

3. The pure sulfonic acids of mesitylene and pseudocumene have been prepared and their properties studied.

4. The refractive index of mixtures of mesitylene and pseudocumene is a linear function of the composition.

5. Pure pseudocumene sulfonic acid may be obtained by washing the mixture of mesitylene and pseudocumene sulfonic acids with hot chloroform but pure mesitylene sulfonic acid cannot be obtained in this way.

6. A method for separating mesitylene from pseudocumene has been devised which gives both hydrocarbons in good yields and in a high state of purity, and which can be applied to the mixture of trimethylbenzenes resulting from the methylation of xylene.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE POLYMETHYLBENZENES. VI. THE SEPARATION OF DURENE FROM ISODURENE¹

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The fifth paper² of this series contained reports on methods for the separation of mesitylene and pseudocumene, the two hydrocarbons occurring in the trimethylbenzene fraction resulting from the methylation of xylene. The present paper reports a method for separating durene (1,2,4,5) and isodurene (1,2,3,5), the two hydrocarbons present in the tetramethylbenzene fraction of the methylation mixture.

The tetramethylbenzene fraction, b. p. 79–91° at 15 mm., represents from 25 to 35% of the product of the methylation of xylene. When this material is cooled to –15° or lower, durene crystallizes out and can be filtered off: about a third of the tetramethyl fraction can be recovered as crude durene, m. p. 75–77°, in this way. The filtrate from the durene is isodurene saturated with durene at the temperature of filtration—no prehnitene (1,2,3,4) is present in it. A very careful search for prehnitene was made both in the filtrate from the cold filtration, and in the “after drip”—the filtrate obtained on allowing the crude durene, while under suction, to warm slowly to room temperature in the Buchner funnel. The filtrate and after drip were first examined by fractionally distilling them and studying the detailed boiling point curves and refractive indices of the various cuts. Next, the filtrate and after drip were sulfonated, and the sulfonic acids isolated and examined for prehnitene sulfonic acid. Finally,

¹ Abstracted from a thesis by Oliver W. Cass, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1931.

² Smith and Cass, *THIS JOURNAL*, **54**, 1603 (1932)

the material in the aqueous acid filtrates from the crystallization of the sulfonic acids was hydrolyzed, and the resulting oils examined by means of boiling point curves, and refractive indices. In no case was any prehnitene found, although check experiments on samples of known composition showed that as little as 1% of prehnitene could be detected in a mixture of the tetramethylbenzenes by sulfonating the mixture, precipitating the sulfonic acids by dilution, filtering and hydrolyzing the sulfonic acids *remaining in the filtrate*. The oil resulting from this hydrolysis contains all the prehnitene and, by subjecting this to a careful fractionation, the presence or absence of prehnitene is revealed by the boiling point curve and the refractive indices of the different fractions.

Since the filtrate and "after drip" resulting from the removal of the durene contained no prehnitene, only the separation of the two hydrocarbons durene and isodurene needed to be considered. The filtrate and the after drip were combined and carefully fractionated through an efficient column. The boiling range was 79–87° at 15 mm., and the portion boiling from 82–84° (90% of the total) was used for the separation. This material had a freezing point of -25.0° , corresponding to about 90% isodurene and 10% durene; n_D^{20} 1.5120.³

As the first step in the experiments on the separation of the hydrocarbons, each of the pure hydrocarbons was converted to the sulfonic acid and the properties of these sulfonic acids were studied. No pronounced differences in solubilities were found: all three sulfonic acids were insoluble or only slightly soluble in the following cold solvents: 50% H₂SO₄, 20% HCl, concentrated HCl, benzene and petroleum ether. When heated, the three acids were soluble in all these solvents except petroleum ether, but isodurene sulfonic acid began to hydrolyze when heated with the first three solvents. In cold chloroform, only prehnitene sulfonic acid is soluble, and then only slightly, while in hot chloroform, prehnitene and isodurene sulfonic acids are very soluble, and durene sulfonic acid only slightly soluble. In no case was the difference in solubility sufficient to lead to an efficient separation of the sulfonic acids. The barium salts of durene and prehnitene sulfonic acids were difficultly soluble in cold water, while that of isodurene sulfonic acid was very soluble. This difference could be made the basis of a convenient method for the separation of durene and isodurene on a small scale, but on a larger scale the difficulty of preparing and handling large amounts of these barium salts, especially when contaminated with much barium sulfate, would render the method very inconvenient.

