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

DIRECT CONVERSION OF DERIVATIVES OF DICHLORO-ACETIC ACID INTO DERIVATIVES OF TRICHLORO-ACETIC ACID

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In a paper just published by us[2] it was shown that nitrodichloro-acetanilides are formed when the isomeric nitro-anilines are treated with dichloro-acetic acid in the presence of phosphorus pentoxide. During the progress of this study it was observed that the reaction between *o*-toluidine and dichloro-acetic acid took a different course when no dehydrating agent was present. When the substances are brought together at 0° or below in the molecular ratio of 1:1, a simple salt of *o*-toluidine and dichloro-acetic acid is formed, analogous to aniline acetate. On the other hand, when an excess of acid is used and the heat of the reaction is allowed to take its course, a complex reaction takes place, the product being a trichloro-acetic acid derivative which appears to be a salt of *o*-toluidine and trichloro-acetic acid. We then turned our attention to other amines and found the same to be true of aniline, *p*-toluidine, α-naphthylamine and *m*-nitro-aniline.

Very little study has been made of the reaction between dichloro-acetic acid and aromatic amines. Beamer and Clarke[3] state that they prepared aniline dichloro-acetate, melting at 122°, and aniline trichloro-acetate melting at 140°, but do not substantiate their claims by any analyses; hence their work is of little significance. Our aniline trichloro-acetate melts at 163°, and not at 140°. Baralis[4] describes a *p*-toluidine dichloro-acetate, m. p. 140–141° and a *p*-toluidine trichloro-acetate, m. p. 137°. We prepared the latter compound and find that it melts at 135°. The journal containing this article is not in the Chemical Abstract list and we have so far been unable to locate it in any library.

A number of articles have been published which describe reactions of dichloro-acetic acid and aromatic amines yielding products containing no chlorine, such as those of Meyer,[5] Duisburg[6] and Heller.[7]

The production of trichloro-acetic acid derivatives from dichloro-acetic acid proceeded so smoothly that we felt it necessary to examine the purity

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[1] This paper constitutes a portion of Part II of a thesis by Samuel C. Smith submitted in candidacy for the degree of Doctor of Philosophy in June, 1923, at the University of North Carolina.

[2] Wheeler and Smith, THIS JOURNAL, **45**, 1839 (1923).

[3] Beamer and Clarke, *Ber.*, **12**, 1066 (1879).

[4] Baralis, *Rev. chim. med. farm.*, **2**, 301.

[5] Meyer, *Ber.*, **16**, 925 (1883).

[6] Duisburg, *ibid.*, **18**, 190 (1885).

[7] Heller, *Ann.*. **332**, 253 (1904).

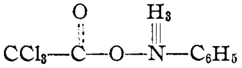
of our dichloro-acetic acid. It was redistilled and the portion boiling at 191° was used in our work.

Calc. for $C_2H_2O_2Cl_2$ (mol. wt., 129): Cl, 55.03. Found: 55.09.

The further precaution was taken of treating the same amines with trichloro-acetic acid. The compounds were identical in every case with those made from dichloro-acetic acid. Again, the composition of the trichloro compounds was proved by regenerating the constituents. For example, aniline trichloro-acetate obtained from dichloro-acetic acid was decomposed by sodium hydroxide, aniline being set free, whereas treatment of an alcoholic solution with sulfuric acid gave the ethyl ester of trichloro-acetic acid. The identity of the latter was proved by its conversion into trichloro-acetamide; m. p., 141°.

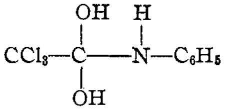
A complete analysis was made in one case only, that of *o*-toluidine trichloro-acetate made from dichloro-acetic acid.

The constitution of the compounds may be represented by one of the following formulas.

I 

$$CCl_3—\overset{\overset{O}{\|}}{C}—O—\overset{\overset{H_3}{|||}}{N}—C_6H_5$$

or

II 

$$CCl_3—\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}——\overset{\overset{H}{|}}{N}—C_6H_5$$

In I we have a pentad nitrogen and therefore an ammonium salt. In II we have a triad nitrogen and a compound of the chloral hydrate type, in which 2 hydroxyl groups are attached to one carbon atom, the stability of such a compound being due to the strong negative environment of the 3 chlorine atoms. The decomposition products which we have obtained throw no light on whether one is better than the other, but we lean to Formula II.

