[Contribution from the Department of Chemistry of the University of Buffalo]

THE ACTION OF ANILINE AND ITS HYDROCHLORIDE ON CERTAIN ORTHOCARBONATES[1]

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INTRODUCTION

In 1866, Hofmann (1) found that aqueous ammonia and ethyl orthocarbonate reacted to form guanidine. Later, Bender (2) reported that aniline and ethyl orthocarbonate formed carbanilide when heated in a sealed tube. It was the purpose of this investigation to trace the steps in the formation of carbanilide from the orthocarbonate and aniline, and to follow up possible side-reactions.

DISCUSSION

In the preliminary experiments in this laboratory, ethyl orthocarbonate was refluxed with aniline for several hours. Carbanilide and triphenylguanidine were both isolated. It was later found that small amounts of aniline hydrochloride acted as a catalyst for the formation of the latter compound. For the purpose of isolating any possible intermediates, aniline and ethyl orthocarbonate were refluxed in 1:1 molar ratio under an efficient fractionating column. The progress of the reaction was noted by collecting the ethyl alcohol as formed and the reaction was stopped when an amount of ethyl alcohol had been collected which indicated reaction in a 1:1 molar ratio:

$$\text{(II)}\ C(OC_2H_5)_4 + C_6H_5NH_2 \rightarrow C_6H_5NHC(OC_2H_5)_3 + C_2H_5OH$$

However, fractionation of the residue at reduced pressure gave a compound which was later identified as diethyl phenylimidocarbonate. Evidently the reaction had gone farther:

$$\text{(II)}\ C_6H_5NHC(OC_2H_5)_3 \rightarrow C_6H_5N{=}C(OC_2H_5)_2 + C_2H_5OH$$

Experiments were then carried out to determine whether or not aniline hydrochloride could act as a catalyst for the formation of this intermediate or for any other step. First, aniline hydrochloride was refluxed with ethyl orthocarbonate for forty five minutes (reaction 6, Table I). At the end of this time the reaction appeared to have gone to completion:

$$\text{(III)}\ C(OC_2H_5)_4 + C_6H_5NH_3Cl \rightarrow C_6H_5NHCOOC_2H_5 + C_2H_5Cl + C_2H_5OH$$

Ethyl chloride was isolated in a salt and ice trap but was not identified beyond the determination of its boiling point (11–15°). A small amount of diethyl phenylimidocarbonate was also isolated here. Using butyl orthocarbonate, the yield of butyl chloride amounted to 79%, of butyl alcohol 79%, and of butyl

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N-phenylcarbamate 37%. By reference to reactions 1 through 5 of Table I, it will be seen that relatively small amounts of aniline hydrochloride seem to catalyze the formation of diethyl phenylimidocarbonate, while stoichiometric amounts set up a reaction in an entirely different direction, as shown in equation III.

The temperature was maintained at a value sufficient to cause continued gentle refluxing. It is obvious however that continued refluxing was detrimental to the yield of diethyl phenylimidocarbonate—as a matter of fact this compound has been shown definitely to undergo pyrolysis at the temperatures used.

Smith (3) has found that dimethyl phenylimidocarbonate reacts with aniline in the cold to form carbanilide. More information relative to this reaction seemed desirable. It has been found in this work that diethyl phenylimidocarbonate undergoes pyrolysis when heated to 240–260° giving phenylurethan and ethylene:

TABLE I

VARIATION OF YIELDS WITH AMOUNT OF ANILINE HYDROCHLORIDE

REACTANTS, GRAMS				TIME, HRS.	YIELD, GRAMS	
No.	$C_6H_5NH_2$	$C(OC_2H_5)_4$	$C_6H_5NH_3Cl$		C_2H_5OH	$C_6H_5N=C(OC_2H_5)_2$
1	12.1	25	0.0	12	9.0	6.0, 24%
2	12.1	25	0.0	5	6.0	11.7, 47%
3	11.7	25	0.5	2	11.0	18.0, 72%
4	11.7	25	0.5	1	11.0	18.0, 72%
5	11.3	25	1.0	0.25	10.0	15.5, 62%
6	0.0	25	16.8	0.75	10.5	2.5, 10%