Fractional sulfonation of durene–isodurene mixtures also failed to separate the two substances, for although the pure hydrocarbons showed a pronounced difference in the ease with which they were sulfonated, when the sulfonation was carried out on a mixture of the two, both sulfonated.

³ Smith with MacDougall, *THIS JOURNAL*, **51**, 3001 (1929).

Thus 5 g. of isodurene was sulfonated completely in thirty seconds by 10 cc. of concentrated sulfuric acid, while 5 g. of durene was only about 5% sulfonated after shaking for twenty minutes with 10 cc. of concentrated sulfuric acid. But when a mixture of 5 g. of isodurene and 2.5 g. of durene was shaken for three minutes with 12.5 cc. of concentrated sulfuric acid, all of the isodurene and over half the durene was sulfonated.

Fractional hydrolysis of the mixture of sulfonic acids was also a failure as a method of separation, and for the same reasons that fractional sulfonation failed; although there is a pronounced difference in the ease with which the pure durene and isodurene sulfonic acids hydrolyze, when they are mixed, it is impossible to hydrolyze one completely without also hydrolyzing the other partially. Isodurene sulfonic acid can be hydrolyzed with 20% hydrochloric acid at temperatures as low as 60°, while durene sulfonic acid is unaffected by even concentrated hydrochloric acid at these temperatures. But when mixed and steam distilled with 20% hydrochloric acid, both sulfonic acids hydrolyze, and in an hour about two-thirds of the isodurene and half of the durene have distilled over.

Nevertheless, although neither fractional sulfonation nor fractional hydrolysis of the sulfonic acids was alone sufficient to separate durene and isodurene, it was found that by a careful combination of the two, a fairly efficient separation could be brought about. This method gives the best results when applied to the re-fractionated filtrate resulting when durene is frozen out of the original tetramethylbenzene fraction. This filtrate, b. p. 82–84° at 15 mm., n_D^{20} 1.5120, consists of about 90% isodurene. The method will give 60–65% yield of "crude" isodurene (96–97% pure) and about 5% yield of durene; or, if the "crude" isodurene is re-sulfonated and the sulfonic acid again hydrolyzed, the yield is about 45% of pure isodurene practically equal in quality to the synthetic product.

Experimental Part

The Pure Hydrocarbons: Durene.—This was obtained directly by freezing out the tetramethylbenzene fraction from the methylation of xylene. It was recrystallized from alcohol until the m. p. was 78–79°.

Isodurene.—This was synthesized from mesitylene by the method of Smith and MacDougall.⁴ The bromomesitylene used as an intermediate was very carefully purified. It had a b. p. of 105.0° at 16 mm., freezing point of 0.01°; n_D^{20} 1.5510 ($dn/dt = -0.00041$ per degree rise in temperature between 15 and 30°). The purified isodurene had a freezing point of -24.1°; n_D^{20} 1.5134 ($dn/dt = -0.00043$ per degree rise in temperature between 15 and 30°).

Prehnitene.—This was prepared from pentamethylbenzene by the method of Smith and Lux.⁵ The sample used had a freezing point of -7.0 to -7.1°; boiling point 96.5° at 25 mm., n_D^{20} 1.5202 ($dn/dt = -0.00040$ per degree rise in temperature between 15 and 30°).

⁴ Smith and MacDougall, *THIS JOURNAL*, **51**, 3001 (1929).

⁵ Smith and Lux, *ibid.*, **51**, 2994 (1925).

Durene Sulfonic Acid, $C_8H(CH_3)_4SO_3H \cdot 2H_2O$.—Durene (10 g.) was placed in a small beaker and covered with 50 g. (27 cc.) of a mixture of 1 part of 60% fuming sulfuric acid and 2 parts of concd. sulfuric acid. The reaction mixture was stirred vigorously, and the lumps of durene were broken up with a glass rod. The temperature rose about 20° during the sulfonation. After five minutes, the reaction mixture was poured onto 250 g. of ice and vigorously stirred. The liquid was filtered at once from the unmelted ice and the traces of unsulfonated durene. To the cold filtrate concd. sulfuric acid was slowly added, until the material set to a mass of pearly white crystals. During the addition of the sulfuric acid the temperature was kept always below 20°, and after the addition of the acid the reaction mixture was cooled to 0° and filtered with suction through cloth, pressed as dry as possible, and dried on a porous plate; yield 18.6 g. (94%), m. p. 110–112°. For purification, the acid was dissolved in the least possible quantity of 20% hydrochloric acid at 80°, the solution then cooled to 0°, filtered through cloth and dried in the air; yield of pure acid, 14 g. (70%), m. p. 113°.

