yields. There was no evidence of the formation of the isomeric, higher-melting compound, diphenyl-carbam-hydroxamic acid. The latter would have been formed, had β-phenyl-hydroxylamine possessed any tendency to dissociate at the phenyl linking, $C_6H_5 \vdots \text{NHOH}$.

Summary

Evidence is submitted that supports the hypothesis of Jones and Hurd, which stated that if the radical "R," which "wanders" in a Beckmann rearrangement, is potentially a free radical, the rearrangement occurs with greater ease than otherwise. Diphenyl-carbam-hydroxamic acid derivatives are discussed in this connection; diphenyl nitrogen is the "free radical."

Derivatives of monophenyl-carbam-hydroxamic acid (phenyl-hydroxyurea) could not be made to rearrange. The structure of carbanilidophenyl-hydroxy-urea is discussed and is preferred to the optional "diphenyl-hydroxy-biuret" structure. It is definitely proved that the assumption that phenyl-hydroxy-urea dissociates into phenyl isocyanate and hydroxylamine, is untenable.

Hydroxy-urea, and hydroxy-biuret are similarly discussed in this connection.

A preliminary study has been made of the reaction between phenyl isocyanate and monohydroxamic acids. The addition seems to be at the α-hydroxylamino hydrogen rather than at the β.

Additional data are obtained for the "diphenylamine reaction."

A method is given which uses hydroxylamine sulfate in the preparation of hydroxylamine in alcoholic solution, when hydroxylamine hydrochloride is not available.

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[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, NO. 67]

A SYNTHESIS OF THYMOL FROM PARA CYMENE. II

BY MAX PHILLIPS

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In an earlier article published from this Laboratory[1] a synthesis of thymol from *p*-cymene was described. The yields obtained according to the method outlined in that paper were far from satisfactory. In the present article certain modifications and improvements in the process are given.

It will be noted from the results presented in this paper that, aside from certain improvements in the yields of some of the intermediates used in this synthesis, the present method differs primarily from the previous one in the manner in which the amino group of cymidine-sulfonic acid is eliminated. Instead of converting the cymidine-sulfonic acid into diazocymene-sulfonic

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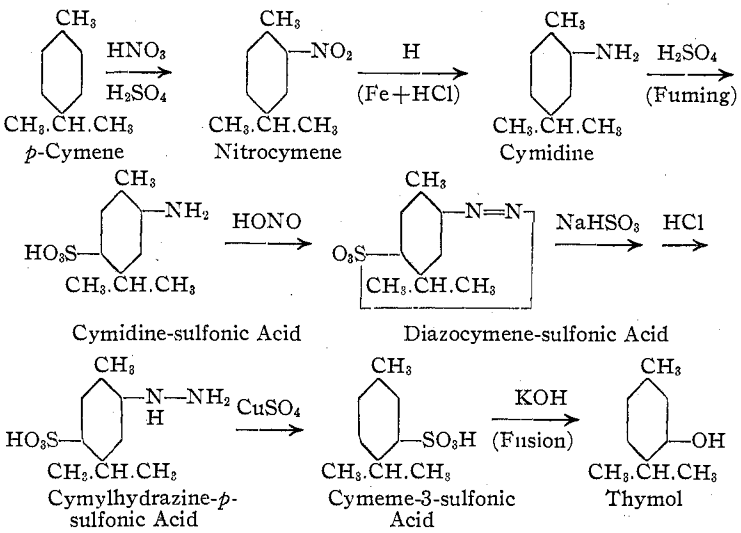
[1] *J. Ind. Eng. Chem.*, **12**, 733 (1920).

acid and then removing the diazo group with alcohol and copper powder, far better results were obtained by first converting the diazocymene-sulfonic acid into cymylhydrazine-*p*-sulfonic acid and subsequently removing the hydrazine group with boiling copper sulfate solution. The various steps involved in the synthesis may be represented as follows:



Experimental Part

Preparation of Nitrocymene.—The nitrocymene used in all of this work was prepared from *p*-cymene, obtained from so-called sulfite turpentine, following the method of nitration fully described in a previous article.[2]

Reduction of Nitrocymene to Cymidine.—One and six-tenths kg. of iron powder and 1.5 liters of boiling water were placed in an 8-liter flask, provided with an inverted condenser. After the addition of 100 cc. of conc. hydrochloric acid, 1 kg. of nitrocymene was added slowly while the mixture was shaken. The addition of nitrocymene was so regulated that the reaction mixture boiled quietly. Whenever the reaction became too violent, it was moderated by cooling the flask with water. When the reaction was finished (shown by no further rise in temperature as the material was shaken) the mixture was made alkaline with sodium hydroxide, and distilled in a current of steam. The cymidine, which is lighter than water, was separated. The product thus obtained was slightly contaminated with nitrocymene and other non-basic impurities. Although these do not seriously interfere with the preparation of the next intermediate, nevertheless, it seemed desirable to remove them. Therefore, the crude cymidine was dissolved in an excess of dil. sulfuric acid, and distilled in a current of steam until the non-basic impurities were completely removed. The residue was made alkaline with sodium hydroxide and the cymidine distilled in a current of steam. The product was dried over solid potassium hydroxide and used directly for the preparation of cymidine-sulfonic acid. In some of the experiments, however, no effort was made to obtain the free base.

