done was that obtained by Lebo[3]: $0.78556\ ^{20^\circ}_{4^\circ}$. Later determinations by Brunel[4] gave the value $0.7808\ ^{25^\circ}_{4^\circ}$.

## Summary

1. First order velocity constants have been determined for the reactions between *iso*propyl alcohol and benzoyl chloride and the following derivatives of benzoyl chloride: *p*-chloro, *p*-bromo, *p*-iodo, *o*-nitro, *p*-nitro and *p*-methyl.

2. A comparison of the activating influence of substituents on the reactivity of the carbon–chlorine bond in derivatives of benzoyl chloride and of diphenylchloromethane shows that negative atoms (Cl, Br, $NO_2$) increase the lability of the bond in acyl chlorides and decrease the lability of the bond in derivatives of diphenylchloromethane. The positive methyl group increases reactivity in the acyl and decreases reactivity in the alkyl compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

# NITROGEN TRICHLORIDE AND UNSATURATED KETONES. II

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The reaction of nitrogen trichloride with benzalacetophenone[2] forms among other products 2-chloro-1-dichloro-amino-1,3-diphenylpropanone-3. The addition is probably to the —C=C— bond as in the corresponding reaction with the unsaturated hydrocarbons[3] and does not involve the carbonyl group.

The reaction has now been studied with benzalacetone. The products obtained with this compound are 2-chloro-1-dichloro-amino-1-phenylbutanone-3 (I), the dichloride of benzalacetone, ammonium chloride and a large amount of nitrogen gas. Product I was reduced by concentrated hydrochloric acid[4] to the corresponding amino chloro ketone II. If the reaction mixture containing I is allowed to stand for several days at room temperature, II will crystallize out as the hydrochloride. Its formation is no doubt due to the hydrochloric acid produced by the decomposition of

[3] Lebo, THIS JOURNAL, **43**, 1005 (1921).

[4] Brunel, *ibid.*, **45**, 1336 (1923).

[1] This paper is an abstract of a part of the thesis submitted by David Craig in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

[2] Coleman and Craig, THIS JOURNAL, **49**, 2593 (1927).

[3] Coleman and Howells, *ibid.*, **45**, 3084 (1923).

[4] The reducing action of hydrochloric acid on chloro-amines was reported by Berg. His best reference is *Ann. chim. phys.*, [7] **3**, 338 (1894).

benzalacetone dichloride. Evidence regarding this decomposition is given in the Experimental Part. This is a more satisfactory method for obtaining the hydrochloride than the treatment with concentrated hydrochloric acid. It is interesting to note that the method may be applied to benzalacetophenone but is not as satisfactory for this compound as the concentrated hydrochloric acid method.

In proving the structure of II, its hydrochloride was reduced with sodium amalgam to the corresponding amino alcohol III. Several attempts to prepare this amino alcohol by other methods were not successful. Its isomer IV was therefore made from 2-amino-1-phenylbutanone-3 by reduction with sodium amalgam. The properties of the two compounds were quite different. Derivatives of both were prepared and analyzed and their molecular weights determined. The reactions for the addition and for the proof of structure of the product are as follows

$$C_6H_5CH{=}CHCOCH_3 + NCl_3 = C_6H_5CH(NCl_2)CH(Cl)COCH_3 \qquad (I)$$

$$C_6H_5CH(NCl_2)CH(Cl)COCH_3 + 2HCl = 2Cl_2 + C_6H_5CH(NH_2)CH(Cl)COCH_3 \qquad (II)$$

$$C_6H_5CH(NH_2)CH(Cl)COCH_3 + 4H = HCl + C_6H_5CH(NH_2)CH_2CH(OH)CH_3 \qquad (III)$$

$$C_6H_5CH_2CH(NH_2)COCH_3 + 2H = C_6H_5CH_2CH(NH_2)CH(OH)CH_3 \qquad (IV)$$

This addition is in agreement with other addition reactions of benzalacetone in which the negative part of the adding molecule attaches itself to the carbon atom farthest from the carbonyl group. Such reactions are those with amines,[5] *p*-toluenesulfinic acid[6] and cyanoacetic esters.[7]

The reaction of nitrogen trichloride with benzalacetone is more rapid than with benzalacetophenone under the same conditions. The yield of addition product obtained with benzalacetone is less and the amount of ammonium chloride greater.

