

TABLE OF AQUEOUS AND OILY DISTILLATES OF TWIGS (BALES 3 AND 4=174<sup>1</sup>/<sub>2</sub> LBS.).

	Water, gals.	Wt. of oil, Gm.
Original distillate.....	64 <sup>1</sup> / <sub>2</sub>	275.2=0.34 p. c.
After 1st cohobation.....	26 <sup>1</sup> / <sub>2</sub>	384.9=0.52 p. c.
After 2nd cohobation.....	12 <sup>1</sup> / <sub>2</sub>	
After 3rd cohobation.....	6 <sup>1</sup> / <sub>2</sub>	
After 4th cohobation.....	2 <sup>1</sup> / <sub>2</sub>	
After 5th cohobation.....	1 <sup>1</sup> / <sub>2</sub>	
After 6th cohobation.....	1 <sup>1</sup> / <sub>3</sub>	55.7
Total.....		715.8=0.90 + p. c.

Whereas 288 lbs. of leaves yielded a total of 658 Gm. or 0.52 p. c. of oil, 174<sup>1</sup>/<sub>2</sub> lbs. of twigs yielded 715.8 Gm. of oil or 0.90 + p. c.

The densities of the leaf oils determined at 22° are herewith tabulated for comparison.

	Original oil.	Oil from Cohobations 1, 2 and 3.	Oil from Cohobations, 4, 5, 6, and 7.
Bale No. 1.....		{ 1.0547 1.0530 }	
Bale No. 5.....	1.0525	1.0540	1.0514
Bale No. 2.....	1.0523	1.0535	
The corresponding data for the twig oils:			
Charge No. 1.....	1.0400	1.0477	1.0473
Charge No. 2.....	1.0420	1.0477	
Charge No. 3.....	1.0393	1.0465	
Charge No. 4.....		.....	

Schimmel & Co.<sup>1</sup> record that the leaves (incl. stalks) and young twigs yielded 0.77 p. c. of an oil the specific gravity of which (apparently at 15°) was 1.055. (Aldehyde content 93 p. c.)

According to the results here recorded, the leaves yielded a total oil of 0.52 p. c. with a density of about 1.054 at 22°, whereas the twigs yielded a total of 0.90 p. c. of oil with a density of about 1.047. It will be seen that the twigs yielded a somewhat larger amount of oil with a slightly lower density than the leaves. The ratio in which leaves and twigs occur on the Cassia shrub does not seem to have been recorded.

## CONTRIBUTIONS TO THE KNOWLEDGE OF FOREST PRODUCTS.

### V. ON NITRO-2, AND AMINO-2 CYMENE.\*

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As has been emphasized in the preceding article, the study of cymene and its derivatives forms a unit in the scheme for the development of a more comprehensive policy of forest utilization. This and the succeeding paper are therefore continuations of the effort to shed more light on the chemistry of cymene.

One way of attacking the general problem involved in these researches is to reason by analogy. The idea is not new that cymene can be nitrated, the nitro-compound reduced to an amino-compound, and the latter in turn involved in

\* Based on part of a thesis presented by W. A. D. to the Graduate Faculty of Vanderbilt University in partial fulfilment of the requirements for the Degree of Master of Science, June 1922.

characteristic reactions, just as in the case of benzene. It has already led to many experiments.<sup>1</sup> It is only recently, however, that amino-2 cymene has been readily available for synthetic purposes.<sup>2</sup> One of the many possibilities suggested by the behavior of aniline, but so far not studied, is the preparation of cymylhydrazine. This very reactive compound would in its turn lead to many other substances. It was with the object of preparing this hydrazine derivative that the experiments here recorded were made. The writers feel that their experiences in learning how to produce amino-2 cymene in sufficient quantity for synthetic purposes may be of some service to others. We began by following the directions of Andrews.

