

From the dihydroxy compound, the dichloride was prepared by boiling the former with several parts of conc. hydrochloric acid for an hour. The chloride separates as a yellow oil which solidifies as it cools. It was recrystallized from hot alcohol and melted at  $64^{\circ}$

Calc.: S, 29.26. Found: 29.87. Calc.: Cl, 32.36. Found: 30.99.

This shows that some of the hydroxy compound was present. It is readily hydrolyzed.

Similarly the bromide was obtained and melted at  $90-94^{\circ}$ .

Calc.: S, 20.81. Found: 21.42. Calc.: Br, 51.88. Found: 50.73.

By heating the dihydroxy compound with acetyl chloride a liquid was obtained which seemed to be the di-acetate.

### Physiological Effects

On account of the higher molecular weight, the volatility is less and the vapors would not be expected to show the activity of the monosulfide. When a tiny particle is placed on the human skin, a burn is produced, but its effect is considerably less than that of mustard gas.<sup>8</sup>

Conjunctivitis of the eyes and a rash over hands and face were suffered by the operator while working with it.

### Summary

An analog of mustard gas,  $(\text{ClCH}_2\text{CH}_2\text{SCH}_2)_2$ , m. p.  $64^{\circ}$ , has been prepared and found to have decided vesicant action. The corresponding dihydroxy compound, m. p.  $114-117^{\circ}$ , was made as an intermediate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF AMHERST COLLEGE]

## TRihalogen-Methyl Reactions. IV. Reaction of Trichloro-acetic Acid with Copper

By Howard Waters Doughty and Benjamin Freeman

Received December 12, 1921

For several years the senior author has been interested in the behavior of compounds which contain the trichloro- or tribromo-methyl group, with copper in presence of aqueous ammonia.<sup>1,2,3</sup> With the exception of benzotrichloride, all of this class of compounds which have been tested react with copper more or less rapidly in the presence of aqueous ammonia, all our samples were indefinite. Mr. Hoffman, by the use of thionyl chloride, has obtained the crude dichloride melting at  $53^{\circ}$  agreeing well with Bennett and Whincop who give  $54^{\circ}$  as the melting point of the unrecrystallized chloride.—E. E. R.

<sup>8</sup> Our thanks for the physiological tests are due to Lt. Harry A. Kuhn, Chief of the Dept. of Toxicology, Edgewood Arsenal.

<sup>1</sup> Doughty, *THIS JOURNAL*, **39**, 2685 (1917).

<sup>2</sup> Doughty, *ibid.*, **41**, 1129 (1919).

<sup>3</sup> Doughty and Freeman, *ibid.*, **43**, 700 (1921).

the copper passing into solution as ammonio-cupric chloride, while mono- or dihalogen methyl compounds react much less readily or not at all in similar environment, except ammonium dichloro-acetate, which does also react.<sup>4</sup> Ammonium trichloro-acetate is particularly noticeable for the violence of its reaction, and the present writers therefore decided to investigate the behavior of trichloro-acetic acid and its derivatives with copper, intending to conduct a similar investigation of the behavior of other substances which contain the trihalogen-methyl group, in the hope of finding some relation between the intensity of reaction and the "negativity" of the fourth substituent of the methane molecule in compounds of the general formula  $RCX_3$ , where R is a radical or hydrogen, and X a halogen atom. As the present writers are no longer in a position to carry on the work together, it is deemed advisable to make a statement of what has been accomplished by them so far.

Berthelot<sup>5</sup> prepared acetylene by passing chloroform vapor over heated copper. Cazeneuve,<sup>6</sup> in 1891, found that bromoform and iodoform react much more energetically with copper and that bromoform, gently warmed with silver powder, gives acetylene and the silver becomes incandescent, while iodoform reacts still more vigorously. On the other hand, chloroform, according to Cazeneuve, does not react at all with silver.

