

**Hydrolysis of the Methylated Celluloses (A') and (B').**—The fully methylated celluloses (A') and (B') (weights 3.45 and 3.49 g.) were dried thoroughly in the vacuum oven and hydrolyzed by heating under pressure with 50 cc. of methanol containing anhydrous hydrogen chloride (1%), first for sixty hours at 100° and then for fifty hours at 125°. Only a very slight residue remained. Each solution was neutralized with silver carbonate, filtered, evaporated under reduced pressure to 25 cc., diluted with 25 cc. of anhydrous ether, boiled with activated charcoal, filtered and the solution evaporated under reduced pressure to constant weight. Weights of crude products from (A') and (B'), 3.55 g. (89.0%) and 3.62 g. (89.7%), respectively. The identity of these products was shown by their boiling point, 106–108° (0.015 mm.). Yields of the pure distilled products were 3.25 g. and 3.30 g., respectively.

### Summary

1. The difficulties encountered in effecting

complete methylation of refined sulfite wood pulps from spruce and maple, by means of dimethyl sulfate and sodium hydroxide, can be overcome readily by dissolving the partially methylated products in chloroform, reprecipitating into petroleum ether and subsequent remethylation with the same reagents.

2. Using this technique no chemical differences can be noted in the behavior of cotton and refined wood pulps, respectively, nor in their hydrolysis products.

3. The previous assumption of the presence of a "resistant" type of cellulose in wood pulps responsible for incomplete methylation and differing therefore from cotton cellulose does not appear to be warranted.

MONTREAL, CANADA

RECEIVED APRIL 24, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

## The Olefin-Benzene Condensation with the Sulfuric Acid Catalyst

BY H. L. WUNDERLY, F. J. SOWA AND J. A. NIEUWLAND

A number of investigators<sup>1</sup> have employed sulfuric acid alone and with other combinations as a catalyst in the olefin-benzene condensation.

The purpose of this investigation was to show the influence of: boron fluoride as a promoter, the amount of sulfuric acid, time and temperature on the olefin-benzene condensation and to study the mechanism of the reaction.

Ipatieff, Corson and Pines<sup>1e</sup> claimed that the propylene-benzene condensation proceeded in exactly the same manner when sulfuric acid was used alone as it had in the presence of boron fluoride and sulfuric acid. It seemed doubtful that the conditions of the experiments of Ipatieff, Corson and Pines<sup>1e</sup> and of Slanina, Sowa and Nieuwland,<sup>1d</sup> were sufficiently comparable to draw this conclusion. Two series of experiments were performed, similar in every detail, except in the first case 80 g. of sulfuric acid alone, while in the second case 80 g. of sulfuric acid with 10 g. of boron fluoride, was used; two moles of benzene was employed. The rate of addition of propylene was controlled carefully and the temperature was

maintained at  $4 \pm 1^\circ$  for all experiments. The results are given in Table I.

TABLE I  
THE EFFECT OF BORON FLUORIDE AND TIME ON OLEFIN-BENZENE REACTION

Time, hrs.	BF <sub>3</sub> g. used	Isopropylbenzene		
		Mono	Di	Tri
2	0.0	62.9	22.8	7.7
2	10.0	91.1	32.7	5.2
4	0.0	97.1	56.2	20.3
4	10.0	97.1	82.4	22.9

It should be noted that boron fluoride exerted a remarkable influence on the propylene-benzene condensation. The effect of time upon this reaction is also shown in Table I. Again, the effect of boron fluoride was pronounced in the ethylene-benzene reaction. Although ethylene did not condense with benzene in the presence of sulfuric acid alone under the conditions employed in this investigation, it was interesting that condensation took place when the mixed catalyst composed of sulfuric acid and boron fluoride was used.

A series of propylene-benzene condensations using sulfuric acid as the catalyst are shown in Fig. 1.

The reactions were all performed under identical conditions except that the quantity of sulfuric acid

(1) (a) Kraemer and Spilker, *Ber.*, **23**, 3269 (1890); (b) Brochet, *Compt. rend.*, **117**, 115 (1893); (c) Ipatieff, U. S. Patent 2,006,695; *C. A.*, **29**, 5456 (1935); (d) Slanina, Sowa and Nieuwland, *THIS JOURNAL*, **57**, 1547 (1935); (e) Ipatieff, Corson and Pines, *ibid.*, **58**, 919 (1936).

was varied. Maximum yields of mono-, di- and triisopropylbenzenes were reached with approximately the same quantity of sulfuric acid (82 g.). These maxima correspond to a 100% yield based on the quantity of propylene added.

