

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).

hydrocarbons were mixed with phosphorus pentoxide, or simply kept in a desiccator over this reagent, the reaction proceeded as usual. But if the hydrocarbons themselves were boiled with phosphorus pentoxide, or kept in a desiccator over either phosphorus pentoxide or sulfuric acid, no change occurred even after standing for months. Durene sulfonic acid was acted upon almost at once by warm concd. sulfuric acid, while durene, which is only slowly sulfonated by concd. sulfuric acid, would undergo the Jacobsen reaction only very slowly. On the other hand, fuming sulfuric acid, which sulfonates durene rapidly, also acted rapidly on either durene or its sulfonic acid with liberation of much sulfur dioxide, causing the Jacobsen reaction to take place. Warm, concd. sulfuric acid, which sulfonates isodurene rapidly, caused the Jacobsen reaction to take place with either isodurene or its sulfonic acid. Furthermore, the reagent—phosphorus pentoxide or sulfuric acid—is necessary, for both the hydrated and the dehydrated durene and isodurene sulfonic acids were perfectly stable when kept in a sealed tube for a period of eight months, while all of the hydrated sulfonic acids have been kept in glass stoppered bottles for over a year with no decomposition whatever. Nor does the water of hydration have any effect upon the reaction, for both the hydrated and dehydrated sulfonic acids behave in the same way toward phosphorus pentoxide or sulfuric acid.

In all the Jacobsen reactions, much sulfur dioxide is evolved, and the next experiments were directed toward determining the amount of this gas, and whether or not it was the only gaseous product. The reaction between durene and sulfuric acid was allowed to take place at room temperature, and the gaseous products were swept out with a stream of dry air, free from carbon dioxide. The exit gases were then passed through potassium hydroxide solution, which was analyzed from time to time. The experiment was run for twenty-five days, as at room temperature the reaction is a very slow one. The gas evolved was found to be chiefly sulfur dioxide. In spite of the oxidizing stream of air used to sweep the apparatus, the ratio of sulfate sulfur (total sulfur dioxide as barium sulfate after iodine titration) to sulfite sulfur (sulfur dioxide by direct iodine titration) was only 1.13 to 1.00, showing that sulfur trioxide could not be present in the evolved gases in very appreciable amounts. In a second quantitative experiment, durene sulfonic acid was used with phosphorus pentoxide and the apparatus swept with a current of pure, dry hydrogen. In this case the ratio of sulfate to sulfite sulfur was 1.03 to 1.00. It therefore was apparent that the sulfur is liberated as sulfur dioxide, and that this came from the reduction of the sulfonic acid group, and not from the sulfuric acid, as reported by Smith and Lux in the case of pentamethylbenzene. In none of these experiments was any hydrogen sulfide or free sulfur found.

The mole ratios between the durene sulfonic acid used and the sulfur dioxide formed when phosphorus pentoxide acted upon the sulfonic acid,

were, in two separate experiments, 1 to 0.342 and 1 to 0.356. In the twenty-five day experiment with durene and sulfuric acid, the ratio between the durene used and the sulfur dioxide produced in twenty-five days was 1 to 0.290, but this particular reaction was very slow under the conditions of the experiment and at the end of twenty-five days it was not complete. Whether the ratio of about three moles of hydrocarbon or sulfonic acid to 1 of sulfur dioxide is really a constant, and what bearing this has upon the mechanism of the reaction, cannot yet be decided. But the evolution of sulfur dioxide in large amounts does appear to be an essential part of the Jacobsen reaction (or of a simultaneous reaction, the conditions for which are the same as those for the Jacobsen reaction) because in every case in which no rearrangement of methyl groups took place, no sulfur dioxide was evolved, while in every case of actual rearrangement, large amounts of sulfur dioxide were evolved.

Since the sulfur dioxide was formed by the reduction of the sulfonic acid group, experiments were next directed toward determining what was oxidized in the process. This was done in the streaming experiments by checking the gain in weight of the potassium hydroxide bulb against the total sulfur calculated back as sulfur dioxide, and it was found that 95% of the total gain in weight was accounted for by the sulfur as sulfur dioxide, leaving only about 5% for carbon dioxide. This 5% difference in weight, which should be due to carbon dioxide, amounted to 0.0019 mole of carbon dioxide, which was only 7% of the number of moles of sulfur dioxide produced. Hence the oxidation product was not carbon dioxide, but most likely was water formed by the oxidation of hydrogen. If so this hydrogen must have been eliminated from a methyl group, or from the open positions on the benzene ring, which might well lead, in either case, to the linkage of several durene residues, producing compounds of high molecular weight. The fact that the reaction took place only under strong dehydrating conditions is not inconsistent with the hypothesis that water is one of the products of the reaction which leads to the sulfur dioxide, but there is the possibility that the amorphous by-products may be the oxidation product, as these have not yet been shown to be oxygen free.