*Purification of p-Cymene.*—Technical cymene procured from the Eastman Kodak Co. was purified by shaking with concentrated sulphuric acid until fresh acid scarcely darkened in contact with the hydrocarbon. The latter was then given a final washing with water, dried over anhydrous sodium sulphate, and distilled through a column. From 907 grams there were obtained 805 grams of cymene which had the following constants:

B.  $p_{769} = 173-4^{\circ} \text{C.}$ ;  $d_{20} = 0.8540$ ;  $n_{20} = 1.4872$ ;  $\alpha = \pm 0.00^{\circ}$ .

This material was used in part of the nitrations. By this process of purification some sulphonation occurs, as cymene sulphonic acid was later separated in crystalline form from the acid residues.

Run.	H <sub>2</sub> SO <sub>4</sub> , <sup>1</sup>	HNO <sub>3</sub> .	Gas.	Crystal.	Temp.	Cymene, <sup>2</sup> Gm.	Nitro, <sup>3</sup> Gm.	P. c. yield.
1	1.82	1.42	+	—	-5 to 0°	25.0	..	..
2	1.82	1.42	+	—	-5 to 0°	35.5	10.0	19.1 <sup>4</sup>
3	1.84	1.42	+	—	-5 to 0°	67.0	25.0	27.7
4	1.90	1.42	+	—	-5 to 0°	67.0	8.0	8.8
5	1.84	1.42	+	—	0 to 10°	67.0	..	.. <sup>5</sup>
6	1.84	1.42	+	+	-5 to 0°	67.0	26.0	28.5
7	1.84	1.42	+	+	-5 to 0°	67.0	28.0	31.0
8	1.82	1.42	+	—	-5 to 0°	67.0	15.0	19.0
9	1.82	1.42	+	—	0 to 5°	67.0	22.0	24.4
10	1.82	1.42	+	—	-5 to 0°	67.0	27.5	30.3 <sup>6</sup>
11	1.82	1.42	+	—	0 to 5°	67.0	30.5	34.0
12	1.84	1.42	—	+	-5 to 0°	67.0	35.0	37.5
13	1.84	1.42	—	—	0 to 5°	67.0	38.0	41.5
14	1.83	1.42	—	+	-5 to 0°	67.0	45.5	50.5
15	1.83	1.42	—	—	0 to 5°	67.0	47.5	52.5
16	1.83	1.42	—	—	0 to 3°	67.0	54.5	60.4
17	1.83	1.42	—	—	0 to 3°	67.0	58.7	65.2

<sup>1</sup> Densities were determined by a Mohr-Westphal balance at room temperature, approximately 23° C.

<sup>2</sup> Purified cymene was used in runs 1-9, incl., and in 11-15 incl. Technical cymene was used in all other nitrations.

<sup>3</sup> The weight of nitrocymene given corresponds to that of the steam distilled oil heavier than water.

<sup>4</sup> 0.5 gram of urea was added to No. 2.

<sup>5</sup> The mixed acids were added from an ice packed burette.

<sup>6</sup> An electric stirrer was used in Runs 10-17, incl.

<sup>1</sup> See preceding for bibliography of various lines of endeavor, p. 224, March Jour. A. Ph. A.

<sup>2</sup> Andrews, *Jour. Ind. Eng. Chem.*, 10, 453, 1918.

*Nitration of p-Cymene.*—In the first attempt at nitration Andrews' directions were followed as literally as possible. The reaction ended with a copious evolution of oxides of nitrogen, a flat failure. According to our information, others have had a similar experience. In the belief that the adjustment of some factor or factors was not quite accurately reproduceable from the original directions, we modified conditions slightly in various ways. The concentrations of the acids, the temperature, the efficiency of the agitation, were all varied; technical cymene was used in place of highly purified, and urea was added in one instance in hope of arresting the oxidative effect of nitrous oxide. A tabulation of the results is given in the preceding table.

