

ican whiskey, but had the taste of spirits, and little difference could be noted between the two-year old sample and the eight-year old.

The judgment of No. 2623 was that it was a good flavored whiskey, but with very light body.

No. 2689 was pronounced a good flavored whiskey.

Nos. 2625 and 2627, the samples aged in uncharred packages, were both called immature whiskey, even when the eight-year old sample was tested. But this judgment was based on a comparison with those aged in charred packages.

On that basis the eight-year old sample was thought to be about 1 to 2 years old. This shows what a marked effect the storage in charred wood has upon the flavor of the whiskey.

#### Conclusions.

1. There are important relationships among the acids, esters, color, and solids in a properly aged whiskey, which will differentiate it from artificial mixtures and from young spirit.

2. All of the constituents are undergoing changes as the aging process proceeds, and it is evident that the matured whiskey is the result of these combined changes.

3. The amount of higher alcohols increases in the matured whiskey only in proportion to the concentration.

4. Acids and esters reach an equilibrium, which is maintained after about three or four years.

5. The characteristic aroma of American whiskey is derived almost entirely from the charred package in which it is aged.

6. The rye whiskeys show a higher content of solids, acids, esters, etc., than do the Bourbon whiskeys, but this is explained by the fact that heated warehouses are almost universally used for the maturing of rye whiskeys, and unheated warehouses for the maturing of Bourbon whiskeys.

7. The improvement in flavor of whiskeys in charred packages after the fourth year is due largely to concentration.

8. The oily appearance of a matured whiskey is due to material extracted from the charred package, as this appearance is almost lacking in whiskeys aged in uncharred wood.

9. The "body" of a whiskey, so-called, is due largely to the solids extracted from the wood.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

### THE CONDENSATION OF CHLORAL WITH PRIMARY AROMATIC AMINES. II.

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A number of condensation products of chloral with primary aromatic

amines have already been described. The first mention of such a reaction is probably that of Maumené,<sup>1</sup> who hoped to obtain indigotin by the action of chloral (2 mols.) upon aniline (3 mols.). His product was a brownish black uncrystallizable substance containing no chlorine. Schiff and Amato<sup>2</sup> first described a condensation product of chloral (1 mol.) and aniline (2 mols.) with the formula  $\text{CCl}_3\text{CH}(\text{NHC}_6\text{H}_5)_2$ . In the same year Wallach<sup>3</sup> described this compound. Later,<sup>4</sup> he gave a full description of the products obtained from aniline, *p*-toluidine, and a sample of xylydine boiling at 212–216°. Eibner<sup>5</sup> studied the condensation of chloral with *p*-nitraniline, *m*-chloraniline, *p*-chloraniline, and 1,2,4-dichloraniline and showed that 1,2,4,6-trichloraniline and 2,6-dichlor-4-nitraniline do not react. Wheeler and Weller<sup>6</sup> prepared the *o*- and *m*-nitraniline compounds and Wheeler and Daniels<sup>7</sup> showed that only addition products could be obtained with the naphthylamines. Niementowski and Orzechowski<sup>8</sup> found that one molecule of chloral condensed with one molecule of anthranilic acid but later<sup>9</sup> obtained the expected diphenamine compound. Finally Rügheimer<sup>10</sup> describes the compounds with *o*- and *p*-phenylenediamine and 1,2,4- and 1,3,4-toluylenediamine. He also states that only addition products are obtained with the naphthylamines.

The chloral diphenamine compounds vary considerably in stability. Most of them may be kept for years. They possess great crystallizing power. Their behavior toward alkalis is variable. The aniline derivative is decomposed by alcoholic potash into aniline, chloroform and phenyl cyanide according to Wallach. The *p*-nitraniline derivative, on the other hand, is converted into a hydroxy compound, one chlorine atom being replaced by a hydroxyl group according to Wheeler and Glenn.<sup>11</sup> They are not stable in the presence of strong mineral acids, which split them so as to re-form the amine. Eibner has shown that boiling acetic anhydride and benzoyl chloride give the acetyl or benzoyl derivative of the original amine. Finally, the writer has found that all of them react with great readiness with bromine in the cold. There is a substitution of one hydrogen atom in those which have been analyzed. This substitution probably occurs in the methylene group of the chloral residue.