In addition to the gaseous reaction products and the rearranged polymethylbenzenes there were formed two other products whenever the Jacobsen reaction took place. One of these products was an intensely black, water-soluble substance, formed in small amounts, which could be removed from the aqueous solutions only by repeated treatments with decolorizing carbon. The other product was a brownish red amorphous material, insoluble in water, which was formed in amounts corresponding to 10 to 30% of the weight of the starting material. Attempts to purify this material were unsuccessful: it does not melt or sublime even when heated to a red heat (*i. e.*, until the melting point tube softened and col-

lapsed) and all attempts to secure pure products of any melting point by recrystallization from various organic solvents failed. From its behavior on heating, and its qualitative analysis, it is believed to be a sulfur-free material of high molecular weight.

The only sulfonic acid that was isolated in large amounts from the Jacobsen reaction upon durene, isodurene or pentamethylbenzene was prehnitene sulfonic acid. Since both durene and isodurene give the same product as a result of the Jacobsen reaction, the mixture of the two hydrocarbons offers a much more convenient source for making prehnitene than the method using pentamethylbenzene, as previously described by Smith and Lux, for this mixture is much more easily obtained in quantity than is pentamethylbenzene.

When the action of aluminum chloride and methyl chloride in the methylation of hydrocarbons is compared with the results of this study on the Jacobsen reaction, the curious fact appears that the orientations of the methyl groups in the comparable products is opposite in the two cases: the direct methylation has been found repeatedly to give little or no *ortho* methylated benzenes (no 1,2,3-trimethylbenzene, no 1,2,3,4-tetramethylbenzene), while when the tetramethylbenzenes undergo the Jacobsen reaction, the shift is completely in the direction of the 1,2,3,4-compound.

These studies are being continued in this Laboratory, and investigations of the reaction with other classes of compounds are under way, as well as investigations designed to throw light on the mechanism of this reaction.

Experimental

Hydrocarbons Not Undergoing the Jacobsen Reaction.—Into a 100-cc. flask was placed 10 g. of the sample, together with 30 cc. of concd. sulfuric acid. The flask was fitted with a calcium chloride tube, and then allowed to stand for ten days with occasional shaking.

- (a) Pseudocumene, b. p. 68° at 22 mm. Sulfonated at once, going into solution.
- (b) Mesitylene, b. p. 66° at 22 mm. Sulfonated at once, going into solution.
- (c) Prehnitene, m. p. -7.1°. Sulfonated at once, going into solution.
- (d) Hexamethylbenzene, m. p. 160-162°. No apparent change.

In no case did the material blacken, though in all cases a light yellowish-brown color developed. There was no odor of sulfur dioxide from any of the samples except the hexamethylbenzene, and in this case it was very slight. At the end of ten days, a, b and c had crystallized. Each sample was treated with 50 g. of ice, the sulfonic acid filtered off and dried on porous plates. From a there resulted 12.5 g. of pseudocumene sulfonic acid-5; m. p. 110-11°; from b, 13.2 g. of mesitylene sulfonic acid, m. p. 76-78°; from c, 11.8 g. of prehnitene sulfonic acid, m. p. 101-103°. Sample d was washed out into 200 cc. of water, filtered, washed with water and dried. There remained 10 g. of hexamethylbenzene, m. p. 158-160°. In none of the four cases had any rearrangement taken place.

The Jacobsen Reaction upon Durene, Using Concd. Sulfuric Acid at Room Temperature.—Into a small flask was placed 12.5 g. of durene (0.093 mole) and 25 cc. of concd. sulfuric acid was then added. The flask was arranged so that dry carbon dioxide-free air could be swept through it and the gaseous products of the reaction then passed

through an absorption bulb containing aqueous potassium hydroxide solution. This bulb was weighed from time to time, and the gain in weight noted. The reaction was allowed to proceed at room temperature for twenty-five days, with intermittent sweeping, during which time the absorption bulb was refilled twice. After each refilling, and at the end of the experiment, the contents of the bulb were analyzed, as follows: the alkaline solution from the bulb was made up to 500 cc. and aliquots removed for titrations. One portion was tested with lead acetate for sulfides, with negative results. Two portions were analyzed for sulfite ion by acidifying with sulfuric acid and titrating with standard iodine solution. Two other portions were then treated with an excess of iodine solution, and the total sulfate content determined by precipitation as barium sulfate in the usual way. These analyses were carried out each time the bulb was refilled, and at the end, and the results are given in the table.

