

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

**STUDIES ON THE POLYMETHYLBENZENES. V.  
THE SEPARATION OF MESITYLENE FROM PSEUDOCUMENE<sup>1</sup>**

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The preceding papers of this series<sup>2</sup> have dealt with the preparation, purification and some physical properties of most of the polymethylbenzenes containing three or more methyl groups. The work described in this paper had for its object the investigation of some derivatives of mesitylene and pseudocumene, with a view to finding a method for the preparation of these two hydrocarbons in a pure state, using as a source the mixture of the two which can be so readily obtained by the methylation of xylene.

In addition to several methods of isolating derivatives of these trimethylbenzenes from various sources, there are in the literature reports of two methods for separating the trimethylbenzenes from each other as derivatives, followed by regeneration of the pure parent hydrocarbons. The method of Jacobsen<sup>3</sup> involving fraction crystallization of the sulfonamides, followed by hydrolysis, was discarded because it was too long and involved. Similarly, this method as modified by Schultz<sup>4</sup> was found to be not only too laborious but to involve a great loss of material. Finally, the method of Armstrong and Miller<sup>5</sup> involving the partial sulfonation of the mixture followed by a fractional hydrolysis of the sulfonic acids, was found to be unsuitable, at least when applied to the trimethylbenzene fraction from these methylation reactions, for no pure hydrocarbons resulted when the method was used.

Nevertheless, the sulfonic acids appeared to be the most promising derivatives with which to work, for these hydrocarbons are easily sulfonated, and the sulfonic acids are well defined solids, easy to handle. Therefore it was decided to prepare the pure sulfonic acids of pseudocumene and mesitylene, and to study their physical properties, particularly the solubilities of the sulfonic acids in various solvents, in the hope of finding a suitable solvent for separating the mixture of sulfonic acids by fractional crystallization, and then to extend the studies to the fractional hydrolysis of the sulfonic acids in the hope of discovering the precise conditions of

<sup>1</sup> 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.

<sup>2</sup> (I) Smith and Lux, *THIS JOURNAL*, **51**, 2994 (1929); (II) Smith with MacDougall, *ibid.*, **51**, 3001 (1929); (III) MacDougall with Smith, *ibid.*, **52**, 1998 (1930); (IV) Smith and Lund, *ibid.*, **52**, 4144 (1930).

<sup>3</sup> Jacobsen, *Ann.*, **184**, 179 (1876); *Ber.*, **9**, 256 (1876).

<sup>4</sup> Schultz, *ibid.*, **42**, 3603 (1909).

<sup>5</sup> Armstrong and Miller, *J. Chem. Soc.*, **45**, 148 (1884); *Ber.*, **11**, 1697 (1878).

hydrolysis which would lead to a clean-cut separation of the two hydrocarbons in good yields. Only the two hydrocarbons mesitylene and pseudocumene needed to be considered as components of the mixture obtained by the direct methylation of xylene, for a very careful search for hemimellitene (1,2,3) in this product failed to indicate that any was present. This is another instance of the one rule which has been repeatedly found to hold in all the methylation experiments in this series, *viz.*, in the methylation of aromatic hydrocarbons with methyl chloride and aluminum chloride, ortho compounds are probably not formed at all, or if formed, occur in very small amounts.

Mesitylene sulfonic acid was found to be very readily dissolved by hot chloroform, while pseudocumene sulfonic acid is nearly insoluble in this solvent. Since the chief component of the mixture of trimethylbenzenes is pseudocumene, a separation of this sulfonic acid in a very pure form can be effected readily by washing the mixture of acids two or three times with hot chloroform. The washings contain all of the mesitylene sulfonic acid, and some pseudocumene sulfonic acid. These can be partially separated by recrystallization from chloroform, or by recrystallization from hydrochloric acid after evaporation of the chloroform, but the mesitylene sulfonic acid obtained in this way is not pure. In addition, if large amounts of material are to be separated, the volume of chloroform required is quite large. Fractional precipitation of the sulfonic acids from concentrated sulfuric acid also failed to give a good separation, for although mesitylene sulfonic acid is much the less soluble of the two, the precipitation has to be repeated several times in order to obtain the pure sulfonic acids. This involved so great a loss of material, and the use of such large quantities of sulfuric acid, that the method was abandoned.

