Summary.

1. Methyl iodide interacts with the sodium salt of 2-*p*-nitrobenzyl-mercapto-4-methyl-6-oxypyrimidine to give first a nitrogen substituted derivative, which then interacts with another molecule of methyl iodide to form an addition product. The methyl group substitutes in the 1-position of the pyrimidine ring.

2. Ethyl bromide and allyl bromide interact with the mercapto-pyrimidine in a manner entirely different from that with methyl iodide. In both of these cases, an oxygen ether is formed, and no evidence was obtained of substitution of the alkyl groups on a nitrogen atom of the pyrimidine ring.

3. In the hydrolysis of 2-*p*-nitrobenzyl-mercapto-pyrimidines with acids, *p*-nitrobenzyl-mercaptan is formed melting at 57–58°. If, however, free iodine functions during hydrolysis, this mercaptan is destroyed and the disulfide, melting at 126.5°, is formed by oxidation.

4. The literature concerning *p*-nitrobenzyl-mercaptan is incorrect; in this paper the melting points of this compound, its disulfide and corresponding monosulfide are described correctly.

NEW HAVEN, CONNECTICUT.

PARA-CYMENE STUDIES. III. THE BROMINATION OF 2-AMINO-PARA-CYMENE.

BY ALVIN S. WHEELER AND IRA W. SMITHEY.[1]

The previous two papers dealing with *p*-cymene concerned (1) the production of toluene[2] by the action of aluminum chloride on a mixture of benzene and *p*-cymene and (2) *p*-cymene as a solvent.[3] This paper describes the action of bromine upon 2-amino-*p*-cymene and the preparation of certain derivatives of the monobromo-amino-cymene obtained. The research began with the isolation of cymene from spruce turpentine, a by-product in the manufacture of paper by the sulfite process. In addition to the steps given by one of us in the second paper of this series on the purification of *p*-cymene we find it necessary to shake out the cymene with a limited amount of conc. sulfuric acid. When this is not done the cymene, even though it be a fraction of narrow range in boiling point (176–178°), acquires a yellow color on standing, and fully satisfactory

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reactions such as nitration and bromination cannot be carried out with it. Cymene was nitrated by the method of Andrews,[4] modified by the Eastman Kodak Co., who introduce some glacial acetic acid to prevent the product from freezing out. The nitro-cymene was reduced with tin and hydrochloric acid. 2-Amino-*p*-cymene was prepared by Lloyd[5] who heated carvacrol at 350–360° with ammonium bromide and zinc ammonia bromide. Soderbaum and Widman[6] reduced nitrocymene with tin and hydrochloric acid. Goldschmidt[7] treated *iso*carvoxime dissolved in alcohol with zinc dust and acetic acid. Semmler[8] mixed boiling alcoholic solutions of tanaceton-acetoxime and sulfuric acid. Wallach and Schrader[9] heated at 235° carvoxime with conc. aqueous potash. Wallach and Neumann[10] heated *iso*carvoxime with potash at 235°. The method for quantity production is the reduction of nitro-cymene, now that cymene is available in large amounts.

The acetyl derivative of amino-cymene which melts at 71° is smoothly brominated in carbon tetrachloride solution and less satisfactorily in glacial acetic acid solution. Hydrolysis of the brominated product is best effected with conc. hydrochloric acid. The monobromo-aminocymene thus obtained is a liquid boiling at 169–170° at 20 mm. Its hydrochloride and hydrobromide were prepared.

Considerable effort was made to locate the position of the bromine atom. It did not enter any of the side chains for the product does not possess any properties characteristic of such compounds. The problem was therefore to determine whether it is in Position 3,5 or 6. The acetyl derivative was oxidized with neutral permanganate and analysis indicated the oxidation of the *iso*propyl group to a carboxyl, forming therefore an acetylamino-bromotoluic acid. Hydrolysis gave the hydrochloride of the amino acid and its analysis indicated two acid hydrogens. Finally analysis of the free amino acid agreed with that calculated for a toluic acid. It happens that only one amino-bromotoluic acid is known, the one with bromine at Position 5, melting at 186–187°; whereas our acid melts at 151°. Since an *ortho* compound is far more likely to be formed than a *meta*, we have placed the bromine atoms provisionally at Position 3 and not at 6. We had expected to find it at Position 5. A fuller discussion is reserved for a special part preceding the summary.