<sup>1</sup> Ber., 3, 246 (1870).

<sup>2</sup> Gazz. chim. ital., 1, 376 (1871).

<sup>3</sup> Ber., 4, 668.

<sup>4</sup> Ann., 173, 274.

<sup>5</sup> *Ibid.*, 302, 335.

<sup>6</sup> This Journal, 24, 1063.

<sup>7</sup> J. Elisha Mitchell Sci. Soc., 22, 90 (1906).

<sup>8</sup> Ber., 28, 2812.

<sup>9</sup> *Ibid.*, 35, 3898.

<sup>10</sup> *Ibid.*, 39, 1653.

<sup>11</sup> J. Elisha Mitchell Sci. Soc., 19, 63 (1903).

*Chloral and p-Bromaniline. Trichlorethylidenedi-p-bromphenamine*,  $\text{CCl}_3\text{CH}(\text{NHBrC}_6\text{H}_4)_2$ . With c. w. MILLER.—Ten grams of *p*-bromaniline were dissolved in 50 cc. benzene and 8 grams chloral (4.2 grams required by theory) in 10 cc. benzene were added. The mixture was concentrated one-half on the water bath and cooled. A white flocculent precipitate came down, giving a melting-point of  $135^\circ$ . On further evaporation a second and much larger crop was obtained, showing a melting-point of  $119^\circ$ . By several recrystallizations from benzene the melting-point was raised to  $140^\circ$ . The yield was very high. Analysis: calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{Cl}_3\text{Br}_2$ , C 35.45, H 2.34, N 5.93, Cl + Br 56.24; found, C 35.03, H 2.46, N 6.38, Cl + Br 55.58.

Trichlorethylidenedi-*p*-bromphenamine consists of fine colorless needles, melting at  $140^\circ$  and decomposing at  $205^\circ$ . It is extremely soluble in alcohol, acetone, glacial acetic acid and hot benzene. It is sparingly soluble in cold benzene and insoluble in ligroin. It is readily purified by using a mixture of benzene and ligroin. It is not decomposed by boiling water but is split by boiling concentrated hydrochloric acid with the regeneration of *p*-bromaniline. A bromine derivative is easily obtained by adding bromine to a glacial acetic acid solution. The product, consisting of colorless plates, melts at  $203^\circ$  after several recrystallizations from glacial acetic acid. Determinations of carbon, hydrogen and nitrogen give very satisfactory figures for a monobrom compound. Chlorine gives a similar reaction. The product, crystallizing in long colorless needles, melts at  $93^\circ$  after recrystallization from glacial acetic acid. A study of the constitution of these halogen derivatives is under way.

*Chloral and o-Anisidine. Trichlorethylidenedi-o-methoxyphenamine*,  $\text{CCl}_3\text{CH}(\text{NHOC}_6\text{H}_4)_2$ . With w. s. DICKSON.—Two molecules (12.3 grams) of *o*-anisidine were dissolved in 50 cc. benzene and one molecule (7.3 grams) of chloral was added. After warming a short time on the steam bath a small quantity of colorless needles deposited. These decomposed at about  $215^\circ$  and weighed 0.95 gram. On concentration of the filtrate in a desiccator a mass of fern-like crystals was obtained mixed with a thick liquid. After filtering, the crystals were pressed on a porous tile. The product was white, melted at  $112\text{--}114^\circ$  and weighed 9.7 grams. On recrystallizing from benzene the melting-point was raised to  $121^\circ$ . The thick liquid finally solidified, considerably increasing the yield. Analysis: calculated for  $\text{C}_{15}\text{H}_{17}\text{O}_2\text{N}_2\text{Cl}_3$ , Cl 28.35, N 7.47; found, Cl 28.35, N 7.30.

