dye) and the extremely soluble 1-amino-4-phenol-sulfonic ester (0.46 mole per mole of dye). The yield ratio of the latter two products was identically the same as obtained in the cleavage of the unsulfonated dye.

Cleavage of 4-Hydroxyazobenzene-4-sulfonic Acid at 140 to 145°.—The sodium salt of the dye and sodium sulfite solution of approximately 0.75 *M* concentration were heated in a steel autoclave at 140 to 145°. At the end of twenty hours cleavage was found complete. Analytical determinations yielded very nearly the same results: 3.6% of the consumed sulfite was changed to sulfate, a little more than was formed at the lower temperature.

Summary

1. A new type reaction of monoazo dyes has been observed. They combine with two moles of a neutral sulfite, in solution, suffering cleavage into a primary amine and the salts of N-sulfonic and N-disulfonic acids.

2. 4-Hydroxyazobenzene yielded approximately 0.78 mole of aniline, 0.22 mole of an N-sulfonic acid of aniline, 0.78 mole of an N-disulfonic and 0.22 mole of an N-monosulfonic acid of 1-amino-4-phenol and no trace of unsulfonated aminophenol.

3. 4′-Hydroxyazobenzene-4-sulfonic acid reacted similarly, sulfanilate being formed as a result of cleavage.

4. Hydrolysis and rearrangement of free N-sulfonic acids resulted in complete recovery of the primary dye component in its original form; the secondary component yielded 1-amino-4-phenol-5-sulfonic acid and an extremely soluble, stable 1-amino-4-phenol-sulfonic ester, a compound not previously reported.

5. An explanation of the cleavage reaction has been suggested, founded on an assumption of functional differences between the two nitrogen atoms of the azo group.

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STUDIES ON THE POLYMETHYLBENZENES. I. A STUDY OF THE JACOBSEN REACTION WITH PENTAMETHYLBENZENE, AND THE PREPARATION OF PREHNITENE[1]

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I. Introduction and Historical

In 1887 Oscar Jacobsen[2] discovered that pentamethylbenzene when treated with concd. sulfuric acid undergoes a rather curious reaction in which a methyl group migrates from one molecule to another, leading to hexamethylbenzene and a tetramethylbenzene, prehnitene (1,2,3,4-),

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

[2] Jacobsen, *Ber.*, **20**, 896 (1887).

which appears in the form of its sulfonic acid. This reaction is expressed by Jacobsen as follows

$$2C_6H(CH_3)_5 + H_2SO_4 \longrightarrow C_6(CH_3)_6 + C_6H(CH_3)_4SO_3H + H_2O$$

Jacobsen extended this reaction to other alkylated benzenes and found that it also took place with durene,[3] giving pentamethylbenzene and two trimethylbenzene-sulfonic acids, and with penta-ethylbenzene,[4] which gives hexa-ethylbenzene and the sulfonic acid of 1,2,3,4-tetra-ethylbenzene. Jacobsen also found that analogous reactions occurred when some of the halogenated benzenes were treated with concd. sulfuric acid, only in these cases it is the halogen which migrates instead of the alkyl group. Thus monobromodurene[5] gives dibromodurene and durene, the latter, of course, reacting at once to give higher and lower methylated benzenes.

The hexa-substituted benzenes obtained in these reactions are apparently end products and are stable toward sulfuric acid, even after several months' contact. In the case of the methylated benzenes, the reaction appears to be limited to the tetra- and pentamethylbenzenes, for the trimethylbenzenes are simply sulfonated by concd. sulfuric acid without any rearrangement; but in the case of the halogenated benzenes, even monobromobenzene will rearrange when treated with sulfuric acid, giving dibromobenzene and (presumably) benzene,[5] dibromobenzene giving tetra- and hexabromobenzene, and tribromobenzene giving hexabromobenzene. Similar migrations of halogens have been noted in the case of iodobenzene, *o*- and *p*-iodotoluene and *o*- and *p*-iodophenol.[6]

