In order to keep these tubes from dangling about, a deep groove a little narrower than the glass tube was made in an ordinary cork and the cork nailed to the box at I. The tube can then be pushed into the groove and fits very firmly. If found necessary, small steel springs may be made to fit over the cork, holding the glass connection in place. The following is a cross-section showing the use of the spring:

Instead of the corks, a strip of board, notched similar to a universal shelving may be constructed, similar to the following illustration:

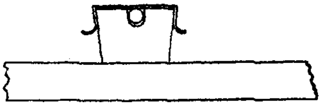

Fig. 2.

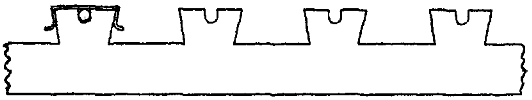

Fig. 3.

Enamelled pans were placed beneath the tubes to catch any waste liquid.

The inside of the box may be used for storing a reserved supply of solutions.

The apparatus, after having been tried out, has been found to have the merits of safety, convenience and neatness. We have planned to have a series of bottles similarly constructed for the reagents used in water analysis, and in general analysis of foods and cleansing reagents.

MARY L. FOSSLER.
FOOD AND SANITARY LABORATORY, DEPARTMENT OF CHEMISTRY.
UNIVERSITY OF NEBRASKA.

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

ACETYLATIONS IN ETHER SOLUTIONS.

BY WILLIAM M. DEHN.

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Though innumerable reactions of acetyl chloride with organic bases are found in the literature, these reactions usually have been produced by direct contact of the substances and furthermore the end products have usually been decomposition products obtained by the action of water or alkalis. The use of an indifferent solvent as ether[1] or chloroform has rarely been employed, hence the mechanisms of the reactions have not been studied thoroughly. The purpose of this study is to throw light on such mechanisms.

The action of acetyl chloride on the various bases was studied in anhydrous ether solutions. The hydrochlorides formed were precipitated by the ether, while the acetyl derivatives—not containing hydrochloric

[1] Claisen employed ether solutions, containing solid alkalis or alkali carbonates, for certain acylations. *Ber.*, 27, 3182.

acid—were usually held in solution.[1] The precipitates formed were purified by dissolving either in absolute alcohol or chloroform and reprecipitating by anhydrous ether. Analyses of the original precipitates usually indicated that they were mixtures of the hydrochlorides and the acetyl chlorides of the bases employed, the percentages of chlorine falling usually between the percentages of these two compounds. Further evidence that the first precipitates were mixtures containing acetyl chloride addition products was indicated by the spinning motions produced when such mixtures or the pure acetyl chloride compounds were floated on water. Such mixtures were best purified by evaporation of their aqueous solutions and recrystallization from organic solvents, the acetyl chloride compounds being hydrolyzed and the hydrochlorides of the bases being obtained pure.

The original ether solutions, containing acetyl derivatives of the base used, were distilled to remove the excess of acetyl chloride; the final fractions contained the mono- or the di-acetyl derivatives. The latter were studied directly or were redissolved in anhydrous ether and then treated with hydrogen chloride, to form salts of the acetyl derivatives if such could be formed.

These studies sometimes proved and sometimes only indicated that *acetyl chloride first adds to the base*, as illustrated by the equation:

$$(1)\quad RNH_2 + CH_3COCl \longrightarrow R(CH_3CO)NH_2HCl.$$

An acetyl chloride addition product is invariably formed with tertiary bases; with primary and secondary amines, sometimes it is the most abundant product, as for instance, with benzylamine; usually, however, products in accordance with the following equations, were obtained:

$$(2)\quad 2RNH_2 + CH_3COCl \longrightarrow RNH_2.HCl + R(CH_3CO)NH$$

$$(3)\quad 2R_2NH + CH_3COCl \longrightarrow R_2NH.HCl + R_2(CH_3CO)N$$

Tertiary bases are described in the literature as having no affinity for the acetyl group. *The acetyl chloride addition products herewith described are not only the first of the kind contributed, but exemplify the general affinity of tertiary bases for acetyl chloride.* Former experiments made to prepare acetyl derivatives of tertiary bases did not involve the entire absence of water. If water is present, even as a trace, reactions typified by the following equations result:

$$(4)\quad R_3N.CH_3COCl + H_2O \longrightarrow R_3N.HCl + CH_3COOH$$

Owing to the difficulty of preparing and working with acetyl chloride so that it does not absorb aqueous vapor from the air, many of the following acetyl chloride addition products are mixed with more or less of the