Beilstein<sup>7</sup> states that benzotrichloride, warmed with copper powder, reacts vigorously, forming first toluene tetrachloride and then toluene dichloride. He does not mention any evidence of the formation of toluene. Evidently the replacement of the hydrogen of chloroform by the phenyl group makes a considerable difference in the course of the reaction, though in both cases the tendency is towards the formation of acetylene derivatives. The problem for us in the present investigation is the determination of the effect of substituting a carboxyl group, instead of a phenyl group, for the hydrogen of chloroform.

#### Some Derivatives of Tetrachloro-succinic Acid

Analogy to the action of chloroform and of benzotrichloride would suggest that the action of trichloro-acetic acid on copper might result in the formation of acetylene dicarboxylic acid or tetrachloro-succinic acid. The latter possibility is of particular interest from the fact that no mention

<sup>4</sup> Thanks to the courtesy of Professor Treat B. Johnson, of Yale University, and Mr. G. W. Pucher, we have obtained a considerable quantity of dichloro-acetic acid, prepared by the latter (*THIS JOURNAL*, **42**, 2251 (1920)). We find that this acid, probably as pure as has ever been prepared, does react with copper and aqueous ammonia, and also with cuprous chloride in aqueous ammoniacal solution.

<sup>5</sup> Berthelot, *Compt. rend.*, **50**, 805 (1860).

<sup>6</sup> Cazeneuve, *ibid.*, **113**, 1054 (1891).

<sup>7</sup> Beilstein, "Handbuch der organischen Chemie," Leopold Voss, 3rd Ed., vol. II, p. 48.

of tetrachloro-succinic acid, its salts or its esters, is to be found in the literature, excepting "perchloro-succinic ester,"  $C_8Cl_{14}O_4$ , which is formed by the action of chlorine on diethyl succinate in the sunlight. This substance reacts with ammonia gas or liquid ammonia to form a substance which Malaguti<sup>8</sup> formulated as  $C_3HCl_3NO$ , and called chloro-azo-succinic acid while Laurent<sup>9</sup> considered it to be tetrachloro-succinimide,  $C_4Cl_4O_2NH$ . Anschütz and Beavis<sup>10</sup> prepared what they considered to be tetrachloro-succinanil, m. p.  $157^\circ$ , by the action of phosphorus pentachloride on the anil of dichloro-maleic acid. They do not offer any evidence for the formula assigned, other than analysis and the method of preparation. The other chloro-succinic acids have been prepared. The trichloro-succinic acid prepared by Van der Riet<sup>11</sup> is particularly significant as indicating the reason for the non-appearance of tetrachloro-succinic acid in the literature. He found that a mixture of chloro-maleic acid, water, and liquid chlorine in a sealed tube in the sunlight, gave an acid, soluble in ether, very hygroscopic, and hence not obtainable in pure condition. From this he prepared salts of various metals, all soluble in water excepting those of lead and silver, and also the aniline salt, m. p.  $146^\circ$  (with decomp.), which separates as a white crystalline precipitate when aniline is added to an alcoholic solution of the acid, and which is easily purified by recrystallization from alcohol. Analyses of these salts showed the acid to be trichloro-succinic acid.

The reaction of trichloro-acetic acid with copper powder is very vigorous and our first attempts to obtain a product of the reaction were not successful. We therefore turned our attention to the action of the ester, ethyl trichloro-acetate, on copper, thus introducing the carboxy group as R in the general formula,  $RCCl_3$ . The ester was prepared by saturating an alcoholic solution of pure trichloro-acetic acid with hydrogen chloride in the usual way. It boiled at  $165\text{--}167^\circ$ . In the following experiments copper was used in various forms. Copper powder was prepared by reduction of copper sulfate with zinc, with subsequent washing and drying. We also tried copper powder prepared by reducing copper oxide with hydrogen. The most effective form was found to be the "dark copper bronze" prepared for use with bronzing lacquers and obtainable from dealers in painters' and decorators' supplies.