Diazo derivatives of amino-bromocymene were prepared by combining it (1) with itself, (2) with aniline and (3) with *p*-nitro-aniline in two

[4] Andrews, *J. Ind. Eng. Chem.*, **10**, 453 (1918).

[5] Lloyd, *Ber.*, **20**, 1262 (1887).

[6] Soderbaum and Widman, *ibid.*, **21**, 2127 (1888).

[7] Goldschmidt, *ibid.*, **26**, 2086 (1893).

[8] Semmler, *ibid.*, **25**, 3352 (1892).

[9] Wallach and Schrader, *Ann.*, **279**, 374 (1894).

[10] Wallach and Neumann, *Ber.*, **28**, 1660 (1895).

ways, (*a*) by diazotizing the amino-bromocymene and (*b*) by diazotizing the *p*-nitro-aniline.   The azo derivatives of *p*-nitro-aniline are yellow and dissolve in alkaline solutions, with the formation of a rich magenta color which disappears on acidification.   This marked color change indicates a change of structure and is well explained by a shifting of the hydrogen of the imino group to the nitro group, forming a pseudo acid, the alkaline salt having the group: NOONa.   Thus: $C_3H_7CH_3BrC_6H_2N:NNHC_6H_4NO_2$ $\longrightarrow C_3H_7CH_3BrC_6H_2N:NN:C_6H_4NOONa$.   Meldola[11] noticed the same color change with *p*-dinitro-diazo-amino-benzene but he believed that the sodium atom merely replaced the hydrogen of the imino group. Hewitt and Mitchell[12] proposed the better explanation of a pseudo or nitronic acid where the hydrogen of the imino group wanders to the *para* nitro group.   A similar change of structure may be assumed in Grand-mougin and Leeman's[13] hexanitro-hydrazo-benzene, the dipotassium salt giving a blue solution.

Experimental Part.

Nitration of *p*-cymene.—The method of Andrews was followed, but some modifications were necessary to obtain good yields.   The nitration mixture was placed in an iron kettle of about 12 liters capacity, with a wooden lid provided with holes for stirrer, funnel and thermometer.   The kettle was surrounded by ice and salt in a wooden tub of 40 liters capacity.   An 18 cm. iron stirrer running at 200–250 r. p. m. was used to agitate the mixture.   Two kg. of cymene was nitrated at one time.   2010 g. of cymene, b. p. 176–177°, was added slowly with stirring to 2010 g. of conc. sulfuric acid cooled to 0° or below with ice and salt.   The mixture was well stirred to insure the formation of a good emulsion.   Andrews calls it a solution but this is impossible, for in our experience it requires a week to dissolve cymene in sulfuric acid and then it is undoubtedly sulfonated.   To the ice-cold emulsion a mixture of 1500 g. of conc. nitric acid and 3150 g. of conc. sulfuric acid was added from a dropping funnel at the rate of two drops a second, provided cooling by the freezing mixture was efficient. In order to prevent the freezing out of nitrocymene 300 cc. of glacial acetic acid was added to the cymene-acid mixture at the beginning.   The operation of nitration required 15 hours.   Stirring was continued for 30 minutes after the last of the acid had been added.   The product was poured into 6 liters of water containing ice to keep the temperature below 10°.   After thorough stirring the nitro-cymene collected on the surface as a red oil.   It was separated, washed with water, very dilute sodium hydroxide (conc. alkali causes a troublesome emulsion), and again with water.   It was dried with calcium chloride and distilled.   The fraction boiling at 148–162° at 35 mm. represented a fairly pure nitro-cymene.   Wheeler and Smith are now engaged in preparing a purer nitro-cymene by preliminary treatment with a small amount of bromine.