Turning to the conditions for the hydrolysis of the two acids, the statement of Crafts<sup>6</sup> was verified, namely, that mesitylene sulfonic acid is easily and completely hydrolyzed by fuming hydrochloric acid at 80°, but it was found that the fuming acid could be replaced by the constant boiling hydrochloric acid without changing the temperature of hydrolysis. This was a great advantage, for it meant that the mesitylene could be steam distilled out of the reaction mixture without reducing the acid concentration below the limit needed for rapid hydrolysis. Pseudocumene sulfonic acid showed no sign of hydrolysis under these conditions, and could be recovered by chilling the acid solution left after steam distillation of the mesitylene. The use of hydrochloric acid is superior to that of sulfuric acid, for at 60° with 20% sulfuric acid, mesitylene sulfonic acid showed signs of charring, and at 80° there was considerable charring and the hydrolysis was not as rapid as with hydrochloric acid. Pseudocumene sulfonic acid, alone, was found to be perfectly stable when heated with 50% sulfuric acid

<sup>6</sup> Crafts, *THIS JOURNAL*, 23, 248 (1901).

until a temperature of 120–125° was reached, when hydrolysis began, and at 135–145° hydrolysis became rapid and complete, with no sign of charring or tar formation. When the two sulfonic acids were mixed, however, the action of sulfuric acid was much less definite, which probably accounts for the failures to obtain either pure mesitylene or pure pseudocumene by the method of Armstrong and Miller.

The final procedure developed for the separation of these two hydrocarbons is one which takes advantage of the differences in the action of hydrochloric acid and sulfuric acid on the sulfonic acids, and the differences in temperatures at which hydrolysis to the hydrocarbons takes place. It consists in the complete sulfonation of the mixture of trimethylbenzenes, precipitation of the mixed sulfonic acids by careful dilution, filtration of these acids, followed by hydrolysis, first with constant boiling hydrochloric acid at 80°. The mesitylene sulfonic acid hydrolyzes completely under these conditions, and the mesitylene is then removed by steam distillation at 80° under reduced pressure. The residue in the distillation flask, when chilled, deposits pseudocumene sulfonic acid almost quantitatively. This is filtered off, and then hydrolyzed by steam distillation from 50% sulfuric acid at 135–145°.

This method always gave a pure pseudocumene, but frequently the mesitylene was contaminated with a small amount of material of unknown constitution, of lower boiling point (*ca.* 150–155°), much lower refractive index, and a very pungent odor. It was necessary therefore to re-sulfonate the crude mesitylene, reprecipitate the sulfonic acid, wash it with cold chloroform or cold concentrated hydrochloric acid, which removes all impurities, and then hydrolyze it to the hydrocarbon again. In this way a mesitylene which had exactly the same boiling point and refractive index was obtained from every experiment, a duplication of physical constants which cannot be obtained by synthesizing mesitylene in the usual way from acetone.

When carried out with the double sulfonation of the mesitylene, followed by refractionation of the "crude" separated hydrocarbons, the yield was about 12% pure mesitylene, 38% pure pseudocumene, with 30–35% of the mixture returned to the next run, a total recovery of 80–85%.

### Experimental Part

**The Trimethylbenzene Fraction.**<sup>7</sup>—This must be carefully fractionated to insure the absence of xylenes or tetramethylbenzenes, as the success of the method of separation

<sup>7</sup> In preparing these mixtures of trimethylbenzenes, the usual procedure was to methylate using methyl chloride, but if a supply of methyl chloride is not available it is possible to obtain consistent yields of about 15% trimethyl fraction by agitating commercial xylene (4 parts) and aluminum chloride (1 part) together at 130–140° for eight to ten hours. The mixture must be refluxed in an oil-bath, not over a free flame, and there must be vigorous stirring to avoid caking of the aluminum chloride on the bottom of the flask.

depends upon having present only mesitylene and pseudocumene. The crude trimethylbenzene fraction (b. p. 150–180°) was twice fractionated through a four-foot packed and jacketed column, only the fraction boiling at 66–68° under 22–23 mm. pressure being used for the separation.

### Preliminary Experiments

**Mesitylene Sulfonic Acid**,  $C_6H_2(CH_3)_3SO_3H \cdot 2H_2O$ .—Mesitylene (100 cc.) (b. p. 66.0–66.2° at 22 mm.,  $n_D^{20}$  1.4965, prepared from acetone) was vigorously shaken with concentrated sulfuric acid (200 cc.) in a 500-cc. flask fitted with a short air condenser. The temperature rose rapidly to 60°, and the oil went into solution completely in five to ten minutes. A clear yellowish liquid resulted. While still warm, the contents of the flask were poured into 400 cc. of concentrated hydrochloric acid, kept at 10° or lower, or into 300 g. of ice, with constant and vigorous stirring. The sulfonic acid precipitated, and was filtered with suction through a cloth filter, pressing as dry as possible. The air-dried crude acid usually had a light pink or violet color; yield, 151 g. (90%), m. p. 76–78°. When purified by recrystallization from chloroform (50 g. acid, 200 g. chloroform), the acid (46 g.) melted sharply at 78° and was snow white. The sulfonic acid is soluble in warm concentrated or 50% sulfuric acid, warm hydrochloric acid (concentrated or 20%) and hot chloroform, and is almost insoluble in all these solvents in the cold. On heating the hydrated acid at even as low a temperature as 60° for one hour, it began to decompose, hydrolyzing to mesitylene and sulfuric acid, with some charring. The hydrate loses water over concentrated sulfuric acid at room temperature, and the dehydrated acid quickly absorbs water from the air. No definite melting point could be obtained for the anhydrous acid; the highest value obtained was 98.5–100°.