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[2] This Journal, **44,** 1775 (1922).

but the residue from the steam distillation of the acid solution was concentrated on the steam-bath, the cymidine sulfate collected on a filter, dried at 110° and used as such for the preparation of cymidine-sulfonic acid. The yield of cymidine varied from 80 to 85% of that calculated.

Cymidine-sulfonic Acid.—One part by weight of cymidine was treated with the calculated amount of sulfuric acid (d., 1.84) required for its conversion to cymidine acid sulfate, and to this 2 parts of fuming sulfuric acid (20% oleum) were added. The addition of the oleum and cooling of the reaction mixture were so regulated that the temperature did not exceed 140°. The sulfonation mixture was then placed in an oil-bath and heated to 130–140° with the thermometer in the reaction mixture. The sulfonation was usually complete in from $^1/_2$ to $^3/_4$ hour. The end of the reaction was determined by diluting a small sample with water and making alkaline with sodium hydroxide solution. If no cymidine separated the sulfonation was considered complete. The reaction product was then cooled and poured into thrice its volume of ice water. The cymidine-sulfonic acid separated as a grayish crystalline mass. After standing for about 2 hours it was collected and purified by dissolving it in a slight excess of 20% solution of sodium hydroxide; this alkaline solution was boiled with animal charcoal, and finally the cymidine-sulfonic acid was precipitated with an excess of sulfuric acid. A white crystalline product was obtained. It was collected on a filter and dried at 120°. The yield was 80% of that calculated.

Cymylhydrazine-*p*-sulfonic Acid.—One mole (229 g.) of cymidine-sulfonic acid was suspended in 1 liter of water, and sodium hydroxide solution was added in slight excess. The mixture was heated to dissolve the sulfonic acid. The calculated amount of sodium nitrite (1 mole) was added in the form of a 20% solution which had previously been standardized against 0.1 *N* permanganate solution and the solution cooled to 0°. This mixture was then added slowly from a dropping funnel to a cold (0°) dil. sulfuric acid solution containing 150 g. of sulfuric acid (d., 1.84) in 1000 cc. of water. The solution was well stirred and the temperature throughout the diazotization maintained at 0° to + 5°. The diazocymene-sulfonic acid that separated was collected and added to a cold (0° to +5°) sodium bisulfite solution made by dissolving 300 g. of sodium sulfite in 3 liters of water and saturating this solution with sulfur dioxide. The orange-colored solution was allowed to stand for 1 hour at room temperature. It was then heated to boiling, 500 cc. of hydrochloric acid (d., 1.19) was added, and the solution concentrated on the steam-bath until crystallization of the cymylhydrazine-*p*-sulfonic acid began. This compound was removed and dried at 110°; yield, 70–75%.

Analyses. Subs., 0.2072, 0.2111: CO_2, 0.3714, 0.3794; H_2O, 0.1240, 0.1301. Subs., 0.1571, 0.1576: $BaSO_4$, 0.1500, 0.1576. Subs., 0.2116, 0.2478: 21.9 cc. of N_2 (27°, 767.2 mm.), 25.8 cc. (31°, 761.5 mm.). Calc. for $C_{10}H_{16}O_3N_2S$: C, 49.14; H, 6.60; N, 11.47; S, 13.12. Found: C, 48.89, 49.01; H, 6.69, 6.89; N, 11.64, 11.46; S, 13.15, 13.29.

Cymylhydrazine-*p*-sulfonic acid is soluble in water but insoluble in alcohol or ether. It melts with decomposition at 260°.

The *barium salt* was prepared by boiling an aqueous solution of the acid with barium carbonate. It separated in the form of light yellow plates.

Analyses. Subs., 0.6664, 0.6562: loss at 120° 0.0837, 0.0820. Calc. for $(C_{10}H_{15}N_2SO_3)_2Ba + 5H_2O$: H_2O, 12.61. Found: 12.56, 12.49.

Subs., anhyd., 0.3034, 0.3215: $BaSO_4$, 0.1126, 0.1195. Calc. for $(C_{10}H_{15}N_2SO_3)_2Ba$: Ba, 22.01. Found: 21.84, 21.87.