Reduction of Nitro-cymene.—Nitro-cymene was reduced with tin and hydrochloric acid, the process being the same as that used for nitrobenzene.   Instead, however, of distilling the alkaline solution with steam, it was found better to add enough sodium hydroxide nearly to dissolve the tin salt and extract with benzene.   After drying the solution with solid sodium hydroxide, the benzene was distilled.   350 g.

[11] Meldola, *J. Chem. Soc.*, **49**, 626 (1886).

[12] Hewitt and Mitchell, *J. Chem. Soc.*, **91**, 1254 (1907).

[13] Grandmougin and Leeman, *Ber.*, **49**, 4384 (1906).

of nitro-cymene gave 260 g. of amino-cymene, the calculated yield being 290 g. A fraction boiling a little below and above 240° was used for acetylation with acetic anhydride. The pure acetyl derivative melted at 71°.

2-Acetylamino-3-bromo-*p*-cymene, $C_6H_2CH_3NHCOCH_3BrC_3H_7.$ — One mol. of acetylamino-cymene was dissolved in 5 parts of carbon tetrachloride and treated with one mol. of bromine. The temperature rose to 50–60° and considerable hydrogen bromide escaped. When the reaction had proceeded for a short time, a mass of white crystals separated from the solution, forming a seemingly solid mass. These crystals were filtered off and recrystallized from alcohol, forming needles which melted at 122.5°. The yield was practically quantitative. Bromo-acetylamino-cymene is soluble in ether, alcohol, benzene and acetic acid and insoluble in water. Glacial acetic acid may also be used as a solvent for the reaction but unless the temperature is kept down, some bromine will enter the side chains forming compounds which attack the eyes.

Analyses. Subs., 0.1818, 0.2614: AgBr, 0.1250, 0.1805. Calc. for $C_{12}H_{16}ONBr(270)$: Br, 29.62. Found: 29.26, 29.38.

A sample of crude acetylamino-cymene in carbon tetrachloride was boiled with bromine. A small quantity of greenish material separated from solution. It was recrystallized from alcohol and obtained in golden-yellow leaflets which melted at 188°.

2-Amino-3-bromo-*p*-cymene Hydrochloride, $C_6H_2CH_3NH_2(HCl)BrC_3H_7.$ — The acetyl derivative above was so little affected by boiling alcoholic potash even after 6 hours, that hydrolysis was effected by boiling with conc. hydrochloric acid for 1 hour. The action could be hastened by decanting at intervals from the undissolved portion, cooling, filtering off the hydrochloride and returning the acid to the flask. The hydrochloride is almost completely insoluble in cold hydrochloric acid, moderately soluble in ether and very soluble in acetone and acetic acid. It dissolves readily in cold water but is hydrolyzed by hot water. It crystallizes from alcohol in silvery hexagonal plates which melt at 205–210° with decomposition.

Analyses. Subs., 0.2301, 0.2106: AgCl, 0.1306, 0.1176. Calc. for $C_{10}H_{14}NBr.$ HCl (264.5): Cl, 13.41. Found: 14.04, 13.81.
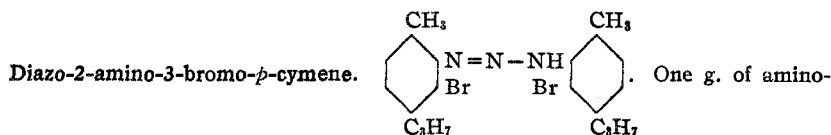
2-Amino-3-bromo-*p*-cymene Hydrobromide, $C_6H_2CH_3NH_2(HBr)BrC_3H_7.$—Pure amino-bromo-cymene was treated with strong hydrobromic acid. A mass of crystals formed instantly. On recrystallizing from alcohol brilliant octagonal plates were obtained which melted at 200–205° with decomposition. This salt is hydrolyzed even by cold water. It is fairly soluble in ether, benzene and acetone.