It has long been known that anhydrous aluminum salts will cause alkyl groups to migrate, not only into different positions in the same molecule but also from one molecule to another, but sulfuric acid is not frequently a reagent which causes migrations of this sort to take place. For this reason we were interested in a study of the Jacobsen reaction and we selected pentamethylbenzene as the object of our first study for two reasons: first, pentamethylbenzene when it undergoes the reaction gives fewer products than any other methylated benzene and, second, the tetramethylbenzene obtained in this way from pentamethylbenzene is prehnitene (1,2,3,4-), a very rare hydrocarbon, and we hoped to discover the conditions which would enable us to use the Jacobsen reaction with pentamethylbenzene as a method for making prehnitene in quantity. The work reported in this paper represents the preliminary investigation of a problem which has for its object: (1) verification of the facts as stated by Jacobsen, (2) determination of the limits of the Jacobsen reaction, and any special conditions which influence the reaction, (3) determina-

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[3] Jacobsen, *Ber.*, **19**, 1209 (1886).

[4] Jacobsen, *ibid.*, **21**, 2814 (1888).

[5] Jacobsen, *ibid.*, **20**, 2837 (1887).

[6] Herzig, *ibid.*, 21, 664 (1888); Neumann, *Ber.*, **20**, 581 (1887); *Ann.*, **241**, 33 (1887).

tion of the mechanism of the reaction and (4) determination of the conditions under which the reaction can be run with pentamethylbenzene to give a good yield of prehnitene.

II. Method of Procedure and Discussion of Results

The procedure, from the initial materials to the final products, may be divided into four steps: (a) the Jacobsen reaction proper, (b) isolation of the products, (c) separation and purification of the products and (d) conversion of the prehnitene-sulfonic acid into prehnitene, together with the purification of the crude hydrocarbon. Each step in this procedure was examined, varying conditions as much as possible and determining the effects of these variations upon the yields of the products.

(a) **The Jacobsen Reaction Proper.**—The three variables studied in this step were the amount of sulfuric acid, the time and the temperature. The last two of these depend upon each other, for the same results are obtained by heating for a short time as are obtained by standing at room temperature for a longer time. In order, therefore, to standardize the procedure, we ran all of our experiments at room temperature, merely varying the time of standing. From the data in the table it is apparent that twenty-four hours is a sufficient time and that no improvement in the yield of products results on longer standing. The amount of sulfuric acid is also of little consequence as far as the final products are concerned, provided enough is used to react according to Jacobsen's equation, but it is more convenient to use more than this amount in order to get a thorough contact between the acid and the solid hydrocarbon.

(b) **Precipitation of the Sulfonic Acid from the Sulfuric Acid Solution.**—This is accomplished by adding ice to the solution; the variables in this step are the amount of ice added and the rate at which it is added, since this controls the temperature. The amount of ice used—enough to dilute the original acid to 50% by volume—was decided on the basis of the different yields of sulfonic acid obtained by using different amounts of ice. In order to avoid charring and the formation of tars, this ice must be added slowly and the mixture cooled in a bath of ice and salt.

(c) **Separation and Purification of the Products.**—The precipitate which forms when the sulfuric acid is diluted consists of hexamethylbenzene, prehnitene-sulfonic acid and tars. The separation of this mixture into its constituents is fairly easy, and is given in the experimental part.