TABLE I
RESULTS OF ANALYSIS OF THE GASEOUS PRODUCTS OF THE REACTION

Time, hours	Gain in weight of the bulb, g.	SO ₂ (titration), g.	SO ₂ (as BaSO ₄ after oxidation), g.
0-198	0.6067	0.4613	0.5329
198-304	.5653	.5105	.5600
304-515	.6412	.5951	.6380
Totals	1.8132	1.5669	1.7309
	Moles SO ₂	0.024	0.027

Hence the chief gaseous product was sulfur dioxide, 95% of the total gain in weight being accounted for by the total sulfur dioxide found by precipitation. The 5% difference in weight, 0.0823 g. which should have been due to carbon dioxide, was equal to 0.0019 mole of carbon dioxide, or only 7% of the number of moles of sulfur dioxide found by precipitation. As 90% of the total sulfur was found as sulfite, in spite of the oxidizing action of the stream of air, it was safe to conclude that the sulfur was liberated as sulfur dioxide and not sulfur trioxide, nor as free sulfur, or hydrogen sulfide, since the tests for sulfides were all negative, and there was never any evidence of free sulfur.

The reaction mixture in the flask was added to 200 cc. of cold water. A reddish-brown, insoluble substance precipitated, which was filtered, washed with water and dried, 2.0 g. This brown powder could be heated to the softening point of glass without melting, and to 220° at 4 mm. pressure without subliming or distilling. The filtrate from this material was jet black. It was decolorized by several treatments with decolorizing carbon and then evaporated in a beaker over an open flame until the boiling point reached 115°. On cooling, the material solidified to a mass of pearly white crystals of sulfonic acid, which was filtered through cloth and dried on a porous plate: wt. 16.2 g., m. p. 97-98°; the mixed m. p. with prehnitene sulfonic acid (103-104°) was 101-103°. It was thus impure prehnitene sulfonic acid. To identify it further, it was hydrolyzed by the "flash" method of Smith and Lux,³ yielding 6.3 g. colorless oil. This oil was then distilled from a small flask. The first few drops came over at 160-163°, and the temperature then rose rapidly to 198° at which point the main portion distilled. The first few drops were nitrated, yielding a trinitro compound, m. p. 183-184°; mixed m. p. with trinitropseudocumene (183-184°), also 183-184°. The small amount of low boiling material was therefore pseudocumene. A few drops of the main distillate were nitrated in the same way, giving a dinitro compound, m. p. 174-175°; mixed m. p. with dinitroprehnitene (174-176°), also 174-175°. The main distillate had a freezing point of -10°, against -6.4° for pure prehnitene. The refractive index, n_D^{22} 1.5194, is also the value for the pure hydrocarbon. There was no doubt, therefore, that the main product of the Jacobsen reaction upon durene was prehnitene sulfonic acid, contaminated

with a small amount of pseudocumene sulfonic acid. The theoretical yield of prehnitene sulfonic acid from 0.093 mole of durene assuming only a rearrangement, is 23.25 g. [$C_8H(CH_3)_4SO_3H \cdot 2H_2O = 250$]. Neglecting the small amount of pseudocumene sulfonic acid, the 16.2 g. prehnitene sulfonic acid obtained is a 70% yield. If the weight of durene used (12.5 g.) is corrected for the 2 g. of brown amorphous powder formed, then the theoretical yield of prehnitene sulfonic acid is 19.6 g. and the amount actually obtained is 83% of this. It therefore follows that in the Jacobsen reaction on durene by far the main reaction is merely rearrangement to prehnitene sulfonic acid; the formation of the brown powder accounts for about one-sixth of the durene used; and finally, pseudocumene sulfonic acid is formed in very minor amounts.