In order to explain why we get a trichloro and not a dichloro compound, we must conceive that 2 molecules of dichloro-acetic acid are rearranged into 1 of trichloro-acetic acid and one of monochloro-acetic acid under the influence of the amine which is basic in character: 2 $CClClHCOOH \longrightarrow CCl_3.COOH + CH_2ClCOOH$.

It may seem inconsistent to employ an outside agent (phosphorus pentoxide) in any of these reactions in view of the basis on which this study is built, but it was found important to do so in order to facilitate the identification of monochloro-acetic acid in the same reaction with trichloro-acetic acid. The last compounds described in the experimental part are the nitroacetanilides of these acids.

Experimental Part

Dichloroacetates

***o*-Toluidine Dichloro-acetate,** $CH_3C_6H_4NH_2.CHCl_2COOH$.—A solution of 5 g. of *o*-toluidine in 20 cc. of carbon tetrachloride was slowly mixed with a solution of 6.1 g. of dichloro-acetic acid in a like amount of the solvent while kept cold with ice. A dense precipitate formed which weighed 8.5 g. It crystallized out of alcohol in prismatic crystals; m. p., 140°. The salt is pure white but turns brown on exposure to the air and light. Continued boiling with water converts it into *o*-toluidine trichloro-acetate.

Analysis. Subs., 0.2496: AgCl, 0.3078. Calc. for $C_9H_{11}O_2NCl_2$ (mol. wt., 236): Cl, 30.08. Found: 30.51.

p-Toluidine Dichloro-acetate, $CH_3C_6H_4NH_2.CHCl_2COOH$.—This compound was prepared in the same way as the *o*-toluidine salt. If care is not taken to hold the temperature down, the reaction takes a different course and a mixture of products is obtained, as shown by its low melting point. This may explain the low melting point, 140°, found by Baralis; our product melts at 160°. Recrystallized from alcohol, the crystals are prismatic and pure white, but turn brown on exposure to the air.

Analysis. Subs., 0.5401: AgCl, 0.6665. Calc. for $C_9H_{11}O_2NCl_2$ (mol. wt. 236): Cl, 30.08. Found: 30.55.

Trichloro-acetates

Aniline Trichloro-acetate, (from Dichloro-acetic Acid), $C_6H_5NH_2.CCl_3.COOH$.—To 5.0 g. of aniline was added 7 cc. of dichloro-acetic acid. A great deal of heat was evolved as the product crystallized. Water was added and heat applied until the product dissolved. As the solution cooled, a mass of colorless crystals formed which melted at 160°. Several recrystallizations from water raised the melting point to 163°; yield of crude product, 7.5 g.

Analysis. Subs., 0.2440: AgCl, 0.4088. Calc. for $C_8H_8O_2NCl_3$ (mol. wt. 256.5): Cl, 41.52. Found: 41.44.

The substance crystallizes from hot water in colorless plates that turn reddish on exposure to the air. It is very soluble in hot water, slightly so in cold water, soluble in alcohol, slightly soluble in ether or benzene. It is decomposed by potassium hydroxide solution, and aniline is set free, as proved by the melting point (198°) of its hydrochloride. It is also decomposed by sulfuric acid. In this case trichloro-acetic acid was proved to be a product by its conversion into ethyl trichloro-acetate, boiling at 170° (756 mm.) and the formation of the trichloro-acetamide from this ester; m. p., 141°.

Aniline Trichloro-acetate (from Trichloro-acetic Acid).—To 5.0 g. of aniline was added 9.0 g. of trichloro-acetic acid. When the mixture was heated gently a vigorous reaction took place. The product crystallized from hot water in plates that melted at 163°. The constituents were also brought together in carbon tetrachloride solution at —3°. The same product, melting at 163°, was obtained. Beamer and Clarke[8] give 145° as the melting point, but they made no analysis.

Analysis. Subs., 0.4878: AgCl, 0.8149. Calc. for $C_8H_8O_2NCl_3$ (mol. wt., 256.5): Cl, 41.52. Found: 41.10.