Sodium Cymene-sulfonate.—One mole (244 g.) of cymylhydrazine-*p*-sulfonic acid was dissolved in hot water and added in small portions to a boiling 10% solution of copper sulfate. With each addition of the cymylhydrazine-*p*-sulfonic acid a rapid evolution of nitrogen took place. Throughout the reaction an excess of copper sulfate was maintained, as determined by the color of the solution. When no more nitrogen was given off, the copper oxide was removed by filtration and the filtrate treated with a slight excess of barium hydroxide solution. The barium sulfate and copper hydroxide were collected on a filter and the filtrate freed from the excess of barium hydroxide with carbon dioxide. The barium carbonate was separated and the filtrate treated with sodium carbonate solution until all the barium was precipitated as barium carbonate. The latter was removed by filtration and the filtrate evaporated to dryness on the steam bath. The material was dried at 140°; yield 79%.

To determine whether or not the sodium cymene-sulfonate thus obtained was free from the other isomer (the sodium salt of cymene-2-sulfonic acid, $CH_3 = 1$), a portion of it was converted into the sulfamide, the latter subjected to a fractional crystallization and the melting point of each fraction determined. In every case the melting point of the sulfamide was found to be 149.9° (corr.) which is the melting point of the sulfamide of cymene-3-sulfonic acid ($CH_3 = 1$). There was no indication of the presence of the other isomer.

Alkali Fusion of Sodium Cymene-sulfonate to Form Thymol.—The fusion apparatus in which all of the following experiments were performed consisted of a small iron pot, of about 500cc. capacity, provided with a cover and stirring device. It was heated in a bath consisting of a eutectic mixture of sodium and potassium nitrates. The whole apparatus was well insulated so that any desired temperature could be maintained constant to within 2–3°. The yield was determined by dissolving the cold alkaline melt in water, acidifying it with dil. sulfuric acid and extracting the solution with ether. The ether solution was dried over anhydrous sodium sulfate, the ether removed by distillation and the residue fractionated.

TABLE I

YIELDS OF THYMOL OBTAINED BY THE FUSION OF SODIUM CYMENE-SULFONATE WITH ALKALI UNDER VARIOUS CONDITIONS

Temp. °C.	Pts. of alkali to 1 pt. of sulfonate	Time Hours	Yield %
320	3[a]	1/2	53.7
290	3[a]	1/2	44.7
270	3[a]	1/2	14.3
350	3[a]	1/2	59.0
350	3[a]	3	51.2
350	3[a]	1	47.9
350	2[a]	1/2	57.7
350	2[a]	2	48.7
350	2[a]	1/4	54.3
350	3[b]	1/2	15.4
320	3[b]	1/2	11.1
350	3[b]	3	9.5
350	1 KOH 1 NaOH	1/2	43.8
350	1 NaOH 2 KOH	1/2	50.1

[a] Potassium hydroxide used.

[b] Sodium hydroxide used.

The thymol fraction was collected in a weighed receiver and the weight of thymol determined. The preceding table shows the results obtained.

It is to be noted from the table that potassium hydroxide is far superior to sodium hydroxide with respect to the yield of thymol. The best yield was obtained using 3 parts of potassium hydroxide to 1 part of sulfonate at 350° with a fusion period of 1/2 hour. However, considering the experimental error, practically the same yield was obtained using only 2 parts of potassium hydroxide. By using mixtures of the two hydroxides better yields were obtained than with sodium hydroxide alone, the yield increasing with the proportion of potassium hydroxide in the mixture.

The synthetic thymol obtained when seeded with a small crystal of natural thymol solidified completely. It was identified by its phenylurethane derivative (m. p., 107°) and its formation of trinitrothymol (m. p., 109°).

Summary

An improved method is described for the synthesis of thymol from *p*-cymene. The yields obtained in the various steps of the process indicate the possibility of utilizing *p*-cymene, the main constituent of so-called sulfite turpentine, as a source for synthetic thymol.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 33]

THE DETERMINATION OF FORMALDEHYDE IN PARAFORMALDEHYDE[1]

BY P. BORGSTROM AND W. G. HORSCH

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The object of this paper is to present the results of a study of certain methods for the determination of formaldehyde in paraformaldehyde. Of the many methods available[2] for the determination of formaldehyde the following will be considered: (1) fixed alkali, (2) iodimetric, (3) peroxide, (4) neutral sulfite, (5) oxidation with permanganate or dichromate in an acid solution and weighing the carbon dioxide produced.

Delepine[3] gives the formula of paraformaldehyde as $(CH_2O)n.H_2O$ showing water as the only impurity. To obtain a standard of composition, a sample of paraformaldehyde was analyzed in the Liebig combustion furnace. In two determinations the carbon dioxide absorbed gave by calculation 96.80 and 96.73 (mean, 96.77%). The water absorbed was very close to 3.23%.

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[1] This work was financed by the National Electrolytic Company and is published with their kind permission.

[2] Lockeman and Corner, *Z. anal. Chem.*, **54**, 11 (1915).

[3] Delepine, *Bull. soc. chim.*, [3] **17**, 849 (1897).