sults among one another will show whether any chlorine escapes or whether any other variable sources of error lie in the chemical reaction itself. The results of four such determinations follow. The weight of dish, cover and rod was less than 70 g.

Exp. A. Dish + $AgNO_3$ minus weight after = 0.5311 g. $w_1 - w = 0.0001$. Wt. sol. 50.0445 g.

Exp. B. Dish + $AgNO_3$ minus weight after = 0.5316 g. $w_1 - w = 0.0004$. Wt. sol. 50.0548 g.

Exp. C. Dish + $AgNO_3$ minus weight after = 0.53105 g. $w_1 - w = 0.0001$. Wt. sol. 50.0391 g.

Exp. D. Dish + $AgNO_3$ minus weight after = 0.5310 g. $w_1 - w = 0.00005$. Wt. sol. 50.0396 g.

Hence, the loss (corrected by companion dish) is respectively, per 50 g. of solution taken: in A 0.53063, in B 0.53062, in C 0.53095, in D 0.53054. Since the balance was sensitive to only 0.05 mg. it is evident that errors of weighing alone account fully for the surprisingly small variations observed. It is, further, clear that these errors may be diminished if there were any object in so doing, by operating with normal instead of 0.2 *N* solutions. The disadvantage that the loss of weight is a smaller quantity than the absolute weight of the HCl determined, so that all errors are multiplied by the factor 1.37, is made unimportant by the great accuracy of the process in itself. In spite of its precision, the method is not time-consuming, as the evaporations require no oversight. The time spent is, practically, only that required by the weighings. Most of this work was done in the laboratory of the Andrews Chemical Works, Davenport, Iowa.

WASHINGTON, D. C.

CORRECTION.

Correction for article on "The Potential of Silver in Nonaqueous Solutions of Silver Nitrate," by Vernette L. Gibbons and F. H. Getman, which appeared in the August number of THIS JOURNAL, page 1645: The last five values in Table X should have been headed Table XI.—Solutions in Pyridine.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

BENZOYLATIONS IN ETHER SOLUTION.

BY WILLIAM M. DEHN AND ALICE A. BALL.

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In a former paper[1] it was shown that acetyl chloride reacts in anhydrous ether solutions with primary, secondary and tertiary bases. The initial products were invariably additive products and these, by simple splitting or by hydrolysis, yielded the ordinary acetylated products.

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[1] THIS JOURNAL, 34, 1399 (1912).

This paper includes analogous studies with benzoyl chloride. With this, as with acetyl chloride, the hydrochlorides of the original base and the acyl chloride additive products of the original bases were precipitated as mixtures. These were often contaminated with the original bases or with benzoylated bases, when such were insoluble in ether; as in cases of the aromatic derivatives benzanilide, benztoluidides, benznaphthalides,[1] benzphenylhydrazine, etc. The courses of these reactions are indicated in the equations:

$$\begin{tikzcd}
(1)\ \mathrm{BzCl} + 2\mathrm{RNH_2} \arrow[r] \arrow[dr] & \mathrm{RBzNH.HCl} \arrow[r, shift left] & \mathrm{HCl} + \mathrm{RBzNH} \arrow[l, shift left] \arrow[dl] \\
 & \mathrm{RNH_2.HCl} &
\end{tikzcd}$$

$$\begin{tikzcd}
(2)\ \mathrm{BzCl} + 2\mathrm{R_2NH} \arrow[r] \arrow[dr] & \mathrm{R_2BzN.HCl} \arrow[r, shift left] & \mathrm{HCl} + \mathrm{R_2BzN} \arrow[l, shift left] \arrow[dl] \\
 & \mathrm{R_2NH.HCl} &
\end{tikzcd}$$