$$\text{(IV) } C_6H_5N{=}C(OC_2H_5)_2 \rightarrow C_6H_5NHCOOC_2H_5 + C_2H_4$$

In later experiments small amounts of phenyl isocyanate and ethyl alcohol were also isolated, perhaps according to the equation:

$$\text{(V) } C_6H_5N{=}C(OC_2H_5)_2 \rightarrow C_6H_5NCO + C_2H_5OH + C_2H_4$$

The urethan is undoubtedly the intermediate as has already been noted (4). It is proposed that decomposition takes place in accordance with equations IV and V, and not along the lines suggested for diphenyl phenylimidocarbonate by Harley-Mason (5). Ethyl N-ethylphenylcarbamate would have been an intermediate if Harley-Mason's mechanism had been followed. This compound was not detected at any time.

It is possible that hydrochloric acid could have been eliminated from aniline hydrochloride, and could then have added to and reacted with diethyl phenylimidocarbonate to form phenylurethan. It has been found here that dry hydrogen chloride is absorbed by diethyl phenylimidocarbonate exothermally with production of phenylurethan and probably of ethyl chloride:

$$\text{(VI) } C_6H_5N{=}C(OC_2H_5)_2 + HCl \rightarrow C_6H_5NHCOOC_2H_5 + C_2H_5Cl$$

On the basis of this evidence the mechanism for the formation of phenylurethan could be constructed as:

$$(\text{VII})\quad \mathrm{C_6H_5NH_3Cl \rightarrow C_6H_5NH_2 + HCl}$$

$$(\text{VIII})\quad \mathrm{C_6H_5NH_2 + C(OC_2H_5)_4 \rightarrow C_6H_5N{=}C(OC_2H_5)_2 + 2\ C_2H_5OH}$$

$$(\text{IX})\quad \mathrm{C_6H_5N{=}C(OC_2H_5)_2 + HCl \rightarrow C_6H_5NHC(Cl)(OC_2H_5)_2}$$

$$(\text{X})\quad \mathrm{C_6H_5NHC(Cl)(OC_2H_5)_2 \rightarrow C_6H_5NHCOOC_2H_5 + C_2H_5Cl}$$

No reaction has been found in this work between pure aniline and pure diethyl phenylimidocarbonate at room temperatures. Smith (3) found carbanilide resulting from the action of dimethyl phenylimidocarbonate and aniline. Smith's results have been verified, only on addition of hydrochloric acid:

$$(\text{XI})\quad \mathrm{C_6H_5N{=}C(OC_2H_5)_2 + HCl + HOH \rightarrow C_6H_5NH_3Cl + CO(OC_2H_5)_2}$$

$$(\text{XII})\quad \mathrm{C_6H_5NH_2 + C_6H_5NH_3Cl + CO(OC_2H_5)_2 \rightarrow CO(NHC_6H_5)_2 + 2\ C_2H_5OH + HCl}$$

It has also been found that refluxing the mixture of aniline and diethyl phenylimidocarbonate produces carbanilide and diphenylguanidine. Inasmuch as diethyl phenylimidocarbonate decomposes pyrolytically into phenylurethan and phenyl isocyanate, this fact may also account for the formation of carbanilide:

$$(\text{XIII})\quad \mathrm{C_6H_5NCO + C_6H_5NH_2 \rightarrow CO(NHC_6H_5)_2}$$

Wilm and Wischin (6) have found that equation (XIII) is valid when the reactants are heated in a sealed tube.

Lakra and Dains (7) and Schiff (8) have also submitted evidence to this end.

Thus there is no evidence of a reaction between aniline and diethyl phenylimidocarbonate at room temperatures, but if the system is heated to the temperature at which the latter decomposes according to Equation IV, triphenylguanidine results. Two mechanisms may be suggested, (A) the stepwise substitution of anilino groups for ethoxyl to form triphenylguanidine and (B) the pyrolytic decomposition of the imino compound giving phenylurethan, followed by a reaction between the urethan and aniline.