Analyses. Subs., 0.4333, 0.5221: AgBr, 0.2653, 0.3199. Calc. for $C_{10}H_{14}$-NBr.HBr (309): Br, 25.88. Found: 26.04, 26.07.

2-Amino-3-bromo-*p*-cymene, $C_6H_2CH_3NH_2Br.C_3H_7.$—Pure amino-bromo-cymene hydrochloride is hydrolyzed with 20% sodium hydroxide and the free amine is distilled with steam. A colorless oil appeared in the upper part of the condenser but it rapidly assumed a yellowish color, being distinctly colored when it dropped from the condenser. The aqueous distillate was saturated with salt and extracted with ether. The ether solution was dried with sticks of sodium hydroxide and the ether was distilled. Pure amino-bromo-cymene was driven over at 169–170° under a pressure of 20 mm. It is a colorless oil at first but soon becomes yellow and after some time red like aniline. It is very soluble in ether, alcohol and acids and insoluble in water. Its specific gravity, determined by the pycnometer method at 21°, is 1.30125. Its refractive index, determined with an Abbe refractometer at 20°, is 1.5781.
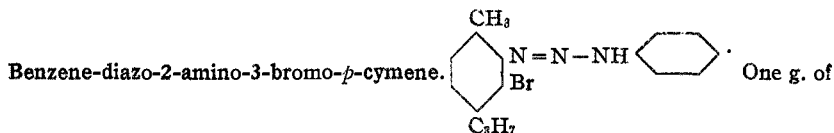
Analysis. Subs., 0.2432: AgBr, 0.2005. Calc. for $C_{10}H_{14}NBr$ (228): Br, 35.04. Found: 35.08.

Diazo Derivatives.

Diazo-2-amino-3-bromo-*p*-cymene.

$$\text{CH}_3 \quad \text{N}=\text{N}-\text{NH} \quad \text{CH}_3$$
$$\underset{\text{C}_3\text{H}_7}{\bigcirc} \overset{}{\underset{\text{Br}}{}} \quad \overset{}{\underset{\text{Br}}{}} \underset{\text{C}_3\text{H}_7}{\bigcirc}$$

One g. of amino-bromo-cymene in 10 cc. of water containing 1.5 cc. of conc. hydrochloric acid, cooled to 0°, was treated with 0.4 g. of sodium nitrite in 5 cc. of water. To this solution was added 1 g. of the amine in 5 cc. of water containing 0.5 cc. of conc. hydrochloric acid. The yellow precipitate which formed was more completely precipitated by the addition of 5 g. of sodium acetate dissolved in 5 cc. of water. The product was recrystallized from petroleum ether from which it separated in yellow prismatic needles which melted at 143–146° with decomposition. Yield, 80%. It is slowly soluble in cold ether, glacial acetic acid, benzene and carbon tetrachloride. It is almost insoluble in cold alcohol.

Analysis. Subs., 0.1193: AgBr, 0.0966. Calc. for $C_{20}H_{25}N_3Br_2$ (467): Br, 34.26. Found: 34.45.

Benzene-diazo-2-amino-3-bromo-*p*-cymene.

$$\underset{\text{C}_3\text{H}_7}{\overset{\text{CH}_3}{\bigcirc}} \overset{\text{N}=\text{N}-\text{NH}}{\underset{\text{Br}}{}} \bigcirc$$

One g. of amino-bromo-cymene was treated with 10 cc. of water containing 1.5 g. of conc. hydrochloric acid. The mixture was cooled to 0° and a slight excess of sodium nitrite solution was added. Some of the amine salt still remained undissolved. It was stirred for 15 minutes and then a solution of aniline hydrochloride was added. An orange-red precipitate was formed, the precipitation being furthered by the addition of 5 g. of sodium acetate in 5 cc. of water. The salt which separated was very soluble in hot alcohol, benzene and glacial acetic acid, and was best recrystallized from petroleum ether, from which it formed yellow needles melting at 161–162° with decomposition. The salt was hydrolyzed with dil. sodium hydroxide solution. The free amine crystallized in the form of flat yellow needles which melt at 152–154° with decomposition.