$$(3)\ \mathrm{BzCl} + \mathrm{R_3N} \rightleftarrows \mathrm{R_3BzNCl}$$

For the purpose of excluding moisture, the benzoyl chloride was redistilled with proper protection from the atmosphere when 60 g. were transferred to two liters of anhydrous ether. The latter was siphoned into a self-filling 100 cc. buret, the flask and buret being supplied with calcium chloride tubes. Glass-stoppered, amber-colored bottles of proper size were previously dried by lumps of fused calcium chloride. Into these, 100 cc. of the ether solution, containing 3 g. of benzoyl chloride, were run, so that the ether solution was at no time in contact with atmospheric moisture. The stopper of each bottle having been sealed with paraffin, the solutions were set aside, to be treated, when desired, with one molecular weight of the anhydrous base. If the base was insoluble in ether, it was powdered and added directly; contact with the latter solutions was promoted by shaking.

When it was found that the amber-colored glass of the bottles retarded the reactions, the contents of the bottles were transferred to colorless, previously desiccated, bottles. In the latter bottles the accelerating influence of sunlight could be observed. It was found that most of the compounds crystallized on the inner surfaces of the bottles facing the direct sunlight. Often the rate of precipitation was retarded when the sides of the containers became coated, but further precipitation could be obtained either when the precipitate was shaken off or when the liquid was transferred to another container.

The precipitates were filtered rapidly, washed with anhydrous ether and dried in desiccators. In some cases the additive products were so hygroscopic that their melting points and analyses could not be obtained without considerable error. In some cases the products were analyzed in the containers in which they were formed; in other cases, as with *p*-

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[1] For the complete analysis of a typical mixture see that of α-naphthylamine.

benztoluidide hydrochloride, indirect methods of analysis were resorted to.

The analyses for halogen were made by the Volhard method. The percentages found were equal to: (1) the percentages of chlorine contained in the hydrochloride of the original base; (2) some percentage lying between this and the percentage of the additive compound; (3) the percentage contained in the additive compound; and (4) some percentage less than the percentage of the additive compound. Thus there were indicated: (1) the hydrochloride of the original base; (2) a mixture of this with the additive compound and sometimes with the benzoylated base; (3) the additive compound; and (4) a mixture of this with a preponderance of the benzoylated base.

The benzoyl chloride additive products of the primary and secondary bases were prepared by two methods: (*a*) as indicated by reactions (1) and (2); and (*b*) by adding hydrogen chloride[1] to anhydrous ether or hydrocarbon solutions of the benzoylated derivatives indicated in (5) and (6). The latter method, of course, yielded pure products; the former method, for reasons indicated, yielded mixtures.

With the additive products of benzoyl chloride as of acetyl chloride, spinning motions[2] were produced when the substances were floated on water. Since these motions were produced even by mixtures with low percentages of the additive products, such movements invariably served as a test for their presence.

Many of these pentavalent nitrogen derivatives of the bases are unstable toward heat and all are extremely unstable toward water. For instance, the benzoyl chloride additive product of *p*-toluidine decomposes in a desiccator at 19°, in accordance with the reaction:

$$(4)\quad CH_3C_6H_4.BzNH.HCl \longrightarrow CH_3C_6H_4.BzNH + HCl$$

Towards water, the benzoyl chloride additive products of the respective bases react as follows:

$$(5)\quad RBzNH.HCl + H_2O \longrightarrow RBzNH + H_2O.HCl$$

$$(6)\quad R_2BzN.HCl + H_2O \longrightarrow R_2BzN + H_2O.HCl$$

$$(7)\quad R_3BzNCl + H_2O \longrightarrow R_3N + BzOH + HCl$$

Thus it is observed that heat and water yield the same dissociated products. On account of their instability toward heat and especially toward water, their preparation and handling required correct physical conditions, especially the rigorous exclusion of moisture. The bases were dried with fused potash and usually were distilled over metallic sodium in thoroughly desiccated vessels. However, owing to the small molecular weight of water

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[1] The best method used for adding the hydrogen chloride was by means of a solution of it in toluene. The concentration of this was determined by titration, and thus equimolecular quantities could be added.

[2] THIS JOURNAL, 34, 1400 (1912).

as compared with that of benzoylated derivatives, even traces of moisture often yielded a preponderance of the secondary products.