The final working conditions which gave the best results, Run 17, were as follows:

Sixty-seven grams of sulphuric acid ( $d = 1.83$ ) was introduced into a heavy porcelain beaker that had been packed in ice. An electrically driven stirrer was started in the acid and 67 grams of cymene were gradually added. When the temperature of the mixture had fallen to  $0^{\circ}\text{C}$ ., a well cooled solution of 50 Gm. nitric acid ( $d = 1.42$ ) and 105 Gm. sulphuric acid ( $d = 1.83$ ) was added drop by drop from a burette at such a rate that the nitration temperature ranged between 0 and  $+3^{\circ}\text{C}$ . At the same time a little salt was added to the ice to produce more efficient cooling. The addition of the mixed acid required about 6 hours. The reaction proceeded very smoothly under these conditions; towards the end the product became reddish brown in color and quite viscous. Stirring was continued 30 minutes after the last of the nitrating acids had been added.

The reaction product was then poured into an equal volume of cold water. The supernatant oil was separated by a funnel and twice washed with water. It was next fractionated by steam distillation into a fraction lighter than water (7 Gm.) and a fraction heavier than water (58.7 Gm.). The former was light yellow in color, the latter was darker and more strongly aromatic.

The crude nitrocymene was dried over anhydrous calcium chloride and was finally purified in larger quantities by distillation *in vacuo*. The constants of the pure product were:

$$B. p_{14} = 130-35^{\circ}\text{C}.; d_{23} = 1.0355; n_{23} = 1.5290.$$

In a summary of our experiences it may be said:

1. That difficulty was encountered in trying to follow Andrews' directions, but that with suitable minor modifications they have proven satisfactory.
2. That sulphuric acid of a density 1.83 and a temperature range of 0 to  $+3^{\circ}\text{C}$ . are more favorable than the conditions originally specified.
3. That we have confirmed the statement of Wheeler and Smithey regarding the necessity of very efficient agitation.<sup>1</sup>
4. That so far it has not been possible for us to attain an 85 per cent. yield of actual nitrocymene.
5. That contrary to Andrews' statement, it was desirable to purify the steam distilled nitrocymene by a further fractionation *in vacuo*. The resultant product not only kept better, but also gave better results on reduction.

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<sup>1</sup> *Jour. Am. Chem. Soc.*, 43, 2611, 1921. This part of our research had been practically completed before their paper appeared.

6. That "technical" cymene appeared to give less trouble during nitration in the way of temperature control and gas formation than a carefully purified hydrocarbon.

*The "Nitration Crystals."*—During the nitration of p-cymene it is not an uncommon occurrence that colorless crystals separate in some quantity. Wheeler and Smithey ventured the opinion that they were composed of nitrocymene frozen out because of the low temperature. They furthermore state that they added acetic acid in order to prevent their separation. Our experiences, particularly our observation that crystal formation in quantity augured for a poor yield, led us to doubt this statement. Since we had already prepared sufficient nitrocymene for subsequent use, we contented ourselves with a few confirmatory observations.

In the first place our pure nitrocymene could not be induced by any means to crystallize at  $-12^{\circ}$  C., a lower temperature than any reached in the course of our nitrations. Secondly we prepared a quantity of crystals with a view to attempted isolation. For this purpose 15 Gm. of purified cymene were nitrated with the usual proportions of acids; the sulphuric acid employed had a density of 1.84 and the temperature of reaction was from  $-8$  to  $-5^{\circ}$  C. After three fourths of the nitrating acids had been added, a mass of crystals, apparently mono-clinic, separated. They were quickly separated by decantation and suction filtration; although readily obtainable in this way, they did not appear to be very stable and gradually shrunk and disappeared as they had a chance to warm up. When water at ordinary temperature was added to some crystals, they melted immediately with a slight evolution of nitrous oxide, but not enough to indicate that they were nitrosyl-sulphuric acid (chamber crystals). When ice water was added they did not melt at once, suggesting that they were not hydrated sulphuric acid. When the crystals were treated with enough water to dilute the solution, an oil separated, but the oil was only a fraction of the mass of the crystals. The oil was nitrocymene as proved by its odor, reduction to amino-cymene and the conversion of the latter into its hydrochloride. It therefore appears that the crystals are not nitrocymene. On the other hand our meager tests do not offer any positive suggestions. All in all, we are inclined to think that the crystals represent either an intermediate or an incidental product of nitration, and we feel that a better knowledge of them would contribute to an understanding of the process of nitration. We shall study this question as opportunity offers.

