethylbenzenes
IV	180–205	2075	tetramethylbenzenes
V	Residue above 205	815	mostly pentamethylbenzene

On cooling to room temperature, Fraction IV solidified partially. It was cooled in a mixture of ice and hydrogen chloride, then rapidly filtered with good suction through a cold filter. The durene was pressed down compactly on the filter and allowed to drain as much as possible. A yield of 605 g. of durene, or 15% of that calculated, was obtained. The durene

TABLE II

RESULTS OF THE METHYLATION OF VARIOUS AROMATIC HYDROCARBONS

Expt.	Hydrocarbon	Wt., g.	Al_2Cl_6	Moles of CH_3Cl	Time, hours	Yield, g., of fractions					Durene	Yield, %
						I up to 135°	II 135–150°	III 150–180°	IV 180–205°	V Residue		
5	Pseudocumene	75	30	2	3	...	...	15	45	10	21	24
6	Xylene	1300	200	45	36	...	109	617	560	85	177	11
8	Fraction III	1640	200	22	...	...	44	585	1006	40	400	21
10	Durene filtrate	110	26	...	6	...	4	22	70	6	11	10
11	Durene filtrate	1080	150	...	10	...	97	273	602	55	200	19
12	Durene filtrate	840	150	...	10	...	...	161	560	40	180	21
13	Fraction III	1250	150	18	...	...	117	545	690	15	180	13
14	Xylene	2260	700	100	40	...	54	542	1110	50	400	14
20	Xylene	3180	900	120	100	...	...	570	2075	815	605	15
21	Xylene	2260	1000	80	60	...	1025	830	75	80	...	..
22	Fraction III	2400	900	40	36	...	...	220	1800	450	507	18
100	Xylene	3000	2000	120	72[a]	217	25	91	676	2098	338	9

[a] Run for three days; heated during the day, with methyl chloride passing through, and allowed to cool and stand overnight.

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[3] Some experiments, using high-speed stirring, were run on a small scale, and there seemed to be no appreciable difference in the time required for absorption of the methyl chloride. With or without stirring, there is an exceedingly rapid absorption at first, until $^1/_4$ to $^1/_2$ of the theoretical amount (depending upon the amount of aluminum chloride used) has been absorbed, and then the absorption becomes very slow, much methyl chloride passing through without reacting.

filtrates may be worked up by heating them with aluminum chloride alone, then decomposing and fractionating in the usual way; and the trimethyl benzenes may be methylated for a short time with methyl chloride, when they are converted almost completely into tetramethylbenzenes. By carrying out one operation on the durene filtrates, and one methylation of the trimethylbenzene fraction, the combined yield of durene in any one run will be between 25 and 35%, based on the xylene used at first. The results of several runs are given in Table II. In each case the weights of the various fractions are those resulting after the second fractionation.

Run 21 shows the effect of a poor grade of aluminum chloride. In this run, the reaction mixture became tarry from the beginning and not much methyl chloride was absorbed.

Run 100 shows the effect of an increased amount of aluminum chloride. This run is practically a duplication of Run 20, except for the amount of aluminum chloride used, and by increasing the catalyst, the absorption of methyl chloride takes place more quickly and completely.

The durene obtained in this way is nearly pure, and one recrystallization from methyl or ethyl alcohol gives a pure white product; m. p., 80°. Solutions of it should not be heated too long, as it is quite volatile with alcohol. It also disappears appreciably on standing in the air, so that crystals of it should be dried as quickly as possible and bottled at once. The alcoholic mother liquors from crystallizations of durene should be distilled off and kept. They contain appreciable amounts of it and should be used for recrystallizing the next batch. The residues from the distillation of these mother liquors can be worked up with the original durene filtrates.

Pentamethylbenzene.—By continuing the methylation beyond the tetramethylbenzene stage, pentamethylbenzene may be made in quantity. The reaction mixture is decomposed and fractionated in the usual way, and then the material boiling above 205° (Fraction V) is separated into three fractions: VI, 205–215°; VII, 215–235° and VIII, the residue boiling above 235°. The first of these is a mixture of tetramethylbenzenes and pentamethylbenzene, the second is pentamethylbenzene, while the residue contains the hexamethylbenzene, other condensation products and tars. The pentamethylbenzene obtained in this way is nearly pure; one recrystallization from ethyl alcohol gives a pure product, crystallizing in large, snow-white leaves; m. p., 52°; b. p., 230°, or 127–129° (20 mm.). Fraction V, Run 100, gave 342 g. of Fraction VI, 1391 g. of Fraction VII and 365 g. of Fraction VIII. The yield of pentamethylbenzene is about 33%, based on the xylene taken in this run.