The trace of water may react in accordance with Equations 5 and 6 forming hydrochloric acid, which in turn may react with the original base, forming the salt and freeing the water. Thus a trace of moisture may catalytically yield a preponderance of salt of the original base. When the speed of reaction is rapid, benzoyl chloride and the base being present in equimolecular quantities, this influence may not operate so largely. This is seen in cases of piperidine and benzylethylamine; the former, precipitating rapidly, yielded 32% and the latter, precipitating slowly, yielded 18% of the additive compounds.

A condition of supersaturation of the ether solution may also intervene, thus favoring the kinetic dissociation of the additive product, so as to yield a preponderance of salt of the original base. That this influence does not operate in cases of the tertiary bases is owing to the absence of hydrogen chloride.

The formation of additive compounds, when benzoyl chloride acts upon bases in anhydrous ether, cannot be explained on the basis of ionization for the reasons: (1) a non-ionizing medium is used; (2) the speeds of reaction vary widely with different bases; (3) sunlight, which is not recognized as an accelerator of ionization, promotes all of the condensations; and (4) other phenomena not reconcilable with ionization are observed.

Of course, it may be maintained that a trace of water promotes the ionization of benzoyl chloride and the bases and, indeed, that ether itself is an ionizing medium. If either or both of these assumptions are true, the speed of reaction should be equal or nearly equal with different bases, for the reason that, while the degrees of ionization of the bases differ but little, the other factors are constants. However, the various precipitations involved times extending from a few seconds to many weeks, hence other variables are involved in the different reactions. That the delayed precipitations were not the results of supersaturation is evident from consideration of the facts that: (1) the precipitations were continuous over the times involved, and (2) the precipitations were promoted by direct sunlight. It appears, therefore, that the important variables involved in reactions of this kind are: (1) the affinity constants of the different bases, and (2) the factor of sunlight energy.

Without involving use of the ionic theory, it may be assumed that the respective bases, with different affinity constants, manifest different tendencies to coalesce with benzoyl chloride; this tendency has its basis in the residual valencies of the two compounds involved. For instance, the bases acted upon are all trivalent but potentially pentavalent; the benzoyl chloride contains the unsaturated atoms oxygen and chlorine. Therefore, it is possible that the initial reaction is:

$$(8)\quad R_3N == + == ClCOC_6H_5 \rightleftarrows R_3N == ClCOC_6H_5$$

This coalescence may be assumed to be partial and reversible, the direct progress depending upon the respective affinity constants of the bases. The molecular compound formed may represent greater or less tendency to undergo molecular rearrangement, as indicated in the equation:

$$(9)\quad R_3N == ClCOC_6H_5 \rightleftarrows R_3(COC_6H_5)NCl$$

and the promotion of this rearrangement may be caused by the energy of sunlight. Of course, the weakness of this hypothesis is the non-isolation of two isomeric additive products; it would seem that among many different reaction products of this kind, some of the unstable form (8) would be precipitated. Since secondary reactions do not occur with the tertiary bases, only reactions as given in (8) and (9), it is expected that they are best suited for the study of this problem. As a matter of fact, these very bases precipitate two crystalline forms, which at first were assumed to be the benzoyl chloride and the hydrogen chloride additive products, respectively, of the base. Since the hydrogen chloride could not be formed, except by hydrolysis of the benzoyl chloride, the absolute exclusion of water will eliminate the possibility of formation of the hydrochloride. This problem will be taken up anew. In the two following reactions:

$$(10)\quad RNH_2 + BzCl \longrightarrow RBzNH.HCl$$

$$(11)\quad RBzNH + HCl \longrightarrow RBzNH.HCl$$

the end products are the same, hence it may be concluded that the reaction will take place with equal ease. However, this was found not always to be the case. For instance, isoamylamine, aniline, *o*-toluidine and α-naphthylamine yielded the additive product with ease, but their respective benzoylated derivatives *failed*[1] *to yield with hydrogen chloride the same additive products.* When it is remembered that hydrogen chloride is more stable toward heat than benzoyl chloride, it may be understood how, in accordance with the coalescent hypothesis:

$$\begin{tikzcd}[column sep=small] (12)\quad R.H_2N = Cl.Bz \arrow[dr] & \\ R.BzHN = Cl.H \arrow[r] & RBzHN.HCl \end{tikzcd}$$

the benzoyl group and the hydrogen atom attached to chlorine may manifest different tendencies to shift to the nitrogen atom and thus to yield the particular additive product. Of course, since the hydrogen chloride in many cases yields the additive product, the affinity of the trivalent nitrogen molecules must exert different influences on the hydrogen atom attached to chlorine. Thus both these different affinity constants and the

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[1] Equimolecular quantities of benzamide and hydrogen chloride in toluene yielded benzamide hydrochloride. Cf. Dessaignes, *Ann.*, 82, 234 (1852); Pinner and Klein, *Ber.*, 10, 1897 (1877); 11, 10 (1878); Meyer, *J. prakt. Chem.*, [2] 30, 122 (1843).

tendency of (H) and (Bz) to dissociate from (Cl) are probably factors of the chemical changes.

Primary Bases.

Isobutylamine.—When equimolecular quantities of isobutylamine and benzoylchloride were brought together in anhydrous ether, an immediate heavy precipitate was formed. It contained 28.07% Cl.

Calculated for $C_4H_9NH_2.HCl$: Cl, 29.66%; for $C_4H_9.C_6H_5CONH.HCl$: Cl, 16.60%.

From these data it was calculated that *isobutyl benzamide hydrochloride* was present as 11.71% of the mixture. Its presence was further indicated by the spinning motions produced when the mixture was floated on water. After being washed with water, dried and concentrated, the ether solution yielded large transparent rectangular plates of isobutylbenzamide[1] melting at 58° and boiling at 305–308°. Anhydrous ether and xylene solutions yielded some oil but no crystalline isobutylbenzamide hydrochloride.

Isoamylamine.—When equimolecular quantities of isoamylamine and benzoyl chloride were brought together in anhydrous ether, pearly flakes, softening at 160°, melting at 201° and containing 16.09% of chlorine, were obtained.

Calculated for $C_5H_{11}.C_6H_5CONH.HCl$: Cl, 15.56%. Calculated for $C_5H_{11}NH_2.HCl$: Cl, 28.69%.

Since both isoamylamine and isoamylbenzamide[2] are soluble in ether, the precipitate contained only *isoamylbenzamide hydrochloride.* Its presence was further indicated by spinning and darting motions produced when the substance was floated on water. The ether solution and some of the precipitate were treated with dilute alkali; the ether solution was separated, dried and concentrated. An oil boiling at 310–315° was obtained; evidently it was *isoamylbenzamide,* $C_5H_{11}.C_6H_5CONH$ with hydrogen chloride in anhydrous ether toluene xylene yielded a liquid hydrochloride.

Aniline.—An immediate precipitate was formed. It was incompletely soluble in water and contained 10.18% of chlorine.

Calculated for $C_6H_5.C_6H_5CONH.HCl$: Cl, 15.18%. Calculated for $C_6H_5NH_2.HCl$: Cl, 27.39%.

Since the percentage of chlorine was lower than either of these, it contained benzanilide.[3] This was obtained by adding water to some of the precipitate—leaflets melting at 161° were obtained. That the original precipitate contained *benzanilide hydrochloride* was further indicated by spinning

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[1] Wheeler, *Am. Chem. J.*, **23**, 142; Titherley, *J. Chem. Soc.*, **79**, 406.

[2] Wurtz, *Ann.*, **75**, 334; THIS JOURNAL, **34**, 1404 (1912).