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[1] Acetanilide, acet-*p*-toluidide, the acetnaphthalides, etc., being sparingly soluble in ether, were precipitated as such with the hydrochloride and the acetyl chloride addition products of the respective bases.

hydrochlorides of the bases used. Though the air contained in flasks and bottles was always dried by a stick of calcium chloride and anhydrous materials and solvents were used, the processes of filtering, washing and drying always involved contamination with aqueous vapor. Furthermore, water derived from the cork stoppers by contact with acetyl chloride, and traces contained in the bases used, contributed to the hydrolytic effect. It must be remembered that, owing to the low molecular weight of water, a little of it will transform much of the acetyl chloride addition product, as indicated in equation (4) above.

Since, on the other hand, the acetyl chloride addition products of tertiary bases, precipitated from ether solution, are sufficiently stable in the absence of water to be separated and analyzed; and since, on the other hand, the acetyl chloride addition product of ammonia (acetamide hydrochloride) is stable in the absence of water, it might be concluded that these and the intermediate acetyl chloride derivatives when formed would not suffer further chemical change. However, the following experiments show that this is not the case: the lower acylated products often secure the hydrochloric acid at the expense of the higher acylated products—the influence of *relative alkalinities* is observed. These effects are illustrated by equations (2) and (3) above and the following:

(5) $2NH_3 + CH_3COCl \longrightarrow NH_4Cl + CH_3CONH_2$

(6) $CH_3CONH_2.HCl + NH_3 \longrightarrow NH_4Cl + CH_3CONH_2$

(7) $2CH_3CONH_2 + CH_3COCl \longrightarrow CH_3CONH_2.HCl + (CH_3CO)_2NH$

(8) $(CH_3CO)_2NH.HCl + CH_3CONH_2 \longrightarrow CH_3CONH_2.HCl + (CH_3CO)_2NH$

(9) $2(CH_3CO)_2NH + CH_3COCl \longrightarrow (CH_3CO)_2NH.HCl + (CH_3CO)_3N$

(10) $(CH_3CO)_3N.HCl + CH_3CONH_2 \longrightarrow CH_3CONH_2.HCl + (CH_3CO)_3N$

(11) $(CH_3CO)_3N.HCl + (CH_3CO)_2NH \longrightarrow (CH_3CO)_2NH.HCl + (CH_3CO)_3N$

(12) $(CH_3CO)_3N + CH_3COCl \longrightarrow (CH_3CO)_4NCl$.

Therefore, in treating an excess of ammonia with acetyl chloride, reaction (5) represents the end product; in treating an excess of acetyl chloride with ammonia, reactions (5) to (12) become involved and products such as:

(*a*)	(*b*)
NH_3	$NH_3.HCl$
CH_3CONH_2	$CH_3CONH_2.HCl$
$(CH_3CO)_2NH$	$(CH_3CO)_2NH.HCl$
$(CH_3CO)_3N$	$(CH_3CO)_3N.HCl$
$(CH_3CO)_4NCl$	

may be found in the mixture. Such a mixture would be formed only if a free exchange of the reacting parts were possible. Owing to the *insolubility* of the above hydrochlorides (*b*) in ether, reactions (6), (8), (10), and (11) will ordinarily be retarded and incomplete, hence a preponderance of the lower acylated products is found in the mixture.

Besides the factors of relative alkalinities and insolubilities of the salts, a third, *the instability of polyacylated products of ammonia,* is involved. For instance, though diacetamide[1] and triacetamide[2] are known, their hydrochloride and acetyl chloride addition products are unknown, hence reactions (8) to (12) are also unknown.