**Diethyl Tetrachloro-succinate.**—Ethyl trichloro-acetate was heated on a water-bath and copper powder was added in 5g. portions, with stirring, at 10-minute intervals until about 3 moles of copper had been added to 2 moles of ester. The heating was continued for 6 to 8 hours. The liquid was then filtered off and the residue extracted with ether. The ether extract was added to the main filtrate, and the whole product

<sup>8</sup> Malaguti, Gerhardt, "Traité chim. organ.," vol II, pp. 466, 477.

<sup>9</sup> Laurent, *Compt. rend.*, **35**, 381 (1852).

<sup>10</sup> Anschütz and Beavis, *Ann.*, **295**, 33, 39 (1897).

<sup>11</sup> Van der Riet, *ibid.*, **280**, 221, 230 (1894).

was fractionated under diminished pressure. A colorless, mobile liquid was obtained, having a pleasant, rather spicy odor, distilling at  $156^{\circ}$  (13 mm.). When heated to  $175^{\circ}$  under atmospheric pressure it decomposed, giving hydrogen chloride and a brown viscous residue.

*Analyses.* Calc. for  $C_6H_{10}O_4Cl_4$ : Cl, 45.54. Found: (Carius) 44.56, 44.58. Mol. wt. Calc.: 312. Found: 293.4. Saponification equivalent (g. of NaOH per g. of ester). Calc.: 0.2564. Found: 0.2676, 0.2504.

These analyses, while not indicating a high degree of purity of product, do show that the ester is in all probability diethyl tetrachloro-succinate. To test this further, the ester was reduced by heating with conc. hydriodic acid for several days in a flask with return condenser. The iodine which separated was filtered off, the solution decolorized by hydrogen sulfide and evaporated to dryness. From 13 g. of ester about 1 g. of an acid was obtained, light brown in color, which melted at  $180-181^{\circ}$ . With the same thermometer succinic acid melted at  $182^{\circ}$  and a mixture of the two in equal parts melted at  $181^{\circ}$ , proving conclusively that the product of reduction of the ester, with accompanying hydrolysis, is succinic acid, from which it appears highly probable that the ester is diethyl tetrachloro-succinate.

Attempts to saponify the ester by boiling with conc. hydrochloric acid were not successful. A dark colored tarry product was obtained from which no definite substance could be isolated.

**Aniline Tetrachloro-succinate.**—When trichloro-acetic acid and copper powder were intimately mixed the mixture became very hot, and a considerable part of the acid was lost by volatilization. By adding the copper in small portions and waiting for the reaction to subside, the temperature was kept below the boiling point of trichloro-acetic acid. The copper was added until 3 atoms of copper were present to 2 moles of trichloro-acetic acid. After cooling, the mixture was extracted with ether. The ether filtrate was evaporated, leaving a green sirupy mass. This was dissolved in alcohol and the copper precipitated by hydrogen sulfide. After filtering, the hydrogen sulfide was removed by partial evaporation under diminished pressure. The remaining solution, dark red in color, contained a strong acid. Aniline was added to this solution, which was then placed in the ice chest. After some hours a small quantity of small, fine, hard, white crystals formed, which melted at  $149-150^{\circ}$  (corr.). Analysis indicates that this substance is aniline tetrachloro-succinate.

*Analyses.* Calc. for  $C_6Cl_4H_2O_4 \cdot 2C_6H_5NH_2$ : Cl, 32.12; N, 6.33. Found: Cl (Carius) 32.32, 31.91, 32.29; N (Kjeldahl), 6.22. Subs. (aniline salt), 1.1711: 104.89 cc. of 0.1 N  $BaO_2H_2$  (thymol blue (blue-yellow)). Calc.: 105.94 cc.

Aniline tetrachloro-succinate is soluble in benzene, rather difficultly soluble in water, slightly soluble in ether, very slightly soluble in cold alcohol, but readily on heating. Boiled, or allowed to stand with water, it hydrolyzes easily, giving hydrochloric acid. The analyses might equally well indicate aniline dichloro-acetate, but this salt melts at  $122-123^{\circ}$ .