[3] Wallach and Hoffman, *Ann.*, **184**, 80; Gerhardt, *Ibid.*, **60**, 311; Lossen, *Ibid.*, **175**, 310; Leuckart, *J. prakt. Chem.*, [2] **41**, 306; Beckman, *Ber.*, **20**, 1508, 2581; Nageli, *Bull. soc. chim.*, [3] **11**, 893; Schweder, *Ber.*, **12**, 1613; Berthelot, Fogh, *Ibid.*, **12**, 1613; Cohen, *J. Chem. Soc.*, **59**, 71; Meyer and Sundmacher, *Ber.*, **32**, 2123; Dinglinger, *Ann.*, **311**, 153.

motions when it was floated on water. It could not be prepared by adding hydrogen chloride to a toluene solution of pure benzanilide.

p-Toluidine.—An immediate, voluminous precipitate was formed It was incompletely soluble in water and contained 9.35% of chlorine.

Calc. for $CH_3C_6H_4.C_6H_5CONH.HCl$: Cl, 14.32%. Calc. for $C_7H_7HN_2.HCl$: Cl, 24.70%.

The insoluble portion was identified as *p*-tolylbenzamide, melting at 158°. That the original precipitate contained *p-tolylbenzamide hydrochloride* was indicated by the spinning motions. It was prepared in pure form by passing hydrogen chloride into a xylene solution of *p*-tolylbenzamide. When isolated it was found to be decomposed even in a desiccator at ordinary temperatures into *p*-tolylbenzamide[1] and hydrogen chloride. That the crystals were the additive compound was proven by the following method of analysis: After the crystals were formed in the manner indicated above, the apparatus was aspirated with dry air to remove the excess of hydrogen chloride. Without exposing the contents of the vessel to atmospheric moisture, the xylene was siphoned off and the crystals were washed with more dry xylene, which was also siphoned off. More xylene was added and also some distilled water. The crystalline compound being hydrolyzed, the hydrogen chloride dissolved in the water and the *p*-tolylbenzamide dissolved in the xylene. The former was estimated by titration with silver nitrate; the latter, by evaporating the xylene solution. From these data it was calculated that the crystals contained 14.80% of chlorine.

Calc. for $C_7H_7.C_6H_5CONH.HCl$: Cl, 14.32%.

Equimolecular quantities of *p*-tolylbenzamide and hydrogen chloride in toluene did not yield any precipitate of the hydrochloride.

o-Toluidine.—An immediate precipitate containing 10.47% of chlorine was obtained. Since spinning motions were obtained with water and the insoluble portion melted at 142°, the precipitate evidently was a mixture of *o*-toluidine hydrochloride, *o*-tolylbenzamide[2] and *o-tolylbenzamide hydrochloride.* The last mentioned could not be prepared by passing hydrogen chloride into a xylene solution of *o*-tolylbenzamide.

m-Toluidine.—An immediate precipitate, showing spinning motions on water and containing 11.00% of chlorine, was obtained. That it was a mixture of *m*-toluidine hydrochloride, *m*-tolylbenzamide[3] and *m-tolylbenzamidehydrochloride* is sufficiently evident.

α-Naphthylamine.—When 3 g. of benzoyl chloride and 3.06 g. of *α*-

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[1] Jaillard, *Z. Chem.*, 1865, 400; Hübner, *Ann.*, **208**, 310; Wallach, *Ibid.*, **214**, 217; Apitzsch, *Ber.*, **33**, 3524.

[2] Büchner, *Ann.*, **205**, 130, gives melting point at 142–143°; Güdeman, *Ber.*, **21**, 2553, gives melting point at 131°.

[3] Just, **19**, 983, gives m. p 125°.

naphthylamine were brought together in anhydrous ether, an immediate voluminous precipitate was formed. It was filtered and the ether solution gave, by evaporation, 2.53 g. of a mixture of α-naphthylbenzamide and unchanged benzoyl chloride. The precipitate weighed 3.504 g. and contained 7.84% of chlorine.

Calc. for $C_{10}H_7NH_2.HCl$: Cl, 19.74%. Calc. for $C_{10}H_7.C_6H_5CONH.HCl$: Cl, 12.50%.