When different aryl- and alkyl- amines are involved, products of varied stability result; an increase of aryl groups, as of acyl groups, producing less stability and an increase of alkyl groups producing greater stability of the acetyl derivatives.

The mechanism of the above described loss of hydrochloric acid to the lower bases may be explained by the following equations:

$$(13)\quad CH_3CO.NH_2HCl : : NH_3 \longrightarrow NH_4Cl + CH_3CONH_2$$

The mechanism of reaction involved in the coalescence of acetyl chloride with organic bases may be explained by the following assumptions:

$$(14)\quad R_3N : : Cl.COCH_3 \longrightarrow R_3(CH_3CO)NCl.$$

The initial action on primary and secondary bases is of the same kind:

$$(15)\quad RNH_2 : : Cl.COCH_3 \longrightarrow R(CH_3CO)NH : HCl.$$

Most of the acetyl chloride addition products of organic bases herein described are new; the first acetyl chloride derivatives of tertiary bases are herewith contributed. These compounds when floating on water usually show remarkable spinning and darting motions while undergoing hydrolysis. This property often served for the purpose of recognizing the presence of such compounds.

Acyl Derivatives.

Ammonia.—Anhydrous ammonia, passed into an anhydrous ether solution of acetyl chloride, yielded a heavy precipitate of ammonium chloride and acetamide. After extracting with ether and alcohol and recrystallizing from water, the residue gave 66.11% of chlorine; calculated for NH_4Cl, 66.28. The ether contained acetamide, hence the reaction is expressed by equation (5) above.

Acetamide hydrochloride.—When treated with anhydrous ammonia, acetamide hydrochloride in suspension in anhydrous ether yielded a white crystallin mass, which after extracting with alcohol, proved to be largely ammonium chloride. Since acetamide was found in the ether, equation (6) above is confirmed.

Acetamide.—When equimolecular quantities of acetamide and acetyl chloride were brought together in anhydrous ether, inch-long needles[3] melting at 138° were precipitated slowly. Calculated for $(CH_3CONH_2)_2HCl$: Cl, 22.94; found, 22.91. The ether solution yielded

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[1] Stecker, *Ann.*, 103, 327.

[2] Wichelhaus, *Ber.*, 3, 847.

[3] Pinner and Klein, *Ber.*, 10, 1896.

an oil which on standing in a desiccator gave crystals of diacetamide[1] melting at 78°. These facts conform with equation (7) above.

Benzamide.—When 5 grams of benzamide and 3 grams of acetyl chloride were brought together in anhydrous ether, the solution remained clear for some hours; in direct sunlight an oil was precipitated quite quickly. After standing, 2.4 grams of glistening transparent hygroscopic needles, melting[2] at 75°, were obtained.

Calculated for $C_6H_5CO(CH_3CO)NH.HCl$:	Cl, 18.77.
Analyzed directly, and found:	Cl, 19.50.
After recrystallizing, found:	Cl, 18.88.

Acetylbenzamide hydrochloride is soluble in alcohol and chloroform and hydrolyzes with the spinning motion, yielding acetylbenzamide. The original ether solution yielded an oil which only partially solidified in a desiccator. On pouring into water, a solid was obtained; after recrystallizing, it melted at 135° and proved to be acetylbenzamide. It is concluded that the action of acetyl chloride on benzamide is expressed by the equation:

$$(16)\quad C_6H_5CONH_2 + CH_3COCl \longrightarrow C_6H_5CO(CH_3CO)NH.HCl.$$

Primary Bases.

Ethylamine.—When 1.7 grams of ethylamine was treated in ether solution with 3.3 grams of acetyl chloride, 1.5 grams of a white, crystallin precipitate was obtained. The crystals were hygroscopic but after recrystallizing from chloroform and ether, were found to be stable in air.