This product is therefore identical with the one obtained from dichloro-acetic acid.

o-Toluidine Trichloro-acetate (from Dichloro-acetic Acid), $CH_3C_6H_2NH_2CCl_3COOH$.—Five g. of *o*-toludine and 7 cc. of dichloro-acetic acid were mixed. The reaction proceeded as described above. The product crystallized from hot water in colorless plates; m. p., 167–168° (decomp.).

Analyses. Calc. for $C_9H_{10}O_2NCl_3$ (mol. wt., 270.5): C, 39.92; H, 3.69; N, 5.17; Cl, 39.37. Found: C, 40.04; H, 3.70; N, 5.11; Cl, 38.93.

o-Toluidine trichloro-acetate decomposes at its melting point, two products being identified as chloroform and carbon dioxide. It is slightly soluble in cold water, very soluble in hot water, soluble in acetone, alcohol, insoluble in benzene or ligroin. Potassium hydroxide liberates *o*-toluidine, shown by the melting point of its hydrochloride,

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[8] Ref. 3, p. 1067.

214–216°. Sulfuric acid liberates trichloro-acetic acid, shown by converting it into its ethyl ester and its amide.

o-**Toluidine Trichloro-acetate** (from **Trichloro-acetic Acid**).—Five g. of *o*-toluidine and 8.0 g. of trichloro-acetic acid were heated together. The product was recrystallized from hot water and proved to be identical with the compound described above in melting point (167–168°), crystal form and solubility.

Analysis. Subs., 0.5122: AgCl, 0.8147. Calc. for $C_9H_{10}O_2NCl_3$ (mol. wt. 270.5): Cl, 39.37. Found: 39.34.

p-**Toluidine Trichloro-acetate** (from **Dichloro-acetic Acid**), $CH_3C_6H_4NH_2.CCl_3COOH$.—Five g. of *p*-toluidine was added to 7 cc. of dichloro-acetic acid. Much heat developed and to the mixture while still hot was added 20 cc. of water. A light yellow precipitate formed. This was recrystallized from hot water except for a small insoluble portion. The pure substance consists of colorless prismatic needles; m. p., 135° (decomp.). The solubilities correspond to those of the *ortho* compound.

Analysis. Subs., 0.3385: AgCl, 0.5353. Calc. for $C_9H_{10}O_2NCl_3$ (mol. wt., 270.5): Cl, 39.37. Found: 39.11.

p-**Toluidine Trichloro-acetate** (from **Trichloro-acetic Acid**).—Five g. of *p*-toluidine was mixed with 8.0 g. of trichloro-acetic acid. The product crystallized from hot water in prismatic needles; m. p., 135° (decomp.).

Analysis. Subs., 0.5021: AgCl, 0.7978. Calc. for $C_9H_{10}O_2NCl_3$ (mol. wt., 270.5): Cl, 39.37. Found: 39.31.

α-**Naphthylamine Trichloro-acetate** (from **Dichloro-acetic Acid**), $C_{10}H_7NH_2.CCl_3COOH$.—Five g. of *α*-naphthylamine was mixed with 9.1 g. of dichloro-acetic acid and the mixture warmed a little, since the reaction in this case was somewhat slow. No solution was apparent. The mush of crystals was washed with 50 cc. of water. The crude product, melting at 170°, weighed 10.4 g., the calculated amount being 10.7. After the substance was washed with boiling water or recrystallized from dilute alcohol the melting point was raised to 173°, with decomposition. The compound crystallizes from alcohol in pale violet plates which are only slightly soluble in hot water, are soluble in alcohol or acetone, and insoluble in ether or benzene.

Analysis. Subs., 0.3587: AgCl, 0.4950. Calc. for $C_{12}H_9O_2NCl_3$ (mol. wt., 306): Cl, 34.74. Found: 34.37.

α-Naphthylamine trichloro-acetate was also made from trichloro-acetic acid by gently heating a mixture of the constituents. Recrystallization from dil. alcohol gave pale violet plates; m. p., 173°.

m-**Nitro-aniline Trichloro-acetate** (from **Dichloro-acetic Acid**), $C_6H_4NO_2NH_2.CCl_3COOH$.—To 5.0 g. of *m*-nitro-aniline was added 15 cc. of dichloro-acetic acid which was sufficient to dissolve it. After the solution had been heated on the water-bath for 10 minutes it was poured into 100 cc. of cold water. The crystalline precipitate formed melted at 143°. Recrystallization from hot water raised the melting point to 147° but continued boiling with water caused hydrolysis. The crystals are pale yellow plates, soluble in alcohol, slightly soluble in ether and insoluble in benzene.