The Behavior of Durene Sulfonic Acid Hydrate When Kept over Phosphorus Pentoxide at Room Temperature.—Two 18-g. samples of durene sulfonic acid hydrate ($2H_2O$) m. p. 113° , and free from sulfates, were placed in a desiccator over phosphorus pentoxide for two months. After two weeks the material began to darken, the odor of sulfur dioxide was noticeable, and the phosphorus pentoxide began to turn pink. At the end of six weeks the sulfonic acid was jet black, with shining crystals of durene scattered through it, and the drying agent was a deep brown. At the end of eight weeks the samples were removed. Each had lost 3.0 g. in weight. They were washed with petroleum ether, which, on evaporation, left fairly pure durene (m. p. $75-77^\circ$). The black material insoluble in petroleum ether was treated with 100 cc. of water, the insoluble material filtered off, washed and dried. It was a brown powder which did not melt at 350° . The aqueous filtrate from this was decolorized, evaporated until the boiling point was 115° and cooled. The resulting white solid was filtered through cloth, and dried on a porous plate. It was prehnitene sulfonic acid, mixed m. p. with a pure specimen ($103-104^\circ$), $100-103^\circ$. The results of these two experiments are given in Table II.

TABLE II
RESULTS OF THE ACTION OF PHOSPHORUS PENTOXIDE ON DURENE SULFONIC ACID
HYDRATE AT ROOM TEMPERATURE

Used, g.	Sulfonic acid Lost, g.	Durene recovered, g.	Sulfonic acid, g.	M. p., $^\circ C$.	Insol. brown powder, g.
18.0	3.0	2.8	6.6	99-101	2.2
18.0	3.0	3.0	7.0	99-101	1.8

Thus at room temperature, over a period of eight weeks in a dehydrating atmosphere, durene sulfonic acid gave essentially the same products as are obtained when durene is kept in contact with sulfuric acid. Results entirely comparable to these were obtained when the anhydrous sulfonic acids were allowed to stand over phosphorus pentoxide.

The Behavior of Durene Sulfonic Acid Hydrate in Contact with Phosphorus Pentoxide.—Into a small flask was placed 12.5 g. of durene sulfonic acid hydrate (0.05 mole), then 30 g. of phosphorus pentoxide was dropped upon it, the flask quickly closed with a stopper arranged to admit a current of gas, and the whole apparatus connected to a weighed potash bulb. The gases were swept out with a stream of pure dry hydrogen. The contents of the flask darkened rapidly and the temperature rose. Some durene sublimed on the walls of the flask. After three hours the reaction mixture was worked up as described in the preceding paragraph, and the contents of the potash bulb analyzed for sulfite by direct titration and for total sulfur by precipitation as barium sulfate after oxidation. Found, SO_2 as sulfite, 1.111 g.; total SO_2 as $BaSO_4$, 1.140 g. Mole ratio sulfite to sulfate, 1.00 to 1.03. Mole ratio between the sulfonic acid used and SO_2 formed, 1.00 to 0.356. The contents of the flask, when separated, gave 0.9 g. of durene, 4.0 g. of the brown powder, and 3.8 g. of prehnitene sulfonic acid, m. p. $100-101^\circ$. Again

the results were qualitatively the same as those obtained in the regular Jacobsen procedure, or when the sulfonic acid is kept in a desiccator over phosphorus pentoxide. In another similar experiment, the results were practically the same: the mole ratio of the durene sulfonic acid used to SO_2 evolved being 1 to 0.342.

The Jacobsen Reaction upon Isodurene, Using Concd. Sulfuric Acid at Room Temperature.—Twenty-five grams of isodurene was placed in a flask with 50 cc. of concd. sulfuric acid and shaken for five minutes, when the hydrocarbon went into solution. Sulfur dioxide was evolved, and the mixture slowly turned black. After two days it had solidified, and after standing for eight days longer the mass of crystals was broken up and extracted with petroleum ether. Only a minute amount of high-boiling oil was removed by the petroleum ether. The material insoluble in petroleum ether was diluted with 200 cc. of water and filtered, yielding 7.0 g. of brown, high melting insoluble material. The jet black filtrate was decolorized and then evaporated until the boiling point reached 115° . On cooling, 23 g. of a sulfonic acid resulted, m. p. $97.5\text{--}100.5^\circ$; mixed m. p. with prehnitene sulfonic acid ($103\text{--}104^\circ$), $101\text{--}103^\circ$. The theoretical yield of prehnitene sulfonic acid hydrate ($2\text{H}_2\text{O}$) from 25 g. of isodurene (assuming only the rearrangement and sulfonation) is 46.6 g.; theoretical yield from 18 g. of isodurene (correcting for the 7 g. brown powder formed) 33.5 g. The amount obtained, 23 g., is 50% yield from 25 g. isodurene, and 70% yield from 18 g. of isodurene. Thus the same conclusions may be drawn from the experiments upon isodurene as from those on durene: the main reaction is merely a rearrangement to prehnitene sulfonic acid, and the same high melting brown powder is formed as the chief by-product.