Although tetrachloro-succinic acid undoubtedly exists in the alcoholic solution mentioned above, after saturation with hydrogen sulfide, we have not been able to obtain the free acid in anything approaching pure condition. Apparently it resembles trichloro-succinic acid in being exceedingly hygroscopic, and it is also easily hydrolyzed and probably decomposes easily, to judge from the fact that the ester gives large amounts of hydrogen chloride when heated above  $175^{\circ}$ . The yield of aniline tetrachloro-succinate is small, never exceeding 5% of the weight of the trichloro-

acetic acid used in our experiments. Many attempts were made to increase the yield, by using various solvents to diminish the intensity of the reaction and by varying the conditions as to temperature and mixing, but we have not been able to obtain any considerable amounts of this salt. When water or benzene was used to dissolve the trichloro-acetic acid before adding the copper, no trace of aniline tetrachloro-succinate could be obtained.<sup>12</sup> It was obtained when the reaction took place in ether solution, but the yield was not very different from that obtained by the method described above, and in some experiments none was obtained.

### Preparation of Dichloro-Acetic Acid

The small yield of a salt of tetrachloro-succinic acid led to further study of the products of the reaction between trichloro-acetic acid and copper, particularly in aqueous and in benzene solution, from which it appears that only a relatively small part of the product is tetrachloro-succinic acid, and the principal product is dichloro-acetic acid. Indeed it appears that this reaction affords a very satisfactory means of preparation of the latter acid, either in aqueous solution or in the anhydrous condition.

Trichloro-acetic acid, 15 g., was dissolved in 100 cc. of benzene, and 15 g. of copper powder was added in 5g. portions at intervals of about 15 minutes. The mixture, which soon became warm, was stirred continuously with an electric stirrer for 2 hours. Hydrogen chloride was then passed into the mixture to convert any organic copper salts into cuprous or cupric chlorides, both of which are insoluble in benzene. After filtering from the copper chlorides, the hydrogen chloride was removed by partial evaporation in a vacuum.<sup>13</sup> When 9 g. of aniline was added to the remaining solution, about 12 g. of white crystalline precipitate was obtained, which proved to be aniline dichloro-acetate, m. p. 122–123°. In order to establish the identity of this product, aniline dichloro-acetate was also prepared from Pucher's dichloro-acetic acid<sup>14</sup> which had been subjected to further fractionation. The melting point of the aniline salt thus prepared was identical with that prepared as described from trichloro-acetic acid, and a mixture of the two products melted at the same temperature, 122–123°.

When water was substituted for benzene in the experiment just described, similar results were obtained. In this case, using 15 g. of trichloro-acetic acid and 10 g. of copper powder in 100 cc. of water, the green color appeared in 5 minutes, and in 30 minutes the temperature rose from 23° to 40°. After stirring for 1 hour the solution was filtered from unchanged copper and insoluble copper salts, and evaporated to dryness. The residue was pulverized, suspended in benzene, saturated with hydrogen

<sup>12</sup> In the abstract of the preliminary report of this work, which was presented at the Spring meeting of the American Chemical Society, 1921, and appeared in *Science*, (54, 35 (1921)) it was stated that good results were obtained by carrying out the reaction in benzene solution. The discrepancy in statement is due to the fact that the melting point of aniline trichloro-acetate is 147°, and therefore this salt, which is present if the reaction is incomplete, may be easily mistaken for aniline tetrachloro-succinate, m. p. 149–150°; it was so mistaken in some of the earlier experiments when the latter salt had not been obtained entirely pure and therefore melted slightly low.

<sup>13</sup> This precaution was probably unnecessary. Simply boiling the solution would doubtless have answered as well.

<sup>14</sup> Pucher, *THIS JOURNAL*, 42, 2251 (1920).

chloride, filtered from copper chloride, freed from hydrogen chloride by partial evaporation under diminished pressure and aniline was added. The yield of aniline dichloroacetate was 14.4 g.