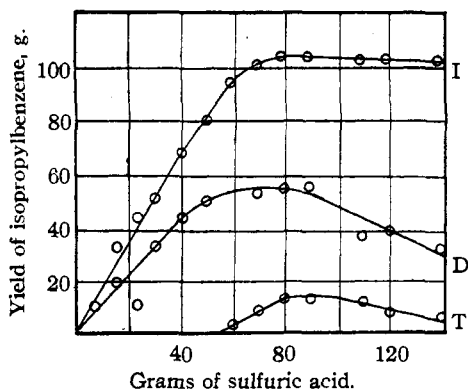


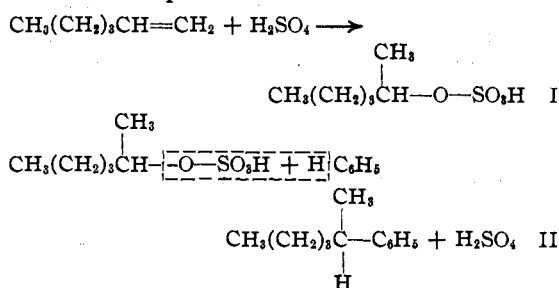
Fig. 1.—Curve I, isopropylbenzene; curve D, diisopropylbenzene; curve T, triisopropylbenzene.

The sulfuric acid always remained as a lower insoluble layer and could be separated and used repeatedly as a catalyst with practically no loss of the acid. At higher temperatures this did not seem to be altogether the case.<sup>1d</sup>

The effect of temperature on this reaction was demonstrated by increasing it from 3 to 15°. Fifty grams of sulfuric acid was used. At the lower temperature 18.5 g. of isopropylbenzene was formed while 93.8 g. was formed at the higher temperature. The diisopropylbenzene changed from 50.0 g. to 40.1 g. while the triisopropylbenzene changed from zero to 8.3 g. with the formation of a trace of tetraisopropylbenzene.

With reference to the mechanism of this reaction it might be said that propylene did not combine with benzene at 5° and atmospheric pressure without a catalyst. It was necessary, therefore, to activate the propylene or the benzene nucleus or both sufficiently to cause their combination. Propylene was added to sulfuric acid to give isopropyl acid sulfate and diisopropyl sulfate. Propylene was condensed with sulfuric acid, under the same conditions employed in constructing Fig. 1, and subsequently added to benzene. By this two-stage procedure any result in Fig. 1 that used over 100 g. of sulfuric acid could be duplicated. Diisopropyl sulfate was purified, added to an excess of benzene and refluxed at the boiling point of benzene for one hour. No reaction took place, as indicated by the failure of a sulfuric acid layer to

appear. A small quantity of sulfuric acid added to the diisopropyl sulfate-benzene solution resulted in a violent reaction and the separation of a large sulfuric acid layer. Sulfuric acid seemed to play an important part in catalyzing the ester reaction with benzene under the conditions of this reaction. The alkylating agent was likely isopropyl acid sulfate. Brochet<sup>1b</sup> indicated that this reaction proceeded through the alkyl acid sulfate stage and that secondly this alkyl acid sulfate double decomposed with benzene as



The latter reaction did not seem likely and so an attempt was made to show that equation (II) was at least incomplete as written. If equation (II) were correct *n*-propyl acid sulfate or di-*n*-propyl sulfate with sulfuric acid should yield *n*-propylbenzene as a product.

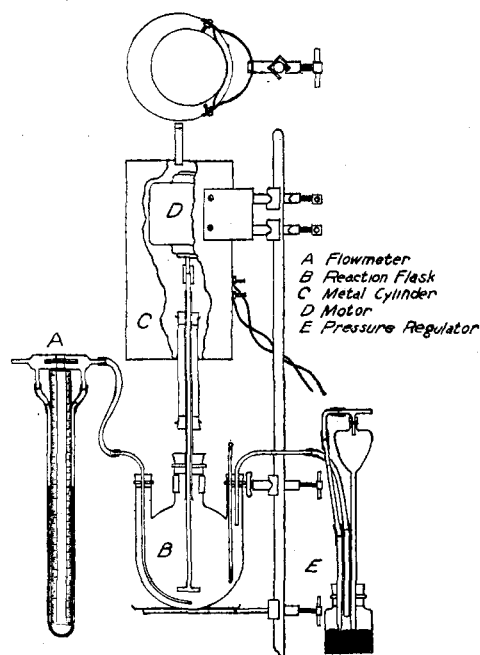
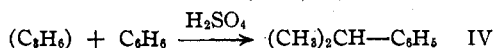
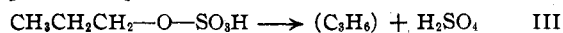


Fig. 2.