*Analysis.* Subs., 0.0960: AgBr, 0.0538. Calc. for $C_{16}H_{18}N_3Br$: Br, 24.09. Found: 23.85.

p-Nitrobenzene-diazo-2-amino-3-bromo-*p*-cymene. 0.96 g. of amino-bromo-

$$\underset{\text{C}_3\text{H}_7}{\overset{\text{CH}_3}{\bigcirc}} \overset{-\text{N}=\text{N}-\text{NH}}{\underset{\text{Br}}{}} \bigcirc \text{NO}_2$$
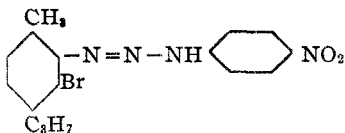
cymene hydrochloride was dissolved in 2 cc. of conc. hydrochloric acid and 2 cc. of water. On dilution to 40 cc. much of the salt crystallized. The mixture was cooled to 10° and 0.28 g. of sodium nitrite in 5 cc. of water was added all at once and the mixture stirred for 30 minutes. Five-tenths g. of *p*-nitro-aniline was dissolved in 2 cc. of conc. hydrochloric acid and 2 cc. of water, and diluted to 40 cc. The two solutions were mixed and stirred for 30 minutes. The solution was filtered from slight impurities and treated with sodium acetate, whereupon a yellow precipitate was formed. The diazo compound was recrystallized from alcohol and obtained in the form of bright yellow needles which melted at 158° with blackening.

Analysis. Subs., 0.0450: AgBr, 0.0228. Calc. for $C_{16}H_{17}O_2N_4Br$: Br, 21.22. Found: 21.56.

This bright yellow compound dissolves in ammonium or sodium hydroxide to form a solution with a rich magenta color, and the color disappears on neutralizing or acidifying the solution. If the neutral colorless solution is warmed, the magenta color comes back, though it is then of less intensity. If the solution is cooled with ice the color disappears again. As suggested in the theoretical part of this paper, the marked change of color must be due to a change of structure, the best supposition being that the salt of a pseudo or nitronic acid has been formed.

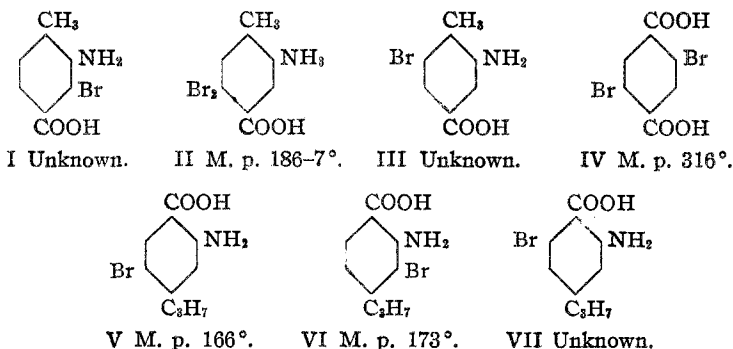$C_3H_7CH_3BrC_6H_2N:N.NHC_6H_4NO_2 \longrightarrow C_3H_7CH_3C_6H_2N:N.N : C_6H_4NO.ONa.$
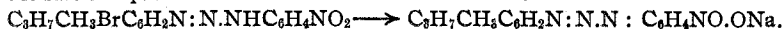
On reversing the process by diazotizing the *p*-nitro-aniline an orange colored precipitate was obtained which was purified by recrystallizing from alcohol. The purified product consisted of orange-red needles with a steel-blue fluorescence, melting at 163° with decomposition. It is soluble in alcohol and benzene. It is soluble in conc. hydrochloric acid and does not readily dissolve in cold aqueous sodium hydroxide. The alkaline solution has a magenta-red color like the other nitro derivative. An analysis could not be made on account of lack of material. We believe that in this compound the azo and imino groups have exchanged places: $C_3H_7CH_3BrC_6H_2NH.N : NC_6H_4NO_2.$

Orientation of the Bromine Atom.