Mechanism A

$$(\text{XIV})\quad \mathrm{C_6H_5N{=}C(OC_2H_5)_2 + C_6H_5NH_2 \rightarrow C_6H_5N{=}C(OC_2H_5)NHC_6H_5 + C_2H_5OH}$$

$$(\text{XV})\quad \mathrm{C_6H_5N{=}C(OC_2H_5)NHC_6H_5 \rightarrow C_6H_5NHCONHC_6H_5 + C_2H_4}$$

$$(\text{XVI})\quad \mathrm{C_6H_5N{=}C(OC_2H_5)NHC_6H_5 + C_6H_5NH_2 \qquad C_6H_5N{=}C(NHC_6H_5)_2 + C_2H_5OH}$$

Mechanism B

Begins with Equation IV

(XVII) $C_6H_5NHCOOC_2H_5 + C_6H_5NH_2 \rightarrow C_6H_5NHCONHC_6H_5 + C_2H_5OH$

(XVIII) $3\ C_6H_5NHCONHC_6H_5 \rightarrow 2\ C_6H_5N{=}C(NHC_6H_5)_2 + CO_2 + HOH$

Equation XVIII has been shown to be correct by Barr (9). Further contributions were made at various times by Dains (10), and by Weith (11).

It seems logical to assume that the reaction between ethyl orthocarbonate and aniline to form the products discussed takes the course indicated by Equations I, II, IV, and XVII in that order.

EXPERIMENTAL PART

Chloropicrin and phenyliminodichloromethane were purchased from the Eastman Kodak Co. and were used after satisfactory determination of physical constants.

Aniline was purchased from the J. T. Baker Co., dried over sodium hydroxide and freshly distilled before each experiment.

Ethyl orthocarbonate and other reagents were prepared as outlined by Tieckelmann and Post (12).

Ethyl orthocarbonate and aniline. Twenty grams (0.1 mole) of ethyl orthocarbonate and 29 g. (0.31 mole) of aniline were heated on an oil-bath to reflux temperatures. At the outset the temperature of the bath was 170° but was gradually raised to 240° at the end of 12 hours. The yield of ethyl alcohol distilling smoothly throughout the reaction amounted to 13 g. (0.28 mole) at the end of the 12 hours, or 68% of the ethoxyl originally present. The residue was dissolved in hot ethyl alcohol and poured into one liter of cold dilute HCl to separate more basic material from the carbanilide. The latter was filtered and washed with water, 29 g., 84% yield. After recrystallization from glacial acetic acid, it melted at 238–239°. N, 13.0 found; 13.2, calculated. On neutralization of the acid filtrate with NH_4OH, 0.8 g. of *sym.*-triphenylguanidine precipitated, m.p. 144–145°, N, 14.5 found; 14.63, calculated, no depression in mixed melting point with sample purchased from Eastman Kokak Company.

Twenty-five grams (0.13 mole) of ethyl orthocarbonate and 12.1 g. of aniline (0.13 mole) were refluxed similarly for 10 hours. Products were 8 g. of ethyl alcohol, 6 g. of a liquid boiling at 126° (12 mm.) and 9 g. of unreacted material. The solid which formed and clogged the fractionating column proved to be carbanilide, m.p. 239°. The liquid distillate was diethyl phenylimidocarbonate, b.p. 247° (751 mm.), n_D^{22} 1.5161.

Anal. Calc'd for $C_{11}H_{15}NO_2$: C, 68.36; H, 8.85; N, 7.25; C_2H_5O, 46.6.
Found: C, 68.9; H, 8.3; N, 7.33; C_2H_5O, 45.2.

Ethyl orthocarbonate and aniline in the presence of aniline hydrochloride. Twenty grams (0.1 mole) of ethyl orthocarbonate, 29 g. (0.31 mole) of aniline, and 0.5 g. (0.04 mole) of aniline hydrochloride were refluxed at temperatures slowly rising to 250° with constant distillation of ethyl alcohol. After 10 hours, 10 g. (0.22 mole) of alcohol had been removed after which 11 g. (0.12 mole) of unreacted aniline distilled over. A hot alcoholic extract of the solid residue was poured into one liter of ice cold dilute hydrochloric acid and the insoluble diphenylcarbanilide filtered and washed with water. Yield 17.5 grams (64%), m.p. 238–239° after recrystallization from glacial acetic acid, nitrogen found 13.2, calculated 13.20. *Sym.*-triphenylguanidine was precipitated from the acid liquors by addition of ammonium hydroxide. It was washed with alcohol and recrystallized therefrom, m.p. 145–146°.