While no attempt was made to determine the maximum yield of dichloroacetic acid by this method, it is evident that it is present in the benzene solution before addition of aniline, and could therefore be obtained very easily by fractional distillation. The method has obvious advantages over the older method<sup>15</sup> of preparation from chloral and potassium or sodium cyanide with the attending unpleasant evolution of large quantities of hydrocyanic acid.

In the preparation of dichloroacetic acid from trichloroacetic acid as described above, hydrogen sulfide can be used instead of hydrogen chloride to remove copper, but we have found hydrogen chloride to be the more satisfactory reagent. This method of preparation of dichloroacetic acid is now under investigation in this laboratory to determine the best conditions for obtaining a maximum yield. The results will be published shortly.

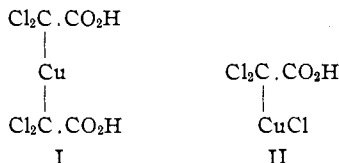
Dichloroacetic acid is also formed when trichloroacetic acid reacts with copper without any solvent. Copper dichloroacetate is found, together with cuprous chloride, in the residue after extraction with ether, and dichloroacetic acid is obtained by suspending this residue in benzene and treating with hydrogen chloride as described above. While we have no numerical data as regards the yield of dichloroacetic acid by this modification, it is apparently not so good as when a solvent is used.

**The Mechanism of the Reaction.**—The formation of dichloroacetic acid from trichloroacetic acid and copper involves the shifting of a hydrogen atom from its labile or ionizable position in the carboxyl group to a position of great stability when joined to the methane carbon atom as in dichloroacetic acid, which raises an interesting question as to the mechanism by which this change takes place. In fairly recent years copper has been used extensively as a condensing agent, particularly by Ullmann.<sup>16</sup> In some cases the action is apparently simply the removal of halogen atoms as in the Würtz or Fittig reaction; thus, with copper powder, iodobenzene gives diphenyl at 230°, and bromobenzene with ethyl chloroacetate gives ethyl phenylacetate at 180–200°. In other cases the action of copper powder appears to be catalytic, as in the reaction of *o*-chlorobenzoic acid with glycooll to form phenylglycine-*o*-carboxylic acid, which is greatly accelerated by the addition of a very minute amount of copper powder. The results obtained in the present investigation appear to us to be somewhat suggestive in this connection.

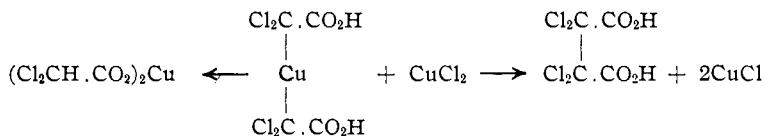
<sup>15</sup> Wallach, *Ann.*, **173**, 288 (1874). Pucher, Ref. 14.

<sup>16</sup> Ullman, *Ber.*, **34**, 2174, 3802 (1901); **36**, 2383 (1903); **37**, 853 (1904); **38**, 729, 2120 (1905); **39**, 1691, 2211 (1906); *Ann.*, **332**, 33 (1904); **350**, 83 (1906). See J. B. Cohen, "Organic Chemistry," Edward Arnold, Part I, p. 199.

When trichloro-acetic acid acted on copper in benzene solution a perfectly clear, dark green solution was obtained after filtering from the insoluble copper salts. After a short time a dark green amorphous precipitate separated from the benzene solution. After filtering again, a dark green, perfectly clear solution was again obtained, from which the dark green amorphous solid soon began to separate. This dark green solid substance, although separating slowly from a clear benzene solution, proved to be totally insoluble in benzene after it had once precipitated. When water was used as solvent in the preparation of dichloro-acetic acid, the copper salt obtained after evaporation of the aqueous solution was also insoluble in benzene. Copper dichloro-acetate, prepared from copper oxide and pure dichloro-acetic acid, is also almost quantitatively insoluble in benzene. It appears, therefore, that the compound which gives the dark green color to the benzene solution cannot be copper dichloro-acetate, nor can it be a chloride of copper, for both cupric and cuprous chlorides are insoluble in benzene. It seems to us that these observations may be satisfactorily explained as follows. Probably the reaction between copper and trichloro-acetic acid involves the formation of a rather unstable compound having the composition of Formula I