(d) **Conversion of Sodium Prehnitene-sulfonate into Prehnitene and Purification of the Hydrocarbon.**—The hydrolysis of sulfonic acids to hydrocarbons in the presence of mineral acids has been studied by a number of investigators, but the most systematic investigation appears to be that of Armstrong and Miller,[7] who found that the reaction depends

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[7] Armstrong and Miller, *J. Chem. Soc.*, **45**, 148 (1884).

primarily upon the temperature and that any mineral acid can be used, provided means are available for obtaining high enough temperatures. These temperatures are all rather critical for given sulfonic acids, and are, in general, in the range of 120–200°—too high for hydrochloric acid unless autoclave conditions are employed. For this reason we chose sulfuric acid as the mineral acid, for any temperature up to the boiling point of sulfuric acid may be obtained by varying the concentration of the acid. Preliminary experiments showed, however, that the sulfonic acid of prehnitene (and also of other highly methylated hydrocarbons) is not only hydrolyzed by hot sulfuric acid but that other decompositions occur, leading to large amounts of tars from which no hydrocarbon can be obtained, and that the formation of these tars is largely a function of the time the sulfonic acid remains in contact with the hot sulfuric acid. Consequently, the only feasible method of hydrolysis appeared to be a "flash" system, in which the sulfonic acid was dropped slowly into hot sulfuric acid and the hydrocarbon distilled out immediately. Such a flash system gave beautiful results when applied to the hydrolysis of durene-sulfonic acid, yielding almost the quantitative amounts of durene; but prehnitene-sulfonic acid is exceedingly sensitive to the hot sulfuric acid and it requires very careful manipulation to get a good yield of hydrocarbon in this way. It was finally discovered, however, that if instead of the sulfonic acid, a water solution or paste of the sodium salt were used, good results could be obtained. The procedure finally developed consisted in passing superheated steam through sulfuric acid, holding the temperature of the acid at 145 to 150° by means of an outside bath, and then running in slowly a paste of the sodium salt of the sulfonic acid at such a rate that the temperature did not fall below 140 or rise above 155°. In this way the yield of hydrocarbon from the sodium sulfonate often runs as high as 90% and the average of a large number of runs is well over 80%. The temperature of hydrolysis is quite critical; below 140° the reaction is very slow, while above 160° there is much decomposition with charring and evolution of sulfur dioxide.

Experimental Part

The Jacobsen Reaction.—One typical run will be described in detail and others are summarized in the table. One-half mole (74 g.) of pentamethylbenzene (m. p. 52° or higher) is heated to 65° and to the resulting oil is added, with vigorous stirring, 200 cc. of concd. sulfuric acid which is at room temperature. By this procedure the hydrocarbon is cooled below its melting point and crystallizes in a finely divided form. This is essential, for if lumps of solid form they are quickly coated over with sulfonic acid or other material and the interior is protected completely against the sulfuric acid. After adding all of the acid, the resulting mush of white crystals and reddish liquid is placed in a cooling bath until it reaches room temperature, after which it is allowed to stand.

After standing for the requisite length of time, the mixture is cooled to 0° in a bath of ice and salt and 165 to 200 g. of cracked ice added in three portions, with vigorous stirring, making certain that the ice and water touch all parts of the mixture. This can be told by the disappearance of the dark reddish-brown color wherever the water touches the solid. After all of the ice has been added, the mixture is cooled to 0° and then filtered with suction through a cloth filter, pressing as dry as possible. The filtrate contains no appreciable amount of organic material and is discarded. The filter cake is leached out thoroughly with about 700 cc. of cold water and the resulting suspension is filtered. The precipitate is light brown and is hexamethylbenzene and by-products, while the red filtrate consists of a water solution of prehnitene-sulfonic acid also containing sulfuric acid.

The filtrate is worked up by converting the acids into the calcium salts by adding powdered calcium carbonate in small portions until there is no further effervescence. The precipitate of calcium sulfate is filtered off, washed thoroughly and discarded. The combined filtrates and washings contain the calcium salt of the sulfonic acid, which is converted into the sodium salt by adding concd. sodium carbonate solution as long as any calcium carbonate precipitates. The precipitate is filtered off, washed with water and discarded, after which the filtrate and washings are evaporated to dryness on the steam-bath, leaving the solid sodium salt of prehnitene-sulfonic acid; weight, about 40 g. or about 68% yield (assuming Jacobsen's equation to be correct). This sodium salt need not be purified before the hydrolysis to prehnitene, but for purposes of identification portions of it from several different runs were converted in the usual manner into the sulfone chloride, m. p. 73–75°, and the sulfonamide, m. p. 187°.[8]