Anal. Calc'd for $C_{19}H_{17}N_3$: C, 79.46; H, 5.97; N, 14.63.
Found: C, 79.7; H, 6.06; N, 14.4.

Using ethyl orthocarbonate and aniline in 1:1 molar ratio and distilling the residue at reduced pressure, the main product was diethyl phenylimidocarbonate b.p. 123–125° (12 mm.), nitrogen, found 7.21; calculated, 7.25. Data on comparative yields will be found in Table I.

Ethyl orthocarbonate and aniline hydrochloride were allowed to react in 1:1 molar ratio, 0.13 mole of each, under reflux conditions, with the temperature slowly rising to 100° over a period of fifteen minutes. After an additional hour's refluxing, 10.5 g. of ethyl alcohol was distilled and five grams of ethyl orthocarbonate was recovered. The residue was distilled at reduced pressure between 124° and 145° at 12 mm., weight 18.2 g. On further fractionation, there was obtained 2.5 g. of diethyl phenylimidocarbonate, b.p. 124–126° (12 mm.) and 12 g. of phenylurethan, m.p. 49–50°, nitrogen, found 8.58, calculated, 8.49. The volatile product of the reaction, collected in an ice and salt trap was undoubtedly ethyl chloride although actual identification was incomplete.

Butyl orthocarbonate and aniline hydrochloride were refluxed as above, using 0.033 mole of each. A product, assumed to be butyl chloride was collected, weight 2 g., b.p. 76–78°, $n_{\rm D}^{20}$ 1.4030, yield 66%. This product gave a negative halogen test with alcoholic silver nitrate but after fusion with sodium and extraction with water, easily precipitated silver chloride. The residue, 3.5 g., when recrystallized from ligroin gave butyl N-phenylcarbamate, m.p. 58–60°, nitrogen, found 7.39; calculated, 7.26.

Thermal decomposition of diethyl phenylimidocarbonate. These decomposition reactions were run in a 200-cc. flask connected with a fractionating column. The column was connected directly with a trap immersed in ice-water. Two 1″ x 10″ test tubes, each containing 18 g. of bromine covered with a little water were connected in series with this trap. The exit tube from the second bromine reaction tube was connected to a funnel inverted over a saturated solution of sodium bisulfite. Thirty grams of freshly distilled diethyl phenylimidocarbonate was placed in the flask, then heated to 260°. A gas was given off and absorbed by the bromine. At the end of two hours, when the evolution of gas had ceased, the contents of the bromine tubes were decolorized with sodium bisulfite, washed with sodium bicarbonate and water, dried over calcium chloride and distilled. Yield of ethylene dibromide 23 g., 79% b.p. 130° (uncorr.), m.p. 9°, $n_{\rm D}^{23}$ 1.5372. The residue in the flask was distilled at reduced pressures, and gave a small amount of phenyl isocyanate and 18 g. of phenylurethan, m.p. 50–51°, nitrogen, found 8.62; calculated, 8.49. A small amount of what may have been carbanilide, m.p. 235° had sublimed on the cold-finger condenser and from the residue in the reaction flask there was obtained a small amount of what may have been triphenyl cyanurate, m.p. 262–265°, literature 270°.