Benzene was treated with *n*-propyl acid sulfate and di-*n*-propyl sulfate along with boron fluoride as a promoter. The products were not *n*-propyl

but were isopropyl substituted benzenes. The following equations are, therefore, proposed in place of equation (II) above



The  $(\text{C}_3\text{H}_6)$  in the above equation represents the intermediate olefin stage, the olefin being in an "activated" state which readily reacted with benzene. The sulfuric acid probably also activated the benzene nucleus slightly but the activated olefin stage, in this case, was of greater importance.

### Experimental Part

**Propylene-Benzene Condensation.**—Two moles of benzene and various quantities (see Fig. 1) of concentrated sulfuric acid were carefully weighed in a 2-liter three-necked round-bottomed flask (see diagram of apparatus, Fig. 2). The flask was immersed in an ice-bath and maintained at a temperature of  $3 \pm 1^\circ$  while propylene was added through a flowmeter at a rate of 21.9 g. of propylene per hour and stirred at a rate of 1100 revolutions per minute.

After propylene had been added for three hours, the flask was removed and the lower layer of sulfuric acid separated. In nearly all cases the weight of the sulfuric acid layer

checked closely with the original quantity of acid added. The upper layer was refluxed for three hours with an equal volume of a 20% solution of sodium hydroxide, separated, dried and fractionated. The fractions collected and the physical properties of the four isopropylbenzenes were the same as those previously reported.<sup>1d</sup> For the yields of products see Fig. 1.

The diisopropylbenzene was converted to terephthalic acid and then to its dimethyl ester<sup>1d</sup> to prove its structure.

Ethylene was condensed with benzene under the same conditions that were employed when propylene was used except that the temperature was between  $10\text{--}20^\circ$ . By using 82 g. of sulfuric acid with 11 g. of boron fluoride as a promoter, 10.2 g. of ethylbenzene and 1.5 g. of diethylbenzene were formed.

### Summary

The influence of the amount of sulfuric acid, the temperature, the time and boron fluoride on the condensation of propylene with benzene has been studied.

Ethylene was condensed with benzene at low temperatures and atmospheric pressure.

A mechanism for the reaction has been proposed.

NOTRE DAME, INDIANA

RECEIVED JANUARY 27, 1936

[CONTRIBUTION FROM THE DIVISION OF INSECTICIDE INVESTIGATIONS, BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

## The Occurrence of Quebrachite in the Stems of *Haplophyton Cimicidum*

BY E. P. CLARK

In an attempt to isolate the insecticidal material reputed to be present in the stems of *Haplophyton cimicidum*,<sup>1</sup> a crystalline material was obtained which proved to be quebrachite (1-methyl inosite).

Since direct comparison of this substance with an authentic sample of quebrachite was impossible, identification was established by comparing the properties of the isolated material and certain of its derivatives with values already recorded in the literature. The results of this procedure and the method employed to obtain the substance are presented here.

### Experimental

**Preparation of Quebrachite.**—Fifteen hundred grams of ground stems of *Haplophyton cimicidum* was moistened with 750 cc. of water and allowed to stand in a tight

(1) This material was obtained through the cooperation of the Mexico City Laboratory of the Division of Fruit Fly Investigations, Bureau of Entomology and Plant Quarantine.

container overnight. The drug was then packed in a percolator and exhausted for approximately two hours with sufficient water to yield 8 liters of extract. This liquid was defecated with basic lead acetate, the excess lead removed with sulfuric acid, and the resulting filtrate concentrated, under reduced pressure, to 300 cc. This was diluted to 2 liters with 95% ethanol. The liquid was filtered and concentrated, under reduced pressure, to a very thick sirup. This was heated and diluted to 200 cc. with ethanol. After some time crystallization commenced and was completed within a week or ten days. The crystals were removed, the mother liquor was diluted with an equal volume of hot methanol, and 1 liter of hot acetone was added. The resulting mixture was shaken rapidly to separate the suspended sirupy material, and the relatively clear solution was concentrated under reduced pressure to a thick sirup. This was dissolved from the flask with 50 cc. of ethanol, and the liquid allowed to crystallize. The total yield of crude quebrachite was usually 10 to 11 g.

The crude material was purified by dissolving 1 g. in 2 cc. of hot water, filtering through Norit, and adding 8 cc. of hot ethanol to the filtrate. Crystallization began at once and was soon completed. By working over the mother liquors, recovery was practically complete.