Hexamethylbenzene.—In the regular procedures, examples of which are given in the table, not very much hexamethylbenzene is formed. One reason for this is that these runs were carried out with a view to the maximum production of tetramethylbenzenes, and so the methylation was not carried far enough to produce much hexamethylbenzene. However, this cannot be the entire explanation, for the reaction gave plenty of high-boiling by-products. Thus, the high-boiling residues (above 205°), accumulated from a great many experiments, gave on fractionation nearly a kilo of pentamethylbenzene, about 700 g. of dark, tarry solid boiling above 200° at 20 mm., but less than 100 g. of hexamethylbenzene. This low yield of hexamethylbenzene obtained in the ordinary experiments appears to be the result of two factors: first, the introduction of the last methyl group is somewhat more difficult than that of the other methyl groups, condensed ring systems tending to form, especially if the reaction is carried out over long periods of time; second, hexamethylbenzene, when strongly heated for any length of time, especially in the presence of the high-boiling by-products, decomposes, forming tarry materials.

Therefore, if it is desired to isolate the hexamethylbenzene formed as a by-product in the production of the lower methylated benzenes, the reaction product should not be strongly heated, but after removing the low-boiling products (Fractions I, II and III) under atmospheric pressure, the fractionation should be completed under reduced pressure. The relative amounts of hexamethylbenzene obtained as by-products by fractionating under atmospheric pressure and in a vacuum are shown by the following parallel distillations.

576 g. of crude reaction product, from the methylation of tetramethyl benzenes to pentamethylbenzene, was divided into two equal parts. The first part, fractionated rapidly under atmospheric pressure, using a Glinsky column, gave 18 g. of hexamethylbenzene and 20 g. of dark, tarry residue. The highest boiling point reached was 250°, at which temperature much decomposition was taking place in the distilling flask. The second part, fractionated in a vacuum (20 mm.), using a modified Claisen flask,[4] gave 37 g. of hexamethylbenzene and 8 g. of residue, the highest boiling point being 150°.

If quantities of hexamethylbenzene are desired, it is best made by the rapid methylation of pentamethylbenzene, using a relatively large amount of aluminum chloride in order to increase the speed of methylation. The following experiment illustrates this preparation.

378 g. of pentamethylbenzene and 200 g. of anhydrous aluminum chloride were treated in the usual way with a rapid stream of methyl chloride for three hours, after which the mixture was allowed to stand overnight at room temperature. The next morning the reaction product had solidified to a compact mass that did not melt on the steam-bath. Hot xylene was added to dissolve the solid material and then the reaction mixture was decomposed in the usual way with water; the oil was separated and the xylene and other low-boiling products were boiled off under reduced pressure (17 mm.), the modified Claisen flask being used for the lower fractions. As soon as the hexamethylbenzene began to come over, the material was transferred to an ordinary

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[4] Noyes and Skinner, This Journal, **39**, 2718 (1917). R. Adams, "Organic Syntheses," John Wiley and Sons, New York, **1921**, Vol. I, p. 40.

Claisen flask and the distillation completed. It is difficult to distil hexamethylbenzene, using a long column, for the material has to be heated so strongly in order to prevent it from solidifying in the column and side tube that quite a little of decomposition occurs. The oil weighed 410 g. (after boiling off the xylene) and gave, on distillation at 17 mm., the products in Table III.

TABLE III

RESULTS OF METHYLATING PENTAMETHYLBENZENE

Fraction	B. p., °C. (17 mm.)	Compounds	Yield, G.
A	80–110	Tetramethylbenzenes	15
B	110–135	Pentamethylbenzene	185
C	135–170	Hexamethylbenzene	197
D	Above 170	Residue	13

The yield of crude hexamethylbenzene is about 48%. One recrystallization of the crude material from an ether-alcohol mixture gave 115 g. of snow-white product; m. p., 155–159°; yield, nearly 30%. Small amounts of impurities lower the melting point of this substance very much, and it requires several crystallizations from large volumes of alchol to get an absolutely pure product. When pure, hexamethylbenzene is a snow-white solid, crystallizing in stout needles which tend to form flat, plate-like clusters; m. p.. 165°. Small amounts of it (25 g. or less) which are nearly pure, are best recrystallized from ethyl alcohol. It requires about 600 cc. of boiling alcohol to dissolve this amount, but on cooling about 20 g. of pure product will be obtained. Ether and benzene dissolve the substance much more readily, but the product obtained is not so pure. Large amounts are best recrystallized from a mixture of ether and alcohol, or of benzene and alcohol.

The residues from these distillations, after all the methylbenzenes have been removed, are dark brownish or black, tarry substances, which boil at very high temperatures and contain much solid material. It has not been possible as yet to isolate any pure products from this mixture.

Summary

1. It has been shown that the methylation of commercial xylene can be carried out so as to obtain durene economically, and directions are given for preparing this substance in quantity. By remethylating the low-boiling fractions, and by working over the durene filtrates, a 30 to 35% yield of durene can be obtained.

2. The methylation, if continued under the proper conditions, gives penta- and hexamethylbenzene. The preparation of these substances is discussed.

MINNEAPOLIS, MINNESOTA