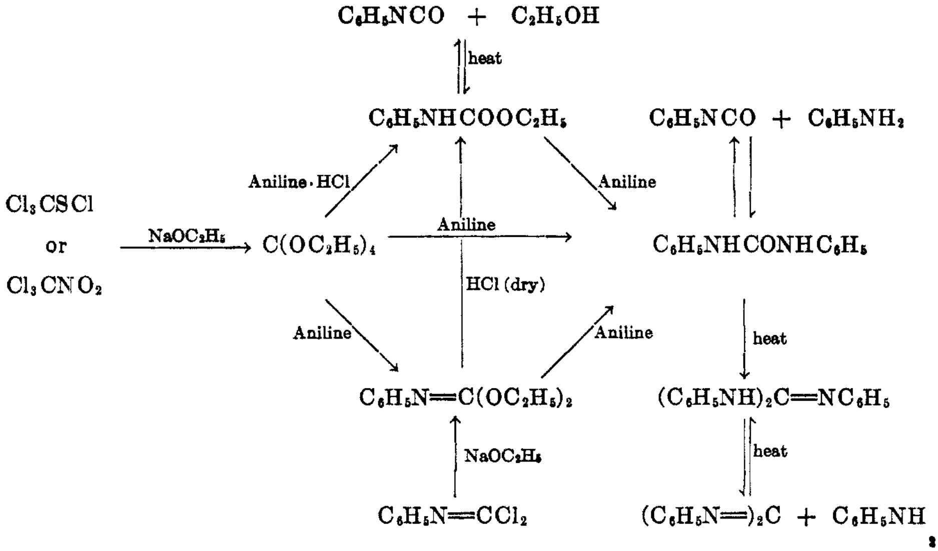
Diethyl phenylimidocarbonate and aniline. Equimolar parts (0.078 mole each) of diethyl phenylimidocarbonate and aniline were refluxed. The outlet of the condenser was provided with two bromine tubes as before. The oil-bath with which the system was heated was kept at 230° for 45 minutes with no evidence of the evolution of ethylene. But at 250° ethylene was produced and was absorbed by the bromine. At the end of two hours the evolution of ethylene had ceased. Ethylene bromide 9.3 g., 63% yield. Ethyl alcohol, 3.2 g., 89% yield was obtained by partially distilling the residue. The solid remaining was recrystallized from glacial acetic acid, weight 4 g., 24% yield, of carbanilide, m.p. 238–239°, nitrogen, 13.1 found; 13.20, calculated. There was also obtained 7.5 g. of *sym.*-triphenylguanidine, 34% yield, m.p. 144–145°, nitrogen, found 14.5; calculated, 14.63. Equimolar parts of these two reactants (0.086 mole) were mixed and allowed to stand at room temperature. There was no visible sign of change at the end of one month. Periodically, 1 cc. of this mixture was removed and treated with 20 cc. of 3 *N* hydrochloric acid. Both carbanilide and phenylurethan are insoluble under these conditions. An odor of ethyl carbonate was easily detected in each test. One drop of concentrated hydrochloric acid was added to 1 cc. of the above mixture of aniline and diethyl phenylimidocarbonate. At the end of 24 hours a thick precipitate had formed, which on filtration and recrystallization from glacial acetic acid gave about 0.6 g. of carbanilide, m.p. 235°. A mixed m.p. with a known sample of carbanilide showed no depression. A small amount of phenylurethan was isolated when the filtrate was poured into water, m.p. 50–51°. The mixed melting point again was identical.

Dry hydrogen chloride and diethyl phenylimidocarbonate. Twenty grams (0.1 mole) of diethyl phenylimidocarbonate was placed in a 250-cc. flask and dry hydrogen chloride gas passed over the liquid surface. The gas was absorbed exothermally, with rise of temperature to 40°. Excess hydrogen chloride and possibly other volatile products were removed by suction and from the residue there was obtained by filtration 17.2 g. of a solid, 17.1 theoretical for phenylurethan, m.p. 50–51° (after recrystallization from ethyl alcohol) no depression on determination of mixed melting point with a known sample.

SUMMARY

1. Aniline reacts with ethyl orthocarbonate to form carbanilide, diethyl phenylimidocarbonate and triphenylguanidine (Chart I).

Chart I



2. Aniline hydrochloride reacts with ethyl orthocarbonate to form phenylurethan (Equation III).

3. Diethyl phenylimidocarbonate decomposes when heated to form phenylurethan and ethylene (Equation IV).

4. Dry hydrogen chloride reacts with diethyl phenylimidocarbonate to form phenylurethan (Equation VI).

5. Diethyl phenylimidocarbonate does not react with aniline in the cold. Carbanilide and phenylurethan are formed in the presence of hydrochloric acid (Equations XI, XII).

6. Pure dry diethyl phenylimidocarbonate reacts with aniline to form carbanilide at 250–260° (Equations IV, XVII).

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