## Experimental Part

Nitrogen trichloride was prepared by the method described by Coleman and Noyes[8] with modifications as described by Coleman and Howells.[3]

**Analysis of Nitrogen Trichloride Solutions.**—Nitrogen trichloride reacts with hydrochloric acid to give ammonium chloride and chlorine. Probably the best method for analyzing nitrogen trichloride solutions utilizes this reaction. The reaction is reversible and the equilibrium adjusts itself very rapidly. However, by the removal of chlorine and the use of a large excess of hydrochloric acid, the reaction can be made to go to completion. It has been found necessary to make special provision for the removal of chlorine when working with the more concentrated solutions. Figure 1 illustrates a satisfactory apparatus for use in analyzing carbon tetrachloride solutions of nitrogen trichloride. C is a 40cc. test-tube half filled with concentrated hydrochloric acid. A is the reaction chamber made from 20-mm. glass tubing and is partially filled with glass beads. B is a side-arm test-tube which is connected to a water pump. For

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[5] Kohn, *Monatsh.*, **28**, 423 (1907).

[6] Kohler and Reimer, *Am. Chem. Jour.*, **31**, 178 (1904).

[7] Kohler and Allen, THIS JOURNAL, **45**, 1987 (1923).

[8] Coleman and Noyes, *ibid.*, **43**, 2211 (1921).

the analysis of 2 cc. of carbon tetrachloride solution containing 3 gm. moles of nitrogen trichloride, 15 cc. of concentrated hydrochloric acid is introduced into A and 10 cc. into B. The sample is introduced into A from a pipet. A and B are then connected by means of a glass tube D and air is drawn through the apparatus rapidly enough so that the yellow color of chlorine and nitrogen trichloride disappears from the mixture in A in about two minutes. A is then heated to about 60° and the current of air continued until the carbon tetrachloride has been carried out of the apparatus. The contents of A and B are united and the amount of ammonia present is determined by distilling from an alkaline solution into 0.1 *N* acid. The mean error of this method is less than three parts per thousand.

**Preparation of the Hydrochloride of 1-Amino-2-chloro-1-phenylbutanone-3.**—One hundred and thirty grams of benzalacetone was dissolved in 500 cc. of dry carbon tetrachloride in a flask fitted with a mercury sealed stirrer and connected to a gasometer. The solution was cooled to −10° and 500 g. of a solution of nitrogen trichloride in carbon tetrachloride, containing 480 mg. moles of nitrogen trichloride, was added through a separatory funnel. The time of addition was about two hours. The evolution of nitrogen began when a small portion of the nitrogen trichloride had been added and continued for a short time after all of the solution had been run in. The reaction mixture was allowed to stand for about five hours. It was then filtered from ammonium chloride and allowed to stand at room temperature for three days. During this time the hydrochloride of 1-amino-2-chloro-1-phenylbutanone-3 crystallized out. The product was nearly pure. It was further purified by dissolving in the least possible amount of absolute alcohol and precipitating by the addition of dry ether. The compound melted with decomposition at 176–177°. The yield of the pure product was about 5%.

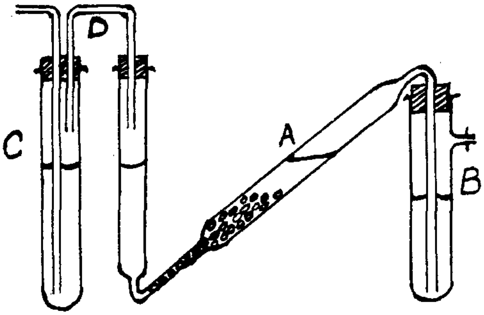

Fig. 1.

*Anal.* Subs., 0.0630: 28.30 cc. of 0.01 *N* HCl. Calcd. for $C_{10}H_{12}OClNHCl$: N, 5.99. Found: 6.29.