Upon adding water to the precipitate, spinning motions indicated the presence of the additive compound. The insoluble portion, consisting of α-naphthylbenzamide[1] and melting at 156°, weighed 1.942 g.; the aqueous solution yielded by evaporation (*a*) 1.4577 g. of α-naphthylamine hydrochloride. The difference between the sum of these weights and the weight of the original precipitate was 0.1043 g. or the hydrogen chloride united with α-naphthylbenzamide in the additive compound, and rendered free by the action of water on the original precipitate. Since this hydrogen chloride is equivalent to (*b*) 0.8111 g. of *α-naphthylbenzamide hydrochloride*, the original mixture consisted of:

	Grams.	Per cent.
(*a*) $C_{10}H_7NH_2.HCl$	1.4577	41.60
(*b*) $C_{10}H_7.C_6H_5CONH.HCl$	0.8111	23.15
(*c*) $C_{10}H_7.C_6H_5CONH$	1.2352	35.25

Making use of the fact that the aqueous portion (1.562 g.) contained 18.30% of chlorine, it may be calculated that 28.45% of the original precipitate was an additive compound. From these two analyses it is concluded that the original precipitate contained 23–28% of *α-naphthylbenzamide hydrochloride*. This compound could not be formed by passing hydrogen chloride into solutions of α-naphthylbenzamide in alcohol-ether, benzene or xylene.

Phenylhydrazine.—An immediate, voluminous precipitate, containing only 3.17% of chlorine was obtained.

Calc. for $C_6H_5N_2H_3.C_6H_5COCl$: Cl, 14.27%. Calc. for $C_6H_5N_2H_3.HCl$: Cl, 24.53%.

With water, the precipitate showed darting motions and yielded insoluble benzoylphenylhydrazine melting at 166°. The precipitate was a mixture of phenylhydrazine hydrochloride, benzoylphenylhydrazine,[2] and *benzoylphenylhydrazine hydrochloride*. The last was prepared by passing hydrogen chloride into xylene containing benzoylphenylhydrazine. When washed by decantation with anhydrous ether and preserved in a desiccator, fumes of hydrogen chloride and a residue containing little chlorine were

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[1] Ebell, *Ann.*, 208, 324, gives m. p. 165°; Kühn, *Ber.*, 18, 1477, gives m. p. 161–162°; Hofmann, *Ibid.*, 20, 1798, gives m. p. 159–160°; Worms, *Ibid.*, 15, 1814.

[2] The melting point is given at 168°. Fisher, *Ann.*, 190, 125; Just, *Ber.*, 19, 1203; Bamberger, *Ibid.*, 27, 162; Holleman and Antusch, *Rec. trav. chim.*, 13, 9423; Baidakowski and Slepak, *J. Russ. Phys. Chem.*, 35, 68.

obtained. Evidently the compound is dissociated at ordinary temperatures.

Acetamide.—Though the solution was kept in the sunlight for most of five months, only a little amorphous precipitate,[1] containing 22.96% of chlorine was obtained.

Calc. for $CH_3CONH_2.HCl$: Cl, 37.12%. Calc. for $C_6H_5CO(CH_3CO)NH.HCl$: Cl, 17.77%.

Urea.—The solution very slowly precipitated clusters of transparent, thick, hexagonal plates clinging to the sides of the bottle, and containing 17.91% of chlorine.

Calc. for $CON_2H_4.C_6H_5COCl$: Cl, 17.68%.

Ureabenzoylchloride melts at 209° with decomposition and dissolves in water with slow motions.

Glycocoll.—After ten weeks, amorphous glycocoll, insoluble in ether, was partially replaced by clusters of transparent, prismatic needles, containing 5.76% of chlorine.

Calc. for $C_2H_3O_2NH_2.HCl$: Cl, 32.08%. Calc. for $C_6H_5CO.C_2H_3O_2NH.HCl$: Cl, 16.45%.

Since no spinning motions were observed, and no benzoic acid could be recovered from the aqueous solution, it is concluded that the crystals were glycocoll hydrochloride[2] mixed with unchanged glycocoll.