It seems well established that the amino-*p*-cymene is 2-amino-*p*-cymene. Bromination of its acetyl derivative in the cold introduces one bromine atom. It may occupy any one of 7 positions, 3 of which are in the nucleus and 4 in the side chains, *i. e.*, in the methyl, in the amino and 2 places in the *iso*-propyl group. Positions in the side chains are ruled out on account of the fact that the reaction is carried out at a moderate temperature thus indicating entrance into the nucleus and also since the product has no characteristics of the benzyl bromide type. Again, the side chains may be removed or converted into other radicals while the bromine atom remains unaffected.

The question therefore is whether the bromine is at Position 3, 5 or 6. The best hope of locating it seemed to lie in oxidizing the substance to a toluic acid. Oxidation might however produce a cuminic acid or a terephthalic acid. Of the three possible toluic acids, Formulas I, II and III, only II is known. Only one bromo-terephthalic acid having any bearing on the question is known, the 2,6-dibromo derivative, Formula IV. Two of the three possible cuminic acids, Formulas V, VI and VII, are known, those represented by Formulas V and VI.

CH₃ / NH₂ / Br / COOH — I Unknown. CH₃ / NH₃ / Br₂ / COOH — II M. p. 186–7°. CH₃ / Br / NH₂ / COOH — III Unknown. COOH / Br / Br / COOH — IV M. p. 316°.

COOH / NH₂ / Br / C₃H₇ — V M. p. 166°. COOH / NH₂ / Br / C₃H₇ — VI M. p. 173°. COOH / Br / NH₂ / C₃H₇ — VII Unknown.

Fileti and Crosa[14] having oxidized nitro-bromo-cymene with nitric acid to a toluic

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[14] Fileti and Crosa, *Gazz. chim. ital.*, **18**, 307 (1888)

acid, we tried nitric acid first. Nitric acid (1:2) converted acetylamino-bromo-cymene into an amino acid melting at 196°, soluble in acids and alkalies, in ether and benzene and very difficultly soluble in water and ligroin. This substance corresponds to none of the toluic or cuminic acids. Neutral permanganate was then tried.

Two g. of acetylamino-bromo-cymene and 4 g. of magnesium sulfate were added to 240 cc. of water, warmed to 80°, and 6 g. of powdered potassium permanganate was finally added. Heating was continued for an hour and a half. The manganese dioxide was filtered off, the excess of permanganate destroyed with alcohol, and the colorless filtrate acidified with sulfuric acid. The abundant white precipitate crystallized from dil. alcohol in fine needles which melted at 215°. The acidity of the product was determined by titration.

Analysis. Subs., 0.1013: KOH (0.05 N solution used), 0.02085 g.

Required for acid derivatives: Acetylamino-bromo toluic acid, $C_{10}H_{10}O_3NBr$ (mol. wt. 272): 0.02085 g. Acetylamino-bromo-cuminic acid, $C_{12}H_{14}O_3NBr$ (mol. wt.) 300): 0.01890 g. Acetylamino-bromo-terephthalic acid, $C_{10}H_8O_5NBr$ (mol. wt. 302): 0.03753 g.

The product is therefore a toluic acid. It was then hydrolyzed, 0.5 g. being boiled for 30 minutes with 40 cc. of conc. hydrochloric acid. The hydrochloride crystallized in leaf-like crystals which melted at 190° with decomposition.

Analysis. Subs., 0.1054: KOH, 0.0419 g. Required for 2 acid hydrogens: 0.0427.

The analysis gives indication of a toluic acid. The substance was finally saponified with sodium hydroxide. From the solution acidified with acetic acid a white precipitate separated which turned pinkish after a time. It crystallized from dilute alcohol in yellowish needles which melted at 151°.