In another run the reaction mixture containing the dichloroamine was shaken with 50 cc. of concentrated hydrochloric acid for thirty minutes. The hydrochloride was obtained in the aqueous layer but was not isolated. By treating with benzoyl chloride according to the Schotten-Baumann procedure two products were obtained, the preparation of which from the pure hydrochloride is described in the next paragraph.

**Benzoyl-1-amino-2-chloro-1-phenylbutanone-3.**—This derivative was obtained in 70% yield by refluxing 0.5 g. of the hydrochloride with 0.5 cc. of benzoyl chloride in 10 cc. of benzene for several hours. After cooling and filtering the product was recrystallized from alcohol or from 140–160° boiling ligroin; m. p. 160–161° (uncorr.).

*Anal.* Subs., 0.0726: 24.40 cc. of 0.01 *N* HCl. Calcd. for $C_{17}H_{16}ClO_2N$: N, 4.64. Found: 4.71.

Subs., 0.2625: 8.53 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{17}H_{16}ClO_2N$: Cl, 11.74. Found: 11.54.

Benzoylation by the usual Schotten-Baumann procedure yielded the benzoyl derivative and a side product. The side product is almost insoluble in high boiling ligroin and melts with decomposition at 204° after being recrystallized from alcohol. It has about the same nitrogen content as the benzoyl derivative. Its structure was not determined.

**Benzoyl-1-amino-1-phenylbutanol-3.**—Since the benzoylation by means of the Schotten-Baumann procedure yielded two products, it was thought advisable to reduce the one which was most likely the true benzoyl derivative, that is, the one melting at 160–161°. The reduction was carried out in warm alcohol by means of sodium amalgam. Meanwhile the solution was kept slightly acid by means of 6 *N* hydrochloric acid. Most of the alcohol was then boiled out, the solution cooled and the product recrystallized from 140–160° boiling ligroin; m. p. 150–151° (uncorr.); yield, 67%.

*Anal.* Subs., 0.0494: 19.15 cc. of 0.01 *N* HCl. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: 5.43.

**1-Amino-1-phenylbutanol-3.**—Three grams of the pure hydrochloride of the amino chloro ketone was dissolved in 20 cc. of water and 189 g. of 2.5% sodium amalgam added in small pieces during an hour. The mixture was stirred and 6 *N* hydrochloric acid added rapidly enough to keep the solution slightly acid to litmus. The solution was poured from the mercury, made alkaline and extracted twice with ether. The ethereal solution was dried with sodium sulfate and evaporated to dryness on the steam-bath. On cooling 1.8 g. (85%) of 1-amino-1-phenylbutanol-3 was obtained. After two recrystallizations from 60–80° boiling ligroin, the product melted at 74–76° (uncorr.).

*Anal.* Subs., 0.0500, 0.0684: 5.91, 8.05 cc. of 0.05 *N* HCl. Calcd. for $C_{10}H_{15}ON$: N, 8.49. Found: 8.28, 8.25.

**Acetylation Value.**—Subs. 0.1842: 1.32 mg. equiv. of acetic anhydride. Calcd. for one $NH_2$: 1.00. Found: 1.18.

The acetate of this amino alcohol is probably soluble in water. At least under the experimental conditions it was saponified.[9]

**Dibenzoyl Derivative of 1-Amino-1-phenylbutanol-3.**—This derivative was prepared by refluxing 0.3 g. of the amino alcohol with 0.54 cc. of benzoyl chloride and 5 cc. of xylene for two hours. On cooling 0.46 g. of the derivative was obtained. After recrystallizing from xylene the product melted at 139–141° (uncorr.). Benzene can be used in this procedure but because of its lower boiling point does not give as satisfactory results.

*Anal.* Subs., 0.0848: 22.90 cc. of 0.01 *N* HCl. Calcd. for $C_{24}H_{23}O_3N$: N, 3.76. Found: 3.79.

*Molecular Weight Determination.*—Subs., 0.0264: 0.4496 g. of camphor. Melting-point depression, 6.2°. Calcd. for $C_{24}H_{23}O_3N$: 373. Found: 379.