Trichlorethylidenedi-*o*-methoxyphenamine crystallizes from ligroin or benzene in magnificent rhombohedra, one-half inch or more long, with a slight yellow color. It is easily soluble in cold benzene and carbon tetrachloride and in hot glacial acetic acid. It is slightly soluble in cold ligroin and fairly soluble in hot ligroin. It crystallizes from alcohol in long slender prisms. One hundred cc. of boiling alcohol will dissolve ap-

proximately 7 grams and at 25° about 2.5 grams. It is insoluble in and unchanged by boiling water. When boiled in concentrated hydrochloric acid the odor of chloral could be detected in the vapors. A bromine derivative is readily obtained by adding bromine to a concentrated glacial acetic acid solution. The product crystallizes in clusters of needles which decompose at about 230°. This compound is being further investigated.

*Chloral and p-Anisidine.* *Trichlorethylidenedi-p-methoxyphenamine*,  $\text{CCl}_3\text{CH}(\text{NHOCH}_2\text{C}_6\text{H}_4)_2$ .—To a solution of 12.3 grams of *p*-anisidine in 20 cc. of benzene (a nearly saturated solution) is added 7.3 grams of chloral. The solution turns to a dark red color at once, much heat is developed and a deposition of 0.22 gram of small colorless crystals occurs. These decompose at about 215° as in the case with *o*-anisidine. After filtering, the reaction mixture is boiled fifteen minutes and then allowed to stand several hours. An abundant crystalline precipitate formed. After filtering and pressing on a clay plate, the product melted at 115° and weighed 10.5 grams. A further yield was obtained from the mother-liquor. Purification by means of the mixed solvent, benzene and ligroin, raised the melting-point to 118–120°. Analysis: calculated for  $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}_2\text{Cl}_3$ , Cl 28.35; found, 28.41.

The *para* compound crystallizes from ligroin in brilliant scales, showing a strong pink color in the mass. It melts at 118–120° and decomposes at 158°. It is fairly soluble in cold benzene, alcohol and ether. It is readily soluble in glacial acetic acid, hot benzene and hot alcohol. The alcoholic solution emits a most disagreeable odor and on spontaneous evaporation to dryness a jet black crystalline mass remains. On treatment with bromine in glacial acetic acid solution a crystalline product is obtained which blackens at about 198°. This compound is being studied further.

*Chloral and Anthranilic Acid.*—The product obtained in this case depends upon the proportions used. One molecule of chloral will condense with one or two molecules of anthranilic acid with the elimination of one molecule of water. The two products have been described by Niementowski but his method yields a mixture and since we wish to prepare the compounds in order to study their bromine derivatives we have improved upon his method.<sup>1</sup>

*Trichlorethylidene-o-aminobenzoic Acid (Chloral-anthranilic Acid)*,  $\text{CCl}_3\text{CH}:\text{NC}_6\text{H}_4\text{COOH}$ . With w. s. DICKSON.—Five grams of anthranilic acid were dissolved in 40 cc. of boiling benzene (a saturated solution) and 5.5 grams chloral in 10 cc. benzene were added. The weights are in the proportion of one molecule to one molecule. The mixture was boiled

<sup>1</sup> Since writing the above, larger quantities of the mono-compound have been prepared in benzene solution and a small amount of the di-compound has been isolated from the product.

