[CONTRIBUTION FROM THE FAYERWEATHER CHEMICAL LABORATORY OF AMHERST COLLEGE]

THE REACTION OF DICHLORO-ACETIC ACID WITH AROMATIC AMINES

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In 1923 Wheeler and Smith[1] published a paper entitled "Direct Conversion of Derivatives of Dichloro-acetic Acid into Derivatives of Trichloro-acetic Acid," in which they state that dichloro-acetic acid and aromatic amines react very smoothly to form amine salts of trichloro-acetic acid. My attention was attracted particularly by the statement that aniline trichloro-acetate is formed merely by bringing together aniline and dichloro-acetic acid, warming the mixture and recrystallizing the product from water. During the past few years aniline dichloro-acetate has been prepared many times in this Laboratory by the addition of aniline to dichloro-acetic acid[2,3] without observing the reaction described by Wheeler and Smith. Our experiments showed that trichloro-acetic acid or its derivatives can be very readily converted into dichloro-acetic acid and in some cases tetrachloro-succinic acid or their derivatives by the action of finely divided copper in water, ether or benzene solution or without any solvent, the reaction being markedly exothermic, and it seemed remarkable that the reverse reaction should proceed so readily. I have, therefore, repeated the experiments of Wheeler and Smith, using samples of dichloro-acetic acid which had been prepared in previous experiments in this Laboratory or used in connection with our previous work. I have not been able to duplicate the results obtained by them.

The results of my experiments show that when dichloro-acetic acid is treated with an aromatic amine, with or without a solvent, the corresponding dichloro-acetate is formed, and is readily obtained by recrystallization. Further heating of the reaction mixture, particularly in the presence of an excess of dichloro-acetic acid, results in the formation of the aryl substituted amide of dichloro-acetic acid, the yield depending on the temperature and the amount of dichloro-acetic acid and the time of heating, a temperature of 140° and an excess of one molecular equivalent of dichloro-acetic acid being in general satisfactory conditions when the heating is continued for 18 to 24 hours. The amine salts thus obtained are in general very soluble in water and alcohol, but very slightly in benzene and carbon tetrachloride, while the amides are readily soluble in benzene and alcohol, less soluble in carbon tetrachloride and very slightly soluble in water. The amides sublime readily, some at water-bath temperature, condensing in long, white

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[1] Wheeler and Smith, THIS JOURNAL, **45**, 1994 (1923).

[2] Doughty and Freeman, *ibid.*, **44**, 640 (1922).

[3] Doughty and Black, *ibid.*, **47**, 1091 (1925).

needles that resemble those of phthalic anhydride. They dissolve in cold, concd. sulfuric acid and precipitate unchanged when the solution is poured into water. Heating the sulfuric acid solution gives dichloro-acetic acid.

Experimental Part

Aniline Trichloro-acetate.—The melting point of this salt has been variously recorded, and our experience in this Laboratory is that it is difficult to obtain precise agreement in using the melting point as a criterion of purity of this salt. For the melting point of aniline trichloro-acetate Beamer and Clarke[4] give 140°, Doughty and Freeman[2] 147°, while later work in this Laboratory indicated 149–150°, and Wheeler and Smith found 163°. I have, therefore, prepared several samples of aniline trichloro-acetate in order to determine its melting point.

Equivalent quantities of trichloro-acetic acid and aniline in benzene solutions were mixed. The salt is nearly insoluble in benzene and crystallized immediately in white flakes. The product was recrystallized from water and from alcohol, forming hexagonal plates and prisms. The dried salt was titrated directly with 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator.

Mol. wt. Subs., 0.6495: 25.38 cc. of 0.1 *N* NaOH. Calcd.: mol. wt., 256.5. Found: 255.9.

This salt has no true melting point. It decomposes at or near its melting point, and this decomposition prevents a true equilibrium between the solid and liquid phases of the salt. By varying the rate of heating of samples taken from the same powdered material I have obtained melting points all the way from 142° to 163°. The lower value was obtained by keeping the temperature at about 135° for approximately ten minutes and then raising it very slowly, while the higher value was obtained by immersing the melting-point tube in the bath already heated to about 140° and heating rather rapidly.

Acid Aniline Trichloro-acetate.—During some previous work[3] it was found that when two molecular equivalents of trichloro-acetic acid and one of aniline were brought together in benzene solution, long, colorless needles separated which melted at 107–108°. These could be recrystallized from monochlorobenzene without change of melting point. Analysis by titration showed that the substance was the acid salt of trichloro-acetic acid.

Equiv. wt. Subs., 0.6277: 29.80 cc. of 0.1 *N* NaOH. Calcd.: equiv. wt., 209.9. Found: 210.4.

We did not succeed in preparing a corresponding acid dichloro-acetate. In all cases the normal salt, melting at 122–123°, was obtained.

The dichloro-acetic acid used in this work was a portion of the acid prepared by Pucher[5] to which reference has already been made in another paper[3] by Doughty and Black. This acid has been carefully tested in this Laboratory during the past three years, and no derivative of trichloro-acetic acid has ever been obtained from it. In the preparation of the aniline and *o*-toluidine dichloro-acetates the behavior of Pucher's acid was checked by comparison with that of dichloro-acetic acid prepared by

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

[5] Pucher, THIS JOURNAL, **42**, 2251 (1920).

Doughty and Black[3] from trichloro-acetic acid and copper. No difference could be observed in the reaction or product.