**2-Amino-1-phenylbutanol-3.**—Ten grams of the hydrochloride of 2-amino-1-phenylbutanone-3, prepared as described by Sonn,[10] was dissolved in water and 184 g. of 2.5% sodium amalgam added in small pieces and with stirring during an hour. The mixture was kept slightly acid with 6 *N* hydrochloric acid. The solution was poured from the mercury, treated with Norit, filtered, and extracted with ether. It was then made alkaline and extracted twice with ether. The ether extractions were united and dried with sodium sulfate. After evaporating the ether on the steam-bath and cooling, 3.2 g. of the amino alcohol was obtained. It melted at 62–64° (uncorr.) after being recrystallized from 60–80° boiling ligroin.

*Anal.* Subs., 0.2086: 25.01 cc. of 0.05 *N* HCl. Calcd. for $C_{10}H_{15}ON$: N, 8.49. Found: 8.40.

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[9] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1904**, Vol. I, p. 152. See also Coleman and Craig, ref. 2, p. 2595.

[10] Sonn, *Ber.*, **40**, 4666 (1907).

The hydrochloride of this compound was prepared and melted at 114–116° (uncorr.).

**Benzoyl-2-amino-1-phenylbutanol-3.**—This compound was obtained by refluxing a mixture of one mole of the amino alcohol with two moles of benzoyl chloride in benzene for three hours. It was also obtained by treating the amino alcohol according to the usual Schotten-Baumann procedure with benzoyl chloride. It melted at 177–179° (uncorr.) after two recrystallizations from 50% alcohol.

*Anal.* Subs., 0.0610: 22.70 cc. of 0.01 *N* HCl. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: 5.21.

*Molecular Weight Determination.*—Subs., 0.0205, 0.0287: 0.3085, 0.3801 g. of camphor. Melting point depression, 9.4°, 11.0°. Calcd. for $C_{17}H_{19}O_2N$: 269. Found: 283, 274.

**1-Chloro-1-phenyl-1-butenone-3.**—The reaction of nitrogen trichloride with benzalacetone produced a large amount of benzalacetone dichloride. Since in the reaction mixture this compound was unstable toward heat and evolved hydrochloric acid, the solvent was evaporated at room temperature under reduced pressure. The yield of the dichloride obtained after recrystallizing the residue from alcohol was about 45%. This slightly impure product on standing for several weeks began to decompose into hydrochloric acid and 1-chloro-1-phenyl-1-butenone-3. At the temperature of the water-bath this decomposition was complete in a few days. This monochloro unsaturated ketone was obtained by distilling the resulting oil under reduced pressure. It boils at 155–156° at 23 mm.

*Anal.* Subs., 0.5691: 32.25 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{10}H_9ClO$: Cl, 19.65. Found: 20.09.

The oxime of this compound was prepared and analyzed. It was obtained in 65–70% yield, using hydroxylamine hydrochloride in alcohol–water solution in the presence of sodium acetate. It melted at 132–134° after being recrystallized from alcohol and its properties agree with those of the compound prepared by Goldschmidt.[11]

Benzalacetone dichloride may be obtained pure from the slightly impure product mentioned above by recrystallizing twice from alcohol. When so obtained it is stable at room temperature and can be distilled without decomposition at 159–160° at 21 mm. It melts at 93–94°.

## Summary

1. Benzalacetone reacts with nitrogen trichloride in carbon tetrachloride solution to form among other products 2-chloro-1-dichloroamino-1-phenylbutanone-3. The addition is to the —C=C— bond and does not involve the carbonyl group. The addition product was reduced to the corresponding amino chloro ketone, the structure of which was established.

2. Benzalacetone dichloride, also formed in this reaction, decomposes in the reaction mixture at room temperature to 1-chloro-1-phenyl-1-butenone-3 and hydrochloric acid.

3. A method is given for the analysis of concentrated solutions of nitrogen trichloride.

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[11] Goldschmidt, *Ber.*, **28**, 1532 (1895).