Purification of the Hexamethylbenzene.—The light brown precipitate of crude hexamethylbenzene weighs about 50 g. and melts gradually from 140 to 160°. It was purified by distillation under reduced pressure, 30 g. of distillate passing over at 170° under 80 mm. or 162° under 55 mm., and solidifying in the receiver to a white solid which, after recrystallizing once from a mixture of chloroform and alcohol, melts at 162°. A mixed melting point with a specimen of hexamethylbenzene, m. p. 162°, showed no depression. The yield, based on Jacobsen's equation, is 74%. The tarry residue remaining in the distilling flask weighed 20 g.

Conversion of the Sodium Prehnitene-sulfonate into Prehnitene, (a) Using Concd. Hydrochloric Acid.—About 10 g. of the sodium salt (or the sulfonic acid itself) was dissolved in 100 cc. of concd. hydrochloric acid. The solution was heated to the boiling point and steam passed through it for two hours. The distillate contained no oil, while the residue in the distilling flask was red and tarry. In another experiment 9 g. of the sulfonic acid was refluxed with 100 cc. of concd. hydrochloric acid for two hours and then distilled with steam. No trace of oil distilled over and the residue was very tarry.

(b) **Distillation of the Sodium Salt with Ammonium Chloride.**—Ten grams of dry sodium sulfonate was ground in a mortar with 50 g. of ammonium chloride, the mixture placed in a distilling flask and heated until the glass began to soften. In this case 1.5 g. of colorless oil distilled over, a yield of only 30%.

(c) **Using Sulfuric Acid.**—Preliminary experiments were carried out on the hydrolysis of durene-sulfonic acid to durene, as we could obtain this sulfonic acid in quantity from durene. These experiments indicated that it was necessary to heat, for very little durene is formed in the cold when the sulfonic acid is shaken with concd. sulfuric acid, contrary to the statement of Jacobsen.[3] By using 50% sulfuric acid and regulating the temperature very carefully, we finally found the conditions which would give a nearly quantitative yield of durene from the sulfonic acid, but when these condi-

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[8] Jacobsen, *Ber.*, 19, 1214 (1886); Kelbe and Pathe, *ibid.*, 19, 1552 (1886), however, give the m. p. of the amide as 177°.

tions were applied to prehnitene-sulfonic acid, only a 50% yield of hydrocarbon resulted. Moreover, if the temperature was increased, the yield diminished, and large amounts of tarry material resulted. After many experiments a procedure was developed which gave excellent results and which consists essentially of a "flash" hydrolysis and distillation with superheated steam. The flask in which the hydrolysis was conducted was an ordinary distilling flask of 500-cc. capacity, with two tubulatures in the bulb, one for carrying a thermometer, and the other for carrying a separatory funnel. The steam was superheated by means of a small superheater of copper tubing placed in the line. A typical experiment is described: the flask is charged with 100 cc. of water and immersed in an oil-bath at about 200°. Then, with superheated steam passing through, concd. sulfuric acid is added through the dropping funnel until the temperature of the diluted acid in the flask reaches 150–160°. At this point a saturated water solution of 40 g. of the sodium prehnitene-sulfonate (or a thin paste of the solid and water) is run in at such a rate that the temperature of the acid mixture remains between 140 and 150°. The hydrolysis takes place rapidly and the hydrocarbon is distilled out immediately by the current of steam. The oil distilling over is a very pale yellow and weighs 20 g. (88% yield based on the weight of the sodium sulfonate). On redistillation over 90% of the oil passes over within a range of 0.5°; b. p. 97 to 98° at 24–25 mm., and the distillate shows a freezing point of −7.4°. (The freezing point of carefully purified prehnitene is −6.4°.)