Calculated for $C_2H_5NH_2.HCl$:	Cl, 43.49.
Calculated for $C_2H_5(CH_3CO)NH.HCl$:	Cl, 28.70.
Calculated for $C_2H_5(CH_3CO)_2N.HCl$:	Cl, 21.41.
Without recrystallization, m. p. 78–84°. Found:	Cl, 41.83.
After one recrystallization, m. p. 83–90°. Found:	Cl, 42.40.
After two recrystallizations, m. p. 100–108°. Found:	Cl, 43.21.

The crystallin mass first formed, therefore, was a mixture of ethylamine hydrochloride[3] with *acetyl-* and *diacetyl*ethylamine hydrochloride. The original ether solution yielded an oil boiling at 195–199°; this was *diacetylethylamine*, since with hydrogen chloride it precipitated glistening, transparent, hygroscopic needles of *diacetylethylamine hydrochloride*, melting at 65° and containing 21.14% of chlorine. Since equimolecular quantities of the reacting substances were used, the following reaction could take place:

$$(17)\quad 3C_2H_5NH_2 + 2CH_3COCl \longrightarrow 2C_2H_5NH_2.HCl + C_2H_5(CH_3CO)_2N.$$

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[1] Hentschel, *Ber.*, **23**, 2395.

[2] Acetylbenzamide melts at 115–120°. Pinner and Klein, *Ber.*, **11**, 9; **25**, 1436; **28**, 2355; *Am. Chem. J.*, **13**, 6; *J. Chem. Soc.*, **79**, 395. Benzamide hydrochloride melts at 178°. *J. prakt. Chem.*, [2] **30**, 122.

[3] Kanonnikow, *J. prakt. Chem.*, [2] **31**, 347; Schiff and Monsacchi, *Z. physik. Chem.*, **24**, 513. The melting point is given at 76–80° by Kanonnikow. All of the melting points of this contribution were made in sealed capillaries.

The above facts are all in agreement with this equation. Calculation of the above analytical data indicates that about 10% of the first crystallin product was formed by some of the following reactions:

(18) $C_2H_5NH_2 + CH_3COCl \longrightarrow C_2H_5(CH_3CO)NH.HCl$

(19) $2C_2H_5NH_2 + CH_3COCl \longrightarrow C_2H_5NH_2.HCl + C_2H_5(CH_3CO)NH$

(20) $C_2H_5(CH_3CO)NH + CH_3COCl \longrightarrow C_2H_5(CH_3CO)_2N.HCl.$

Isoamylamine.—The precipitate first formed contained 25.85% of chlorine. After evaporating its aqueous solution and recrystallizing from alcohol and ether, the crystals[1] melted at 209° and contained 28.55% of chlorine. Calculated for $C_5H_{11}NH_2.HCl$: Cl, 28.69. Calculated for $C_5H_{11}(CH_3CO)NH.HCl$: Cl, 21.41. At first the hygroscopic crystallin mass was a mixture of these two substances. The original ether solution yielded an oil boiling at 220–224°. That this was *acetylamylamine* was proven by the formation of its *hydrochloride*, hygroscopic needles containing 21.41% of chlorine.

Aniline.—When 3.96 grams of acetyl chloride and 4.61 grams of aniline (equimolecular quantities) were mixed in anhydrous ether, sufficient heat was generated to boil the ether. After cooling and standing, 5.9 grams of a solid separated (calculated for aniline hydrochloride, 5.5 grams). At first the solid melted not sharply at 120–125°, contained 17.31% of chlorine and was incompletely soluble in cold water. After washing with alcohol and ether, the solid melted at 198° and contained 27.25% of chlorine. Calculated for $C_6H_5NH_2.HCl$: Cl, 27.39. The ether solution contained acetanilide, hence the reaction was as follows:

(21) $2C_6H_5NH_2 + CH_3COCl \longrightarrow C_6H_5NH_2.HCl + C_6H_5(CH_3CO)NH.$

Acetanilide.—The voluminous ether solution necessary to dissolve the acetanilide remained clear for a day or more. In sunlight and while kept cold, compact crystals of acetanilide hydrochloride[2] separated. Calculated for $(C_6H_5CH_3CONH)_2HCl$: Cl, 11.56; found, 11.47. These crystals soften at 125° and melt at 133°. On concentrating the ether solution, more of these crystals and unchanged acetanilide were obtained. The residue yielded diacetanilide,[3] hence the following reaction takes place:

(22) $3C_6H_5(CH_3CO)NH + CH_3COCl \longrightarrow$
$(C_6H_5.CH_3CONH)_2HCl + C_6H_5(CH_3CO)_2N.$

p-Toluidine.—From 5 grams of *p*-toluidine and 3.7 grams of acetyl chloride, 6 grams of solid separated. With water the precipitate yielded

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[1] Würtz, *Ann.*, **75**, 334.

[2] Noelting and Weingaertner, *Ber.*, **18**, 1340.

[3] Kay, *Ber.*, **26**, 2851, 2853; Blacker, *Ber.*, **28**, 2356; Wheeler, *Am. Chem. J.*, **18**, 698.

p-toluidine hydrochloride[1] and acet-*p*-toluidide,[2] the latter melting at 142–145°. The ether solution gave an oil which with hydrogen chloride precipitated transparent prisms and hexagonal plates.

Calculated for $CH_3C_6H_4(CH_3CO)_2N.HCl$: Cl, 15.59. Found: Cl, 15.31.

Diacet-p-toluidine hydrochloride melts at 120°. Reactions are as follows:

(23) $2CH_3C_6H_4NH_2 + CH_3COCl \longrightarrow CH_3C_6H_4NH_2.HCl + CH_3C_6H_4(CH_3CO)NH$

(24) $3CH_3C_6H_4NH_2 + 2CH_3COCl \longrightarrow 2CH_3C_6H_4NH_2.HCl + CH_3C_6H_4(CH_3CO)_2N.$

α-Naphthylamine.—When 4.1 grams of α-naphthylamine and 2.3 grams of acetyl chloride were mixed in anhydrous ether, 5 grams of a felt-like mass of crystals were obtained at once. This crystallin mass was a mixture of α-naphthylamine hydrochloride,[3] acet-α-naphthalide[4] and probably the hydrochloride of the latter. Calculated for $C_{10}H_9N.HCl$: Cl, 19.74. The mixture contained 10.10% of chlorine. The α-naphthylamine hydrochloride was extracted with cold water. With water the latter two yielded insoluble acet-α-naphthalide, melting at 159°. This, with hydrogen chloride in alcohol-ether solution, yielded *acet-α-naphthalide hydrochloride*, small needles melting not sharply at 137°.

Calculated for $C_{10}H_7(CH_3CO)NH.HCl$: Cl, 16.00. Found: Cl, 16.10.

β-Naphthylamine.—When 4.1 grams of β-naphthylamine and 2.3 grams of acetyl chloride were mixed in anhydrous ether, 5.5 grams of crystals were obtained. This crystallin mass, containing 10.12% of chlorine, yielded β-naphthylamine hydrochloride[5] and acet-β-naphthalide.[6] The former melted at 254°; the latter,[7] at 134°. With hydrogen chloride, the latter yielded prismatic needles of *acet-β-naphthalide hydrochloride*, melting at 152°.

Calculated for $C_{10}H_7(CH_3CO)NH.HCl$: Cl, 16.00. Found: Cl, 16.05.

Preparation of Acet-β-naphthalide.[8]—Equimolecular quantities of β-naphthylamine and acetyl chloride are mixed in anhydrous ether. The mixture is then distilled on the water bath to remove the ether and

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[1] Rosenstiehl, *Bull. soc. chim.*, 10, 199; Bischoff and Walden, *Ann.*, **279**, 134; Krafft, *Ber.*, **32**, 1601; Ullman, *Ber.*, **31**, 1699.

[2] Riche, *Ann.*, **129**, 77; **156**, 74. Feitler gives the melting point at 153°; *Z. physik. Chem.*, **4**, 76. Diacet-*p*-toluidide melts at 41°; Zeiser, *Ber.*, **28**, 1665.