Analysis. Subs., 0.4049: AgCl, 0.5722. Calc. for $C_8H_7O_4N_2Cl_3$ (mol. wt., 301): Cl, 35.32. Found: 34.89.

p-**Nitrochloro-acetanilide** (from **Dichloro-acetic Acid**), $C_6H_4NO_2NHCOCH_2Cl$.—Five g. of *p*-nitro-aniline was warmed with 12 cc. of dichloro-acetic acid. After reaction had taken place (analogous to the reactions described above), 5.0 g. of phosphorus pentoxide was added and the mixture heated on the steam-bath for 10 minutes, then poured into 100 cc. of cold water and allowed to stand overnight for complete crystallization to take place. The precipitate was then extracted with carbon tetrachloride. The insoluble portion proved to be *p*-nitrochloro-acetanilide and the solution contained *p*-nitrotrichloro-acetanilide.

The portion insoluble in carbon tetrachloride was recrystallized from alcohol. It consisted of yellow prisms, m. p. 177°, insoluble in water, soluble in acetone or ether.

Analysis. Subs., 0.3311: AgCl, 0.2191. Calc. for $C_8H_7O_3N_2Cl$ (mol. wt., 214.5): Cl, 16.55. Found: 16.37.

That this compound was *p*-nitrochloro-acetanilide was proved by comparison with the product made directly from monochloro-acetic acid. To 5.0 g. of *p*-nitro-aniline was added 5.0 g. of phosphorus pentoxide and 5.0 g. of monochloro-acetic acid. After the mixture had been heated until fusion took place, 100 cc. of water was added. The precipitate formed was recrystallized from alcohol, as yellow prisms; m. p., 177°.

Analysis. Subs., 0.1974: AgCl, 0.1344. Calc. for $C_8H_7O_3N_2Cl$: Cl, 16.55. Found: 16.37.

***p*-Nitrotrichloro-acetanilide** (from Dichloro-acetic Acid), $C_6H_4NO_2NHCOCl_3$.—The portion soluble in carbon tetrachloride was purified by evaporation of the solvent and extraction of the residue with 50% alcohol. The portion insoluble in the alcohol melted at 135–140°. It was recrystallized from carbon tetrachloride. The pure substance consists of light yellow prismatic needles that melt at 140° with previous softening. It is soluble in acetone, alcohol, benzene or chloroform.

Analysis. Subs., 0.0341: AgCl, 0.0521. Calc. for $C_8H_5O_3N_2Cl_3$ (mol. wt., 283.5): Cl, 37.56. Found: 37.79.

To prove that this was *p*-nitrotrichloro-acetanilide the substance was synthesized from trichloro-acetic acid. To 5.0 g. of *p*-nitro-aniline was added 5.0 g. of phosphorus pentoxide and 7.0 g. of trichloro-acetic acid. The mixture was heated until it melted. To remove any unchanged *p*-nitro-aniline dil. hydrochloric acid was used for precipitation. The substance was purified by recrystallizing from carbon tetrachloride and obtained as light yellow needles; m. p., 140°, with previous softening.

Analysis. Subs., 0.2365: AgCl, 0.3598. Calc. for $C_8H_5O_3N_2Cl_3$: Cl, 37.56. Found: 37.61.

Summary

1. The dichloro-acetates of *o*- and *p*-toluidine were prepared from dichloro-acetic acid.

2. The trichloro-acetates of aniline, *o*- and *p*-toluidine, α-naphthylamine and *m*-nitro-aniline were prepared from dichloro-acetic acid. The same trichloro-acetates were prepared from trichloro-acetic acid.

3. To prove the presence of monochloro-acetic and trichloro-acetic acids in the reaction of dichloro-acetic acid on aromatic amines, the *p*-nitrochloro-acetanilides were prepared, separated and identified.

4. Two molecules of dichloro-acetic acid exchange a hydrogen and a chlorine atom under the influence of these weak bases, thus yielding trichloro-acetic acid derivatives from dichloro-acetic acid.

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