Representative runs are shown in the table. The final run represents an experiment on a large amount of pentamethylbenzene to see whether or not the data obtained from small runs were applicable to larger quantities; the results show that prehnitene can be made in quantity by this method. It is, in fact, the only method for obtaining this hydrocarbon in any quantity, starting with materials which are themselves easily available.

TABLE I

SUMMARY OF THE RESULTS OF THE JACOBSEN REACTION WITH PENTAMETHYLBENZENE

Pentamethylbenzene, g.	Na sulfonate, g.	Crude prehnitene, g.	Crude hexamethylbenzene, g.	Pure hexamethylbenzene, g.	Time of standing, hours
74	45	15	..	..	24
74	40	20	50	30	24
74	35	20	49	30	48
74	45	16	49	..	48
74	40	21	55	..	48
74	45	18	41	34	24
74	35	18.5	45	..	24
74	46	17.5	48	..	24
74	40	19.5	50	..	24
74	37	20.0	50	..	24
74	43	18	55	30	24
1090	..	264	610	434	24

The Mechanism of the Jacobsen Reaction.—In this preliminary study most of the work was directed toward establishing the best conditions for carrying out the Jacobsen reaction in order that it might be used as a method for making prehnitene, and no extensive study of the mechanism of the reaction was made. In connection with another phase of this work, however, a sample of pentamethylbenzene-sulfonic acid was prepared and was placed in a desiccator over sulfuric acid for final drying. At the end of a week it was noticed that the acid had darkened quite a bit, and as the time went on, the color deepened. The sulfuric acid in the desiccator also darkened in color and sulfur dioxide was evolved, but this came from the sulfuric acid and not from the sulfonic acid above it. At the end of eight weeks both the sulfonic acid and the sulfuric acid were dark brown. The sulfonic acid (10 g.) was removed and worked up exactly according to the procedure used in carrying out the Jacobsen reaction. There resulted a brownish solid, insoluble in water or alkali, and an aqueous solution containing sulfonic acids.

The solid was sublimed, giving a white sublimate, m. p. 75 to 101°, which could not be purified because of the small amount. This m. p. is above that of pentamethylbenzene (52°) but below that of hexamethylbenzene (164°). However, some of the solid was mixed with pure hexamethylbenzene and the resulting mixture melted at 122–140°. Hence the solid is probably impure hexamethylbenzene and the impurity is most likely pentamethylbenzene resulting from hydrolysis of the sulfonic acid.

The sulfonic acids contained in the aqueous solution were converted into the sodium salts in the usual way and evaporated almost to dryness. A pasty mass of yellowish solid resulted; when this was hydrolyzed with sulfuric acid, there resulted 1.5 g. of oil in the distillate.

This experiment indicates that the first step in the Jacobsen reaction is a sulfonation and that it is the sulfonic acid, not the hydrocarbon, which rearranges, for the reaction will take place with the sulfonic acid alone in the absence of direct contact with sulfuric acid. Further study of this phase of the problem is in progress and will be reported later.

Summary and Conclusions

1. The rearrangement known as the Jacobsen reaction takes place essentially in the manner reported by Jacobsen, although there are considerable amounts of tarry by-products and Jacobsen's equation does not represent all that happens.
2. The optimum conditions for this reaction with pentamethylbenzene have been determined and when properly handled the reaction can be used as a method for making the rare hydrocarbon prehnitene (1,2,3,4-tetramethylbenzene) in quantity and with a yield of about 65% based on the pentamethylbenzene used. The yield of hexamethylbenzene is over 70%, while somewhat less than one-third of the original pentamethylbenzene is lost, principally as tars.
3. The hydrolysis of prehnitene-sulfonic acid to prehnitene has been studied in detail and a method is described which gives high yields of the hydrocarbon.
4. One experiment is reported which has a bearing upon the mechanism of the Jacobsen reaction.

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