*Preparation of Amino-2 Cymene.*—The nitrocymene prepared as just described was then reduced to the corresponding amine. Two of the usual methods were employed. In the first, tin was the reducing agent. Forty-five grams of tin and 25 grams of nitrocymene were placed in a round bottom liter-flask fitted with an "adapter," which carried a dropping funnel and a reflux condenser. The mixture was heated to  $90^{\circ}$  on a water-bath and 85 cc of concentrated hydrochloric acid was then added at such a rate that the mixture boiled gently without further heating. The flask was shaken constantly. The reduction was finally completed by heating the mixture on the water-bath for an hour. The base was separated by steam distillation from the product made strongly alkaline with sodium hydroxide. The yield varied between 10 and 15 grams, the latter being 75 p. c. of the theoretical.

Profiting by our experiences in nitration, we decided to try mechanical agitation and abandoned this procedure after three runs in favor of iron powder which

we thought could be more easily stirred than granulated tin. Sixty grams of iron powder and 80 cc of hot water were introduced into a liter round bottom flask and the mouth closed with a two holed rubber stopper. Through one hole had been inserted a stirring rod and shaft, the other carried an "adapter" with dropping funnel and reflux condenser. After starting the electrically driven stirrer, a few drops of nitrocymene were introduced, then 5 cc of concentrated hydrochloric acid, and after that in all 50 grams of nitrocymene. The latter was added in the course of an hour at such a rate that the temperature remained at about 90° C. Toward the end of the reaction it was necessary to add 4 cc more of acid and to raise the temperature to about 100° C. The stirring and the heating were continued a half hour after the addition of the nitrocymene ended. The flask was then allowed to cool, its contents were made strongly alkaline with caustic soda, and the base was separated by steam distillation. The aminocymene was recovered from the aqueous distillate partly by mechanical separation and partly by ether extraction. The oil was dried over anhydrous sodium sulphate prior to purification.

This process worked so well that it was used for the production of the necessary amounts of aminocymene. The quantities for a run were increased in proportion to 75 grams of nitrocymene. The best result was a yield of 62 grams of crude base, corresponding to 99 p. c. of the theoretical.

The amino cymene was purified by fractionating *in vacuo*. In one instance 150 grams of oil were resolved into the following fractions:

Fraction.	B. p. 13 mm.	Weight, Gm.
1	80-100° C.	5
2	100-119°	35
3	119-124°	100
4	124-	10 approx.

Fraction 1 appeared to be cymene. Fraction 2 was mainly amino cymene as was proved by its conversion into the hydrochloride and removal of non-basic material by steam distillation. Fraction 3 was pure amino-2 cymene, having the constants:

$$d_{23} = 0.9448; \quad n_{23} = 1.5395.$$

The following values have been previously recorded for the compound:

$$\text{B. p.} = 118-21^\circ \text{ C.}; \quad d_{20} = 0.9442; \quad n_{20} = 1.5387.$$

Amino-2 cymene was further identified by conversion into two derivatives. The hydrochloride melted at 206-7° C., and the acetyl derivative at 70-1° C. Both compounds were purified by recrystallization from 5 p. c. alcohol.

To summarize, it was found that efficient stirring was helpful in the reduction of nitrocymene to aminocymene, and that iron powder as reducing agent gave excellent yields. It was also found necessary to purify the crude base by distillation *in vacuo*, both because the product kept better, and because the success of subsequent reactions depended upon the purity of the base.