which is easily soluble in benzene, giving a dark green solution. Cupric chloride and probably cuprous chloride are formed at the same time. The organo-metallic compound may then react in two ways,



or possibly the initial condensation may give a compound similar to Formula II, two molecules of which may then eliminate cuprous chloride to form tetrachloro-succinic acid, or cupric chloride to form copper dichloro-acetate. There is at present no evidence which would enable one to choose between these possibilities. On either supposition, the relative amounts of tetrachloro-succinic acid and copper dichloro-acetate formed would depend upon the relative velocities of the respective reactions, which would doubtless be greatly affected by temperature and nature of solvent. While the evidence at present available is not sufficient to warrant more than a suggestion, it does seem to us that there is

here some indication as to the possible explanation of the mechanism of reactions in which copper powder or cuprous chloride is used as a condensing agent, not only those of the type mentioned above, but also such as the Sandmeyer and Gattermann reactions in which cuprous salts and copper powder, respectively, are used with diazonium salts. The analogy to the latter reactions is strengthened by the fact that trichloro-methyl compounds also react with cuprous chloride in presence of aqueous ammonia.<sup>2</sup>

So far as we are aware, no compound of the kind suggested has ever been described. Cupric and cuprous acetylides are indeed examples of copper directly linked to carbon, and their instability suggests that this linkage is generally unstable and that compounds of this type may be expected to undergo decomposition or rearrangement very readily to form more stable compounds. It is to be expected, however, that the stability of the copper-carbon linkage would be greatly affected by the nature of the other atoms or groups which are joined to the carbon atom to which the copper atom is also joined. Thus it should not be surprising that a carbon atom may be joined to negative atoms or groups in such a manner as to make the combination sufficiently negative to form a more or less stable linkage with copper, although such combination would be too unstable in most cases to permit isolation and purification of the compound. The relative ionization constants of the chlorinated acetic acids and of the unsaturated acids, such as acetylene dicarboxylic, acrylic, maleic and fumaric, furnish indication that it is precisely among highly chlorinated and unsaturated compounds that we should look for cases of relatively stable linkage between copper and carbon. The acetylides are examples of copper joined to carbon which is joined by the triple linkage to another carbon atom, and the formation of copper acetylides is limited to compounds containing the  $R-C\equiv C-H$  grouping, where copper may replace the hydrogen which is joined to a triply linked carbon. The very great strength of acetylene-dicarboxylic acid, as compared with succinic and maleic acids shows the great negativity of the acetylene linkage. If there is really any truth in the explanation which we offer of the reaction of copper with trichloro-acetic acid, there should be a possibility of similar, and probably more stable compounds of copper with carbon when the carbon atoms are contained in a more "negative" grouping than that represented by "trichloro-ethanoic acid." The replacement of the carboxyl group of this acid by chlorine, or the introduction of an unsaturated linkage in place of the carboxyl group and a chlorine atom would be in the nature of such increase of negativity, and it is precisely in such cases that we have observed the formation of compounds, as yet not further investigated, which appear to support our assumption.

When carbon tetrachloride reacts with copper in presence of aqueous



ammonia, one of the reaction products is a dark brown precipitate, insoluble in water, aqueous ammonia, or the ordinary organic solvents. This substance was washed free from chlorides, suspended in aqueous ammonia through which air was aspirated for 12 hours to remove free copper, and then washed free of ammonia and dried at room temperature. As thus obtained, the dark brown powder dissolved readily in hydrochloric acid, forming a dark maroon solution, which became somewhat lighter in color on addition of an excess of ammonia, but showed no trace of blue, indicating absence of copper ions. When the dark brown powder was heated in a dry tube, however, water was given off and a black residue remained which dissolved readily in hydrochloric acid and gave abundant tests for copper. The substance also apparently contains nitrogen.