Dichloro-acetic Acid and Aniline

Aniline Dichoro-acetate.—Equivalent quantities of dichloro-acetic acid and aniline were dissolved in separate portions of benzene. When these solutions were mixed a white, flaky precipitate of aniline dichloro-acetate was formed; m. p., 122–123°. Recrystallization from water or alcohol did not change the melting point. (A short-stem thermometer was used in all melting-point determinations to avoid the necessity of correction for exposed stem.)

Equiv. wt. Subs., 0.7057: 31.90 cc. of 0.1 N NaOH. Calcd. for $CHCl_2.CO_2H.$-$C_6H_5NH_2$: equiv. wt., 222.05. Found: 221.2.

The same substance is formed by simply mixing aniline and dichloro-acetic acid in approximately equivalent quantities and crystallizing the product from water or alcohol.

Dichloro-acetanilide.—Aniline, 10 g., and dichloro-acetic acid, 16 g., were mixed in a small flask and heated on a metal bath at 140° for 24 hours. The melt was poured into 150 cc. of cold water. The heavy, dark colored precipitate was washed with hot water, dissolved in alcohol, the solution boiled with decolorizing carbon and the material purified by recrystallization. The product was yellow and melted at 115–116°. It sublimes in long, white needles that resemble those of phthalic anhydride; m. p., 118°. Lembling[6] gives 117–118° as the melting point of dichloro-acetanilide.

Dichloro-acetic Acid and *o*-Toluidine

***o*-Toluidine Dichloro-acetate.**—This salt was prepared in the manner described for aniline dichloro-acetate. It is soluble in twice its weight of hot water, from which it crystallizes in colorless, bunched needles or plates; m. p., 132.5°. Wheeler and Smith give 140° as the melting point of this salt, and state that it must be prepared at or near 0°.

Dichloro-aceto-*o*-toluidide.—Dichloro-acetic acid, 25 g., and *o*-toluidine, 20 g., were mixed in a small flask and the mixture was heated on a metal bath at 140° for 18 hours. The melt was poured into 200 cc. of cold water. A heavy oil separated, which solidified when stirred. Filtered and air-dried, this product weighed 29 g. It is very soluble in alcohol, ether, or benzene, less soluble in carbon tetrachloride and very slightly soluble in cold water. It is rather more soluble in hot water than in cold, and small samples can be purified by crystallization from hot water. It is best purified by crystallization from 50% alcohol. It sublimes readily at water-bath temperature, condensing in long, slender, white needles; m. p., 133.°

The same product is formed by heating *o*-toluidine dichloro-acetate alone, or in larger amount by heating with dichloro-acetic acid, at 140°. The melting point, 133°, is practically the same as that of *o*-toluidine dichloro-acetate, 132.5°, but when equal parts of each are mixed, the mixture melts below 112°.

Anal. Calcd. for $C_8H_7ONCl_2$: Cl, 32.58. Found (Carius): 33.16.

Dichloro-acetic Acid and *p*-Toluidine

***p*-Toluidine Dichloro-acetate.**—This salt was prepared as described for *o*-toluidine dichloro-acetate. The salt crystallized from hot water in radial tufts of very long, slender, colorless needles; m. p., 138°.

Baralis[7] gives 140–141° as the melting point of this salt, while Wheeler and Smith give 160°.

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[6] Lembling, *Compt. rend.*, **127**, 189 (1898).

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

Dichloro-aceto-*p*-toluidide.—The same procedure was followed as for the *o*-toluidide and the reaction was entirely analogous. The product crystallized from alcohol in white, flaky plates, m. p. 153°, and sublimed readily, condensing in down-like, fluffy, white masses and long needles; m. p., 154°.

Rügheimer and Hoffmann,[8] made the toluidides of dichloro-acetic acid by heating the acid toluidine malonates with phosphorus pentachloride. Their description of the compounds corresponds to the products that I have prepared. They do not give a melting point for the *o*-toluidide, but do give 153° for dichloro-aceto-*p*-toluidide.

α-Naphthylamine dichloro-acetate was also prepared as directed by Wheeler and Smith. My product crystallized from water and alcohol in hard, grayish-violet crystals; m. p., 136°. Wheeler and Smith by similar treatment obtained α-naphthylamine trichloro-acetate; m. p., 173° (decomp.).

Summary

The behavior of dichloro-acetic acid with aromatic amines is entirely normal, giving amine salts or aryl substituted amides of dichloro-acetic acid, according to temperature and duration of heating. In no case is there any indication of the formation of trichloro-acetic acid or its derivatives.

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PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. VIII. THE REDUCTION OF ALKYL FURYL CARBINOLS[1]

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In a recent paper by Kaufmann and Adams[1d] the reduction of furfural by means of hydrogen and platinum black made from platinum oxide was studied. It was found that the initial product was furyl carbinol. This upon further reduction yielded four products: tetrahydrofuryl carbinol, pentane-diol-1,2, pentane-diol-1,5 and *n*-amyl alcohol. The first substance made up the largest proportion of the reaction mixture while the last was obtained in only small amounts. In the article describing this work, a review of the previous researches on the reduction of furane and its de-

[8] Rügheimer and Hoffmann, *Ber.*, **18**, 2987 (1885).

[1] For previous papers in this field see (a) Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922). (b) Carothers and Adams, *ibid.*, **45**, 1071 (1923). (c) Adams and Shriner, *ibid.*, **45**, 2171 (1923). (d) Kaufmann and Adams, *ibid.*, **45**, 3029 (1923). (e) Carothers and Adams, *ibid.*, **46**, 1675 (1924). (f) Shriner and Adams, *ibid.*, **46**, 1683 (1924). (g) Carothers and Adams, *ibid.*, **47**, 1047 (1925).

[2] This communication is an abstract of a portion of a thesis submitted by J. S. Pierce in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.