under a reflux condenser for three hours, filtered from a small precipitate and cooled. A crystalline deposit, weighing 5 grams and melting at  $148-151^{\circ}$ , separated. The crystals were large elongated tables occurring in clusters. From the filtrate was obtained 3 grams of material, melting at  $145-150^{\circ}$ . Several recrystallizations from benzene raised the melting-point to  $152^{\circ}$ . Niementowski and Orzechowski<sup>1</sup> prepared this compound without the use of any solvent. They used an excess of chloral and got several by-products. We have tried their method but have employed theoretical proportions. Even so we get the same by-products. The mortar was placed in a block of ice and the previously cooled substances rapidly stirred together. The mixture liquefied and then rapidly became very hard. This product decomposed at about  $127^{\circ}$ , after two hours on ice at  $124^{\circ}$  and after three hours more at room temperature at  $118^{\circ}$ . It was then rubbed up with a little water and filtered. The decomposition point rose to  $135^{\circ}$ . Now, taking advantage of the marked difference in solubility in benzene of the mono- and di-compounds (not observed by Niementowski) the crystalline mass, weighing 8.2 grams, was extracted with 45 cc. boiling benzene. From the extract there separated a mass of colorless needles, weighing 3.7 grams and melting at  $149-152^{\circ}$ , consisting therefore of the nearly pure mono-compound. On evaporating the filtrate a residue was obtained, weighing 1.3 grams and melting at  $160^{\circ}$ , a fair quality of the di-compound. A second extraction was made with 35 cc. of boiling benzene. On cooling, this yielded a product weighing 0.8 gram and melting at  $162^{\circ}$  and a residue melting at  $157^{\circ}$  after evaporation. There still remained an insoluble residue, dark purple in color. These results are in marked contrast to those obtained by our method of boiling in benzene, for we get practically only the mono-compound and consequently a much larger yield. We further identified the mono-compound by a chlorine determination. Calculated for  $C_9H_7O_2NCl_4$ , Cl 39.92; found, Cl 39.43.

On treating a glacial acetic acid solution of this compound with bromine a bromo derivative is obtained in large quantity. On cooling a hot glacial acetic acid solution, it deposits in clusters of fern-like crystals which decompose at  $237^{\circ}$ . This compound is under investigation.

*Trichlorethylidenedi-o-aminobenzoic Acid (Chloral Di-anthranilic Acid)*,  $CCl_3CH(NHC_6H_4COOH)_2$ .—Five grams (2 mols.) of anthranilic acid in 40 cc. boiling benzene were treated with 2.9 grams (1 mol.) of chloral in 10 cc. benzene and boiled under a reflux condenser for three hours. During the boiling there separated 3.25 grams of the di-compound, melting at  $164-165^{\circ}$ . On evaporation to dryness the residue was found to weigh 4.0 grams and to melt at  $157^{\circ}$ . The pure compound melts at  $165^{\circ}$ . The

<sup>1</sup> Ber., 28, 2812.

method of Niementowski<sup>1</sup> was tried and although found to be better than for the preparation of the mono-compound, it gave a smaller yield and a larger amount of unknown colored by-products. Analysis: calculated for  $C_{18}H_{13}O_4N_2Cl_3$ , N 6.96, Cl 26.11; found, N 6.76, Cl 26.10.

The di-compound consists of a crystalline powder and may be purified by precipitating its ether solution with ligroin. Upon boiling eight hours with acetic anhydride and cooling, a crystalline substance deposits, melting at  $183^\circ$  and crystallizing from benzene in needles. This corresponds to acetyl-*o*-aminobenzoic acid. On treating a glacial acetic acid solution with bromine, there is almost instantly obtained a heavy precipitate which after recrystallization from glacial acetic acid melts with decomposition at  $236^\circ$ . This behavior is surprisingly like that of the bromo derivative of the mono-compound.