Secondary Bases.

Diethylamine.—An immediate precipitate containing 29.19% of chlorine was obtained.

Calc. for $(C_2H_5)_2NH.HCl$:[3] Cl, 32.36%. Calc. for $(C_2H_5)_2C_6H_5CON.HCl$: Cl, 16.60%.

Since diethylamine[4] is soluble in ether, the percentage of chlorine indicated that the mixture contained 20.14% of *diethylbenzamide hydrochloride;* the presence of this was confirmed by the spinning motions of the mixture on water.

Methylaniline.—Crystals forming quite slowly clinging to the side of the bottle and containing 23.03% of chlorine were obtained.

Calc. for $C_6H_5.CH_3.C_6H_5CON.HCl$: Cl, 14.32%. Calc. for $C_6H_5.CH_3.NH.HCl$: Cl, 24.70%.

If phenylmethylbenzamide[5] was not contained in the mixture, 16.09% was *phenylmethylbenzamide hydrochloride.*

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[1] THIS JOURNAL, 34, 1403 (1912).

[2] Curtius and Göbel, *J. prakt. Chem.*, [2] 37, 157; Schabus, *Jahrsb.*, 1854, 676; Kraut and Hartmann, *Ann.*, 133, 100.

[3] Wallach, *Ann.*, 214, 275; Behrend, *Ibid.*, 222, 119; Pinner, *Ber.*, 16, 1650.

[4] Since diethylbenzamide is a liquid boiling at 280–282° and is soluble in ether, it was not a component of the mixture. Hallman prepared it in the above indicated manner, *Ber.*, 9, 846; Ramburgh, *Rec. trav. chim.*, 4, 387.

[5] Hepp gives m. p. 59°; *Ber.*, 10, 329; Hess gives m. p. 63°; *Ibid.*, 18, 685; Wislicenus and Goldschmidt, *Ibid.*, 33, 1471.

Piperidine.—An immediate, very hygroscopic precipitate, containing 24.70% of chlorine, was obtained.

Calc. for $C_5H_{11}N.HCl$: Cl, 29.17%. Calc. for $C_5H_{10}N.C_6H_5CO.HCl$: Cl, 15.72%.

If not containing benzoylpiperidine,[1] the mixture was composed of 33% of *benzoylpiperidine hydrochloride*. This was prepared by treating the former with hydrogen chloride in anhydrous ether solution. First crystals, then an oil, on standing, white, hygroscopic needles containing 16.50% of chlorine were obtained, hence nearly pure additive compound was obtained.

Benzylethylamine.—A slow-forming precipitate containing 19.30% of chlorine was obtained.

Calc. for $C_6H_5CH_2.C_2H_5NH.HCl$: Cl, 20.66%. Calc. for $C_6H_5CH_2.C_2H_5.$-$C_6H_5CON.HCl$: Cl, 12.87%.

The presence of *benzylethylbenzamide hydrochloride* (17.47%) was indicated by the spinning motions of the mixture on water. *Benzylethylbenzamide,* boiling at 218° at 29 mm., was prepared.

Tertiary Bases.

Triethylamine.—Equimolecular quantities of benzoyl chloride and triethylamine gave an immediate precipitate which was increased on standing. The crystals softened at 180°, melted at 238–240° and contained 15.15% of chlorine.

Calc. for $(C_2H_5)_3N.HCl$: Cl, 25.77%. Calc. for $(C_2H_5)_3NC_6H_5COCl$: Cl, 14.67%.

Evidently the substance was a mixture of triethylamine hydrochloride[2] with *triethylaminebenzoylchloride.*

Triamylamine.—The reaction mixture remained in an amber-colored bottle for three weeks without yielding a precipitate. After standing for five weeks more in a clear-glass bottle, a mass of long needles, melting at 117° and containing 9.55% of chlorine was obtained.

Calc. for $(C_5H_{11})_3N.C_6H_5COCl$: Cl, 9.64%.