**Pseudocumene Sulfonic Acid-5**,  $C_6H_2(CH_3)_3SO_3H \cdot 1.5H_2O$ .—This was prepared from pseudocumene following the same directions as for the sulfonation of mesitylene, except that the sulfonation mixture was cooled before pouring onto ice or concentrated hydrochloric acid; yield, 135 g. from 100 cc. of pseudocumene (about 85%); m. p. 110–111°. Recrystallized from hot 20% hydrochloric acid, the acid crystallized as tiny white glistening plates, m. p. 111–112°. The acid contains 1.5 molecules of water of crystallization, which is slowly lost over sulfuric acid, phosphorus pentoxide, or on heating to 105° for an hour. The hydrate is stable at 80° for at least three hours, and loses only 1% in weight when heated to 90° for two hours. The melting point of the dehydrated acid is not sharp, usually 128–131°. The hydrate is soluble in cold or hot concentrated sulfuric acid, warm hydrochloric acid (concentrated or 20%), and warm 50% sulfuric acid. It is only slightly soluble in hot or cold chloroform, cold 50% sulfuric acid, and cold hydrochloric acid. Of the three isomeric pseudocumene sulfonic acids, only the one, pseudocumene sulfonic acid-5, is obtained by direct sulfonation according to these directions.

**Sulfonation of the Mixed Hydrocarbons.**—The following table shows the results of sulfonating three different fractions of the mixed trimethylbenzenes, according to the directions for sulfonating the pure hydrocarbons.

TABLE I  
SULFONATION OF THE MIXED TRIMETHYLBENZENES

Fraction	Boiling point (23 mm.), °C.	Amount used, cc.	Yield of sulfonic acid, g.	M. p., °C.
I	65.0–67.5	50	60	95–101.5
II	67.5–68.5	50	71	99–103
III	68.5–73.0	25	37	87–93

**Separation of the Sulfonic Acids Using Chloroform Extraction.**—Ten grams of the acid from I was twice washed with 50 cc. of hot chloroform. There remained 6.3 g. of

white sulfonic acid, m. p. 108–110°, mixed m. p. with pure pseudocumene sulfonic acid, 110–111°.

Ten grams of the acid from II similarly yielded 7.0 g. of white sulfonic acid, m. p. 109–111°, mixed m. p. with pure pseudocumene sulfonic acid, 110–111°.

Ten grams of the acid from III, similarly yielded 6.0 g. of white sulfonic acid, m. p. 105–109°, mixed m. p. with pure pseudocumene sulfonic acid, 108–111°.

When combined (19.3 g.) and recrystallized from hot 20% hydrochloric acid, these acids yielded 15.6 g. of pure sulfonic acid, m. p. 111–112°. The chloroform washings, evaporated to 40 cc. and cooled, deposited 8.0 g. of pink sulfonic acid, m. p. 73–76°, but repeated recrystallization brought the m. p. only up to 74–77° (78° for pure mesitylene sulfonic acid) and there was much loss in the crystallization.

These experiments show that pure pseudocumene sulfonic acid can be obtained in about 50% yield from the mixture of sulfonic acids by this method, but pure mesitylene sulfonic acid cannot be so obtained.

**Hydrolysis of the Sulfonic Acids, Using Sulfuric Acid.**—One hundred cc. of the trimethylbenzene fraction was sulfonated in the usual way with 200 cc. of concentrated sulfuric acid. The mixture was then diluted with 300 cc. of water and kept at 80° for thirty minutes, after which it was rapidly steam distilled at 100–120° for fifteen minutes. The distillate contained 8 cc. of an oil, boiling at 165.1–166.1° (corr.) at 760 mm. Pure mesitylene in the same apparatus boiled at 164.1–164.5°. When the temperature of hydrolysis was raised to 140°, 78 cc. more of oil resulted in the distillate. This showed a boiling point of 67.0–71.2° at 23 mm. Pure pseudocumene boiled constantly at 68.5 (23 mm.) in the same apparatus. Thus neither the mesitylene nor the pseudocumene obtained by this method was pure.

**Hydrolysis of the Sulfonic Acids, Using Hydrochloric Acid.**—These experiments showed that mesitylene sulfonic acid was completely hydrolyzed when heated to 80° for one hour with either concentrated or 20% hydrochloric acid, and that pseudocumene sulfonic acid was unaffected under these conditions, and as these experiments led directly to the method of separation finally adopted, the details will be given in the next section dealing with the separation.