The Jacobsen Reaction on Mixtures of Durene and Isodurene.—Since both durene and isodurene gave prehnitene through the Jacobsen reaction, these experiments were designed to utilize the tetramethylbenzene fraction from the methylation of xylene, as a source for prehnitene. After cooling this fraction to about -15° and filtering off the durene, the filtrate so obtained consists of about 90% isodurene and 10% durene. One experiment will be described, and the results of others given in a table: 100 g. of this filtrate (b. p. $82\text{--}84^\circ$ at 15 mm.) was shaken for five minutes with 100 cc. of a mixture of 2 parts of concd. sulfuric acid and 1 part "60% fuming H_2SO_4 ." The hydrocarbons rapidly dissolved, after which the reaction mixture was kept at 80° . After four hours, the mixture solidified, and at the end of nine hours the black solid was broken up and poured out upon 500 g. of ice. The brown insoluble material (wt. 18 g.) was filtered off. The black filtrate was not decolorized, but was at once cooled to $+10^\circ$ and treated with 250 cc. of cold concd. sulfuric acid. The resulting black crystalline precipitate of sulfonic acid was filtered off through cloth and pressed as dry as possible; m. p. $98\text{--}100^\circ$. It was then dissolved in 200 cc. of warm water and hydrolyzed at $145\text{--}150^\circ$ by the "flash" method of Smith and Lux.³ The oil in the distillate, after drying, weighed 65.2 g. After the residue in the distillation flask had cooled, it deposited 7.0 g. of black solid. The 65.2 g. of oil was carefully fractionated, as follows.

TABLE III
FRACTIONATION OF CRUDE PREHNITENE

Fraction	B. p., 25 mm., $^\circ\text{C}$.	Wt., g.	n_D^{25}	Freezing point, $^\circ\text{C}$.
I	66–75	8.0	1.5051	
II	75–94	4.0	1.5110	
III	94–96.4	6.8	1.5167	–16
IV	96.4	41.4	1.5196	–7.2
V	Residue	3.0	1.5210	–10.0

Fraction IV was very good prehnitene, showing a freezing point of -7.2° against -6.4° for the pure hydrocarbon. Fractions I and II contained a trimethylbenzene.

presumably pseudocumene. In the table below the results of some other runs are summarized; these data show that the best yields of prehnitene result when the temperature is from 70 to 90°, and the time about nine hours, although the time may be shortened considerably by operating at the higher temperatures.

TABLE IV

RESULTS OF THE CONVERSION OF DURENE-ISODURENE MIXTURES TO PREHNITENE

Wt. of tetramethyl filtrate, g.	Time	Temp., °C.	Prehnitene obtained, g.
100	3 days	25	Little
50	4 hours	80	13.2
100	2 hours	90	38.6
50	9 hours	70	16.0
50	9 hours	70	21.2
100	9 hours	80	41.4

Thus a yield of over 40% of prehnitene can be obtained in this way, and this is the most convenient method yet discovered for the preparation of this hydrocarbon.

Summary

1. The Jacobsen reaction can be divided into at least two rearrangements: (a) the shift of methyl (alkyl) groups from molecule to molecule, giving higher and lower methylated benzenes, and (b) the shift of methyl groups within a molecule to an arrangement more stable toward sulfuric acid or other strong dehydrating conditions.

2. Of the polymethylbenzenes, only durene, isodurene and pentamethylbenzene undergo the reaction, the first two reacting according to (b), giving prehnitene, and the pentamethylbenzene reacting according to (a), giving prehnitene and hexamethylbenzene.

3. Mixtures of durene and isodurene can thus be used as a source for prehnitene.

4. The hydrocarbons are not the only products of the reaction, but are accompanied by sulfur dioxide, a black, water-soluble material, and a brown amorphous water-insoluble material, the last occurring in amounts of from 10 to 30% of the total material recovered.

5. It is the sulfonic acid which rearranges, and not the hydrocarbon.

6. The dehydrating agent—phosphorus pentoxide or sulfuric acid—is necessary, for the sulfonic acids alone are stable.

7. The shift of the methyl groups is accompanied by reduction of the sulfonic acid group of part of the material used.

8. The orientation effects of the Jacobsen reaction and those of the direct methylation of benzene hydrocarbons, are entirely opposite in the case of tetramethylbenzene.