Isodurene Sulfonic Acid, $C_8H(CH_3)_4SO_3H \cdot 2H_2O$.—Isodurene (10 g.) was sulfonated by shaking it with 20 cc. of concd. sulfuric acid in a small flask for ten minutes. The reaction mixture was poured into 20 g. of ice, the crystals filtered with suction through cloth, and dried on a porous plate; yield 18 g. (91%), m. p. 76–77°. It was purified by dissolving it in 50 cc. of cold water and passing gaseous hydrogen chloride into the ice cold solution. The white crystals were filtered, pressed out and dried in the air; yield of pure acid, 12–14 g. (60–70%), m. p. 79°.

Prehnitene Sulfonic Acid, $C_8H(CH_3)_4SO_3H \cdot 2H_2O$.—Prehnitene (10 g.) was sulfonated according to the directions given for isodurene; yield 18 g. (91%), m. p. 99–100°. The acid was purified according to the directions given for durene sulfonic acid; yield of pure acid, 14 g. (70%), m. p. 104°.

In all these sulfonations no traces of sulfones or other water-insoluble material were found among the reaction products. The solubilities of these sulfonic acids in various solvents, and the conditions under which they hydrolyze, have already been given.

The Separation of Durene and Isodurene.—The mixture of durene and isodurene used for the separation was obtained by fractionating the original methylation mixture twice, collecting the fraction boiling from 79 to 91° at 15 mm. pressure; the durene was then frozen out of this by cooling to –16° and filtering. The filtrate was then refractionated, and the portion boiling from 82–84° at 15 mm. (90% of the material) was used for this separation. The fuming sulfuric acid used in the separation consisted of a mixture of one part of “60% fuming sulfuric acid” and two parts of concd. sulfuric acid. This is the acid meant whenever the term “fuming sulfuric acid” is used.

In a two-liter flask, fitted with a short air condenser, was placed 500 g. of the durene–isodurene mixture. To this was added 500 cc. of the fuming sulfuric acid, and the flask then shaken vigorously for three minutes. The temperature rose to 80°, and nearly all of the oil went into solution. Without cooling, the contents of the flask was poured out, with vigorous stirring, upon 1500 g. of finely chipped ice in a 4-liter beaker. Stirring and cooling were continued until the temperature fell to 5°, and the material was then rapidly filtered with suction through a cloth filter. This separated the unsulfonated material, (R_1), chiefly durene, from the sulfonated material in the filtrate (F_1).

The filtrate (F_1) was at once treated with 250 cc. of concd. sulfuric acid, which was added with vigorous stirring, keeping the temperature below 25°. The whole mixture set to a mass of crystals, which was broken up, cooled to 5°, and filtered with suction through cloth, pressing as dry as possible, (precipitate R_2 , filtrate F_2).

The precipitate R_2 was transferred at once to a two-liter flask arranged for steam distillation, 500 cc. of 20% hydrochloric acid was added, and the mixture steam distilled for one hour. The residue in the flask (R_3) was set aside. The oil in the distillate (D_1)

was separated, washed with bicarbonate and dried over calcium chloride. This oil weighed 319 g. (63.8% of the wt. of starting material); freezing point -26.0 , which corresponds to about 96% isodurene.

This oil D_1 was then re-sulfonated exactly as described for the mixture with which the separation started, using everywhere proportionate amounts of reagents. The sulfonic acid obtained from the re-sulfonation melted sharply at 78.5° (recrystallized isodurene sulfonic acid melts at 79°), and on hydrolysis gave 240 g. (48% of the wt. of the starting material) of dry oil, which was carefully fractionated. At 22–23 mm. 95% of this oil boiled between $90-91^\circ$. The middle fraction was collected (223 g., 44.6%) and this showed a freezing point of -24.08° (the freezing point of synthetic isodurene is $-24.0 \pm 0.1^\circ$).⁴ The low-boiling material from this fractionation, and the residue in the distilling flask, 14 g. in all, were put back in stock for the next run.