Analysis. Subs., 0.1022: KOH, 0.0247 g. Required for the 3 possible acids: Amino-bromo-toluic acid, $C_8H_8O_2NBr$ (mol. wt. 230): 0.0248 g. Amino-bromo-cuminic acid, $C_{10}H_{12}O_2NBr$, (mol. wt. 258): 0.0221 g. Amino-bromo-terephthalic acid, $C_8H_6O_4NBr$ (mol. wt. 260): 0.0440 g.

A toluic acid is again indicated. The 3 analyses point to a toluic acid of molecular weight of 272. We had expected to obtain toluic acid II with bromine in Position 5, but the acid melts at 151° instead of 186–187°. In choosing I instead of III, we are guided by the fact that the bromination of other amino compounds yields *ortho* and *para* compounds and not *meta*. The bromination of 4-amino-*m*-xylene[15] puts bromine *ortho* to the amino group. In this case the *para* place is already occupied. The bromination of 2-amino-*p*-xylene[16] puts bromine *para* to the amino group. Fischer and Windhaus[16] did not however prove it, merely stating that it was "wahrscheinlich." Everything considered we believe that the location of the bromine atom at Position 3 should be regarded as provisional.

Summary.

1. The nitration of *p*-cymene is described and the reduction of 2-nitro-*p*-cymene.

2. The bromination of 2-amino-*p*-cymene yields the new compound, 2-amino-3-bromo-*p*-cymene. Its acetyl derivative, hydrochloride and hydrobromide are described.

3. Diazo derivatives were prepared, including the coupling of amino-

[15] Noelting, Braun and Thesmar, *Ber.*, **34**, 2255 (1901).
[16] Fischer and Windhaus, *ibid.*, **33**, 1974 (1900).

bromo-cymene with (1) itself, (2) aniline and (3) p-nitro-aniline in two ways.

4. Conversion of the amino-bromo-cymene into a hitherto unknown amino-bromo-toluic acid suggests that the bromine atom occupies Position 3.

5. A new toluic acid, 2-amino-3-bromo-p-toluic acid, was prepared; also its hydrochloride and acetyl derivative.

CHAPEL HILL, NORTH CAROLINA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

SOME COMPOUNDS OF PIPERIDINE WITH HALIDES.

BY CLIFFORD S. LEONARD.

I. Inorganic Halides.[1]

A series of new halide compounds may be prepared from piperidine by reaction with halides of trivalent arsenic, antimony, and phosphorus and of tetravalent silicon, tin, and titanium. The solvent used is normal heptane. The complete miscibility of most of the halides employed and of the piperidine with heptane, together with the inert nature of the latter, favor its use. In each case the reaction takes place with as many piperidine molecules as there are halogen atoms available (with the exception of tin chloride, of which two chlorine atoms are inactive).

The reaction appears to be an addition like the formation of ammonium halides from ammonia and hydrogen halides. In general, if M is the metalloid, n its valence and X the halogen, the reaction may be written

$$n C_5H_{10}NH + MX_n \longrightarrow M(C_5H_{10}NH)_n X_n.$$
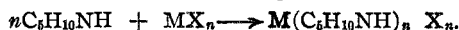
The behaviors of the complexes formed are like those of ammonium compounds, $i. e.$, they appear to be piperidinium compounds. We may write the equation and the structural formula in the following way, taking $AsCl_3$ as the example:[2]

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[1] This work comprises part of a thesis presented in June, 1920, to the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. See the preliminary note, read by Prof. Edward Kremers before the American Chemical Society, in *Science*, 53, 145 (1920). The formula given in this note is incorrect; a typographical error adds an extra arsenic atom.

[2] Whether the mechanism is direct addition or a substitution followed by addition of freed HCl does not matter as to resultant product. It has been the habit to beg the question of the nature of organic amino-halides; thus aniline and HCl give aniline "hydrochloride." Since this work was completed, Schmidt at the University of Wisconsin has studied similar products from $AsCl_3$ and aniline. He has named them as substituted aniline hydrochlorides, as is conventional. Obviously their nature must be similar, however, to the compounds here described. (See Schmidt, THIS JOURNAL, 43, 2449 (1921).)