**The Separation of Pseudocumene and Mesitylene.**—Fifteen hundred grams (1728 cc.) of the trimethylbenzene mixture (b. p. 66–68° at 22 mm.) was sulfonated by shaking it with an equal volume of concentrated sulfuric acid. The temperature rose to 83° and after ten minutes nearly all the oil had gone into solution. The material, while still quite warm, was transferred to a warm separatory funnel and the unsulfonated oil (61 g., 4%) drawn off.<sup>8</sup>

The sulfonation mixture, after removal of this oil, was cooled to room temperature and then poured very carefully onto 1500 g. of crushed ice contained in large beakers surrounded by a freezing mixture. The dilution must be carefully done, with vigorous stirring and keeping the temperature as low as possible. The whole mixture solidified to a mass of light pink crystals which was broken up by stirring. After the temperature of the mass had fallen to 10°, the precipitate was filtered through a cloth filter on a large Buchner funnel, pressed down and sucked as free from liquid as possible. The precipitate was divided into two parts, and each part treated with a liter of 20% hydrochloric acid in a 3-necked five-liter flask, so arranged that steam could be passed through under reduced pressure. The reaction mixture was heated to 80° for thirty minutes, during which time a layer of oil appeared and the remaining sulfonic acids went into solution, giving a light pink to purple solution. Steam at 80–90° (never above 95°) was then

<sup>8</sup> This unsulfonated oil has a peculiar, unpleasant odor, and is probably not a polymethylbenzene, but it is important to remove it as completely as possible at this point, for otherwise it accompanies the mesitylene.

passed into the mixture for ninety minutes. The oil in the distillate was then separated, washed with water, bicarbonate and dried. It weighed 349 g. (23.3%) (from both halves of the precipitate). This was "crude" mesitylene.

The residues from this steam distillation were combined and cooled to 0°, and the solid resulting filtered off through cloth; weight, 1336 g.; m. p. 111° sharply. This solid (pseudocumene sulfonic acid) was then hydrolyzed by steam distillation from 50% sulfuric acid at 140°. The oil in the distillate, when washed and dried, weighed 639 g. (42.6%). This was "crude" pseudocumene.

The various filtrates from the sulfonic acids were combined, enough sulfuric acid added to bring the boiling point to 140°, and steam distilled at this temperature. There resulted 175 g. (11.7%) of oil, consisting of a mixture of the hydrocarbons, which was returned to the next run. The total recovery was therefore 81.6%.

The crude pseudocumene (639 g.) was carefully distilled through an efficient column. About 90% of it (568 g., 37.9%) showed a constant boiling point of 68° at 22 mm.; 168.0–168.2° at 742 mm.;  $n_D^{20}$  1.5048. This is pure pseudocumene.

The "crude" mesitylene (349 g.) is not pure, for it contains some of the pungent oil, most of which was not sulfonated in the first sulfonation. To remove this, the crude product is resulfonated, and then the sulfonic acid precipitated by pouring the reaction mixture into 800 cc. of concentrated hydrochloric acid at 0°. The sulfonic acid so purified melted at 77–78°, and on hydrolysis gave 174 g. of mesitylene. Of this 163 g. (10.9%) boiled at 66.0° under 22 mm.;  $n_D^{20}$  1.4974. The filtrate from the sulfonic acid, when hydrolyzed, gave 141 g. of oil which was returned to the next run.

A summary of this and several other runs is given in Table II.

TABLE II  
SUMMARY OF YIELDS IN THE SEPARATION OF MESITYLENE AND PSEUDOCUMENE

Trimethyl fraction, g.	Yield of crude 1,3,5, %	Yield of crude 1,2,4, %	Pure 1,3,5, %	Pure 1,2,4, %
377	8.4	50.4	5.8	41.9
407	28.0	40.0	17.9	37.5
200	17.9	37.6	..	..
400	21.6	40.4	12.0	35.1
1500	23.3	42.6	10.9	37.9

The purity of the two hydrocarbons was followed by means of the boiling point and the refractive index, which was found by experiment to be a linear function of the composition.

TABLE III  
REFRACTIVE INDICES OF MESITYLENE-PSEUDOCUMENE MIXTURES

Mesitylene, %	Pseudocumene, %	$n_D^{26.6}$ (obs.)	$n_D^{26.6}$ (calculated for linear function)
100	0	1.4942	.....
75	25	1.4961	1.49606
50	50	1.4980	1.49793
25	75	1.4999	1.49981
0	100	1.5017	.....

### Summary

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

2. Trimethylbenzenes can be made by simply refluxing together xylene and aluminum chloride.

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 ISODURENE<sup>1</sup>

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The fifth paper<sup>2</sup> 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,

<sup>1</sup> 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.

<sup>2</sup> Smith and Cass, *THIS JOURNAL*, **54**, 1603 (1932)