*Chloral and o-Toluidine.* Trichlorethylidenedi-*o*-tolamine,  $CCl_3CH(NHC_6H_4CH_3)_2$ . With STROWD JORDAN.—Chloral and *o*-toluidine were brought together directly in the proportion of one molecule to two molecules. No advantage was found in using benzene as a solvent. To 28 grams *o*-toluidine 19.3 grams chloral were added; the mixture turned dark red and the temperature rose to  $80^\circ$ . After standing for some time, often over night, a quite hard crystalline cake formed. This was dissolved up in ether or successively extracted with benzene. In either case, a small residue weighing 0.7 gram remained. This was pale greenish in color and melted at  $213^\circ$ . The main product of the reaction was recrystallized from ether until the melting-point reached  $80^\circ$ . The yield was 70 per cent. of the theoretical. Analysis: calculated for  $C_{18}H_{17}N_2Cl_3$ , Cl 30.95; found, 30.77, 30.40, 30.96. The Stepanow method was employed in the second and third analyses and found to be extremely convenient. With some of our compounds we have found it impracticable on account of the deep color of the solution. We found it advisable to follow the suggestion of Rosanoff and Hill<sup>2</sup> and filter off the silver chloride before titrating.

Trichlorethylidenedi-*o*-tolamine crystallizes in very long silky needles. It is not very stable in solution or when exposed to the light. It is decomposed by water into chloral and *o*-toluidine. It is soluble in cold alcohol, ether, acetone, chloroform, carbon tetrachloride and glacial acetic acid, in hot ligroin and hot benzene. The pure substance melts at  $80^\circ$  and will melt repeatedly at that temperature. A bromine derivative is readily obtained in glacial acetic acid solution. This consists of colorless plates which melt with decomposition in the neighborhood of  $268^\circ$ .

*Physiological Action.*—The tolamine was found to have a physiological action by an accidental observation. Mr. Jordan unintentionally got a

<sup>1</sup> Ber., 35, 3898.

<sup>2</sup> This Journal, 29, 269.

small amount in his mouth and in about an hour a feeling of numbness spread over him to such a degree that pinching the flesh produced little sensation. Mr. Jordan was frightened by his condition but in an hour and a half he returned to a nearly normal state. The physiological action of this and other diphenamine compounds of chloral will be studied with care, some preliminary experiments on rabbits by Dr. MacNider, of this University, having confirmed the observation of such an action.

CHAPEL HILL, N. C.,  
October 16, 1907.

### NOTES.

*The boiling point of isobutane*, which is given in the literature, is based on a determination by Butlerow.<sup>1</sup> He found that the gas begins to condense to a liquid at  $-17^{\circ}$ .

Some years ago Mabery<sup>2</sup> isolated from petroleum a hydrocarbon which boiled at  $0^{\circ}$  and which he considered to be isobutane on the basis of the chloride obtained from it, which boiled at  $68-69^{\circ}$  and which he considered to be isobutyl chloride. Since 2-chlor-2-methyl-propane boils at  $67.3-67.8^{\circ}$ <sup>3</sup> and has a specific gravity closely approaching that of Mabery's product, it seems probable that the chloride which he obtained was in reality a derivative of normal butane, and not of isobutane. This view is further supported by the work of Pelouze and Cahours,<sup>4</sup> who found that a chloride boiling at  $65-70^{\circ}$  is obtained by the action of chlorine on normal butane.

It seemed of interest to prepare isobutane again, and make a new determination of the boiling-point. This was done by Mr. E. F. Phillips under my direction in the laboratory of the Rose Polytechnic Institute several years ago, and the results were reported to Professor Mabery, thinking that he would, at some time, publish something further upon the subject. As he has not done this and informs me that he does not expect to take up the subject again, it seems proper to give the results of our experiments.

The isobutane was prepared by the reduction of isobutyl iodide with zinc and dilute alcohol. The gas was purified and dried by passing it through bulbs containing alcohol and also bulbs containing concentrated sulphuric acid. It was condensed to a liquid by a freezing mixture and the temperature at which the vapor of this liquid exerted a pressure of 760 mm. was determined. This temperature was found to be  $-11.5^{\circ}$ . A considerable part of the liquid was allowed to evaporate and the deter-

<sup>1</sup> Ann., 144, 13.

<sup>2</sup> Am. Chem. J., 19, 247.

<sup>3</sup> Norris and Green, *Ibid.*, 26, 308.

<sup>4</sup> Jsb., 1863, 524.