In a previous communication<sup>17</sup> a color test for tetrachloro-ethylene was proposed, based upon the behavior of this substance with copper in the presence of aqueous ammonia. It was shown at that time that of all substances tested which contain the trichloro- or tribromo-methyl group, only one, benzotrichloride, failed to bring about fairly rapid solution of the copper to form the characteristic dark blue ammono-cupric solution. On the other hand, substances which did not contain this trihalogen-methyl group did fail to bring about solution of the copper, with two notable exceptions, namely, dichloro-acetic acid and tetrachloro-ethylene. The former contains, to be sure, only two chlorine atoms joined to the methane carbon atom, but there is in addition the negative carboxyl group, so that dichloro-acetic acid would be expected to behave in this respect somewhat similarly to chloroform, and it does. Tetrachloro-ethylene contains a double linkage and two chlorine atoms, joined to the methane carbon and, on the basis outlined above, would be expected to behave somewhat similarly to carbon tetrachloride in respect to its reaction with copper, and the experimental verification is striking. When tetrachloro-ethylene and copper are brought together in presence of aqueous ammonia there is evident and fairly rapid action, but no blue color appears. Instead, copper does go into solution slowly forming a dark maroon solution and, gradually, a dark brown precipitate. After long standing (the bottle was set aside for more than a year) the solution does show the dark blue color characteristic of the ammono-cupric ion. It seems probable that in this case there is the formation at first of a fairly stable organo-copper compound from which the copper is not ionized, which subsequently hydrolyzes or rearranges to give a substance which does give cupric ions. These supposed organo-copper compounds will be investigated as soon as circumstances permit.

The reaction of ammonium trichloro-acetate with copper in aqueous ammonia has not so far yielded satisfactory results. We have obtained

<sup>17</sup> Ref. 1, p. 2690.

a small amount of dichloro-acetic acid, separated and identified as its aniline salt, showing that the course of the reaction is probably similar to that when ammonia is not present, but it is evident that the reaction is more complicated, probably by reason of secondary reactions in which ammonia takes part.

### Summary

The reactions of trichloro-acetic acid and of ethyl trichloro-acetate with copper have been studied. Diethyl tetrachloro-succinate has been prepared by the action of copper with ethyl trichloro-acetate. It boils at 156° and 13 mm. pressure. Tetrachloro-succinic acid is formed in small amount by the action of copper with trichloro-acetic acid alone or in ether solution. The acid was not obtained in pure condition. Aniline tetrachloro-succinate was obtained, m. p. 149–150°.

Dichloro-acetic acid is formed in satisfactory quantity when trichloro-acetic acid reacts with copper powder in benzene or aqueous solution, and this reaction is recommended as a means of preparation of dichloro-acetic acid in any desired quantity.

Evidence is presented from which it seems probable that these reactions involve the formation of an intermediate relatively unstable compound in which copper is joined directly to carbon, and that the course of the reaction is determined by the manner in which the copper is eliminated from this intermediate compound. The suggestion is made that the action of copper as a condensing agent, as used by Ullmann, Sandmeyer and Gattermann, may involve the formation of similar intermediate compounds.

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[CONTRIBUTION FROM THE LABORATORY OF PHARMACEUTICAL CHEMISTRY, UNIVERSITY OF WASHINGTON]

## THE ACTION OF NITROSYL CHLORIDE ON NORMAL HEPTANE

BY E. V. LYNN AND O. HILTON

Received December 15, 1921

It has recently been found by one of us<sup>1</sup> that nitrosyl chloride will readily react with normal heptane in the sunlight, a reaction which is apparently general for the paraffin hydrocarbons. From a preliminary study of the products it was assumed that dipropyl ketone is the chief one, but no satisfactory proof was given. In the present work, we have repeated the former investigation and demonstrated the correctness of the assumptions made then as to the course of the reaction.

Since hydrogen chloride is developed in quantity, the assumption was made that the other product is a nitroso compound. All representatives of this class are known to possess a deep blue color; hence the formation

<sup>1</sup>Lynn, THIS JOURNAL, 41, 368 (1919).