The unsulfonated oils, R_1 from the original sulfonation, and a corresponding oil from the re-sulfonation, were combined, washed with bicarbonate and dried; wt., 67.6 g. (13.5% of the starting material). On cooling to -10° and filtering, 28 g. of crude durene (m. p. 70–73) was obtained. The filtrate from this was returned to stock for the next run.

The acid filtrates from the precipitation of the sulfonic acids, as well as the residues from the steam distillations, were all combined, enough sulfuric acid added to bring the b. p. to 140° , and steam passed through at 140° until no more oil was distilled over. The oil in the distillate was separated, washed with bicarbonate, and dried. It weighed 60.2 g. (12% of the starting material), and was added to stock for the next run. Thus the yields in the separation were: 223 g. pure isodurene (44.6%); 28 g. crude durene (5.6%); and 100 g. of mixture (20%) returned to the next run. Total recovery, 351 g. (70%). The loss was thus 30% and this was due almost entirely to inefficient condensation during the long steam distillations and vacuum fractionations. If a trap cooled with carbon dioxide snow had been inserted in the exit of the distilling train, a much higher recovery could probably have been obtained, for there was no organic material left in the final residues from the steam distillations.

It is exceedingly important for a successful separation that the directions as to amounts of reagents, and *particularly the time of contact with the reagents*, be followed exactly, for both durene and isodurene sulfonic acids, in contact with sulfuric acid, undergo the Jacobsen rearrangement, giving prehnitene. The separation should never be interrupted immediately after a sulfonation or after a filtration of the sulfonic acids from the sulfuric acid solution, and the best results are obtained when the whole separation is carried straight through without any interruption. The table summarizes a few runs.

TABLE I
THE SEPARATION OF DURENE AND ISODURENE

Run	Mixture, g.	Crude isodurene (96–97%)	Pure isodurene, g.	Pure (recryst.) durene, g.
1	200	102.2	115.4 (m. p. -24.17°)	11
2	200	103.4		
3	500	319.0	223 (m. p. -24.08°)	16

It was found, in this work, that the only property of isodurene suitable for testing its purity was the freezing point. The refractive index of mixtures of durene and isodurene is practically the same as that of pure isodurene for concentrations of durene as high as 20%, and very little information about the purity of a specimen can be obtained from the boiling point, but the freezing point of the specimen furnishes an accurate method of analysis.

Summary

1. A method for separating durene from isodurene has been devised, which gives a pure isodurene in yields of about 45%, when applied to the refractionated filtrate obtained by freezing out the durene from the tetramethylbenzene fraction resulting from the methylation of xylene.

2. In the methylation of xylene using methyl chloride and aluminum chloride no prehnitene (1,2,3,4) is formed.

3. The pure sulfonic acids of each of the tetramethylbenzenes have been prepared, and some of their properties studied.

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THE JACOBSEN REACTION. II¹

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In the first paper of this series³ a report was made of a preliminary study of the Jacobsen reaction when applied to pentamethylbenzene, but as the purpose of that work was to develop a method for preparing prehnitene, the study was limited to the one hydrocarbon, pentamethylbenzene. This study has now been extended to other polymethylbenzenes, and the present paper reports some of these results.

The results of Jacobsen and other workers in this field, together with references to the literature, have been given in detail in the paper by Smith and Lux. In the case of the hydrocarbons studied so far in this Laboratory, it has been found that the rearrangement of methyl groups caused by sulfuric acid (the "Jacobsen Reaction") is limited to pentamethylbenzene, durene and isodurene. The hydrocarbons mesitylene, pseudocumene, prehnitene and hexamethylbenzene do not rearrange when in contact with concd. sulfuric acid at room temperatures for over ten days. Of the three hydrocarbons which did undergo a rearrangement, pentamethylbenzene was the only one from which the chief products of the reaction were a more highly methylated benzene and a less highly methylated one. Durene and isodurene gave prehnitene sulfonic acid as the main reaction product, involving only a shift of a methyl group within the molecule.

In the case of durene and isodurene, it was found to be the sulfonic acid which rearranged, and not the hydrocarbon, as Jacobsen maintained. If the pure sulfonic acids (either the anhydrous or hydrated forms) of these

¹ Paper VII on the Polymethylbenzenes. VI, *THIS JOURNAL*, **54**, 1609 (1932).

² Abstracted from a thesis by Oliver W. Cass, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1931.

³ Smith and Lux, *THIS JOURNAL*, **51**, 2994 (1929).