These were nearly pure[3] crystals of *triamylaminebenzoylchloride.* Upon water they gave the characteristic spinning and darting motions.

Dimethylaniline.—In sunlight, transparent, prismatic crystals were gradually formed on the sides of the bottle. They were very hygroscopic and contained 12.90% of chlorine.

Calc. for $(CH_3)_2C_6H_5N.HCl$: Cl, 22.50%. Calc. for $(CH_3)_2C_6H_5N.C_6H_5COCl$: Cl, 13.55%.

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[1] Schotten, *Ber.*, **17**, 2455; **21**, 2238, gives m. p. 48°; Cahours, *Ann. chim. phys.*, [3] **38**, 76.

[2] Schiff and Monsacchi, *Z. phys. Chem.*, **24**, 516.

[3] "Triisoamylamine Hydrochloride," Hofmann, *Ann.*, **79**, 22; Malbot, *Ann. chim. phys.*, [6] **13**, 504.

These crystals were nearly pure[1] *dimethylaniline benzoylchloride.*

Diethylaniline.—Crystals melting[2] at 115–120° and containing 14.20% of chlorine were obtained.

Calc. for $C_2H_5(C_2H_5)_2N.HCl$: Cl, 19.10. Calc. for $C_6H_5(C_2H_5)_2N.C_6H_5COCl$: Cl, 12.24%.

Diethylaniline benzoylchloride was present as 71% of the mixture.

Antipyrine.—Clusters of transparent needles melting at 138° to a blood-red liquid were obtained. The substance contained 11.08% of chlorine.

Calc. for $C_{11}H_{12}N_2O.C_6H_5COCl$: Cl, 10.47%.

Antipyrine benzoylchloride is very soluble in water.

Quinoline.—Precipitated slowly, reddish crystals melting at 112–116° and containing 16.10% of chlorine.

Calc. for $C_9H_7N.HCl$: Cl, 21.42. Calc. for $C_9H_7N.C_6H_5COCl$: Cl, 13.15%.

Evidently *quinoline benzoylchloride* was present as 65% of the mixture.

Pyridine.—A slow-forming precipitate containing 26.30% of chlorine was obtained.

Calc. for $C_5H_5N.HCl$: Cl, 30.69. Calc. for $C_5H_5N.C_6H_5COCl$: Cl, 16.15%.

Pyridine benzoyl chloride was present as 31% of the mixture.

α-Picoline.—Star-like clusters of needles containing 17.60% of chlorine were obtained.

Calc. for $C_5H_4N.CH_3.HCl$: Cl, 27.37%. Calc. for $C_5H_4N(CH_5).C_6H_5COCl$: Cl, 15.18%.

Picoline benzoyl chloride was present as 80% of the mixture.

SEATTLE, WASH.

THE SALTS OF ACRIDINE, PYRIDINE AND QUINOLINE.[3]

[SECOND PAPER.]

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In a previous paper[4] some experiments were described which indicate a very close analogy between the acridyl salts, *e. g.*, salts of diphenyl acridol (I), and the salts of triphenylcarbinol and its analogues (II). The analogy lay in the character of the reaction of the respective halides with metals. Triphenylmethyl chloride and its analogues in solution react with silver and other metals to form highly unsaturated free radicals of the type of triphenylmethyl. These free radicals absorb oxygen from the air to form

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[1] Dimethylaniline hydrochloride melts at 83–85°, Scholl and Escales, *Ber.*, 30, 3134; Menschutkin, *J. Russ. Phys. Chem. Ges.*, 30, 252; Perkins, *J. Chem. Soc.*, 69, 1235; Bredig, *Ber.*, 30, 673.

[2] Diethyl aniline hydrochloride melts at 145°, Reynolds, *J. Chem. Soc.*, 61, 457; THIS JOURNAL, 34, 1408 (1912).

[3] Presented at the spring meeting of the American Chemical Society, Cincinnati, April, 1914.

[4] THIS JOURNAL, 34, 1695 (1912).