[3] Zinin, *J. prakt. Chem.*, **27**, 140; Young and Clark, *J. Chem. Soc.*, **71**, 1200.

[4] Liebermann, *Ann.*, **183**, 229; Biedermann and Andreoni, *Ber.*, **6**, 342; Tommasi, *Bull. soc. chim.*, **20**, 20; Pinnow, *Ber.*, **33**, 418; Holleman, *Rec. trav. chim.*, **13**, 289.

[5] Liebermann, *Ann.*, **183**, 264.

[6] Merz and Weith, *Ber.*, **14**, 2343.

[7] Cosiner gives the melting point at 132°; *Ber.*, **14**, 58.

[8] Merz and Weith's method of preparation consists of heating to 280° β-naphthol, acetic acid and ammonium acetate.

excess of acetyl chloride. The residue is extracted first with a little water to remove the naphthylamine hydrochloride and then recrystallized from hot water. Yield about 80% of the naphthylamine used.

Benzylamine.—From 4 grams of benzylamine and 3 grams of acetyl chloride, 4.6 grams of solid were precipitated at once. At first it contained 20.22% of chlorine; after recrystallizing from chloroform and ether, it melted[1] with decomposition at 134° and contained 19.08% of chlorine. Calculated for $C_6H_5CH_2(CH_3CO)NH.HCl$: Cl, 19.11. With water *acetylbenzylamine hydrochloride* yields an oil. Distillation of the original ether gave an oil boiling at 220–230°. Evidently the main reaction is as follows:

$$(25)\ C_6H_5CH_2NH_2 + CH_3COCl \longrightarrow C_6H_5CH_2(CH_3CO)NH.HCl.$$

Secondary Bases.

Diethylamine.—Equimolecular quantities reacted with warming and yielded hygroscopic transparent needles and plates containing 28.09% of chlorine. Calculated for $(C_2H_5)_2NH.HCl$: Cl, 32.36; $(C_2H_5)_2$-$(CH_3CO)N.HCl$: Cl, 23.39. After recrystallizing they melted[2] at 215°, hence the original solid contained diethylamine hydrochloride and probably *acetyldiethylamine hydrochloride.* The original ether solution gave an oil; this with hydrogen chloride gave only an oily precipitate.

Diamylamine.—From 1.5 grams of diamylamine and 0.9 gram of acetyl chloride, 0.8 gram of solid, melting at 285° and containing 16.46% of chlorine, was obtained. After dissolving in water and concentrating, pearly flakes were obtained. They melted at 288° and contained 18.20% of chlorine. Calculated for $(C_5H_{11})_2NH.HCl$: Cl, 18.31. Evidently the first precipitate was a mixture of diamylamine hydrochloride[3] with *acetyldiamylamine hydrochloride.* Though, when treated with hydrogen chloride, the latter did not form in the original ether solution, this ether solution gave by direct distillation an oil boiling at 240°, probably *acetyldiamylamine*, in accordance with the equation:

$$(26)\ (C_5H_{11})_2NH + CH_3COCl \longrightarrow (C_5H_{11})_2NH.HCl + (C_5H_{11})_2(CH_3CO)N.$$

Methylaniline.—When 5.4 grams of methylaniline and 3 grams of acetyl chloride were brought together in anhydrous ether, 6.6 grams of a crystalline precipitate were obtained (calculated for methylaniline hydrochloride, 7.25 grams). After recrystallizing from chloroform, needles,[4] melting at

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[1] Various authors give the melting point between 140° and 158°. Spica gives 240° (*Ber.*, **10**, 889); Curtius and Lederer give 246° (*Ber.*, **19**, 2463); Hoogewerff and Dorp give 255.5–258° (*Rec. trav. chim.*, **5**, 253); Konowalow gives 246–250° (*Ber.*, **28**, 1861).

[2] Diethylaminehydrochloride melts at 215–217°; Wallach, *Ann.*, **214**, 275; Behrend, *Ibid.*, **222**, 119; Pinner, *Ber.*, 16, 1650.

[3] Hofmann, *Ann.*, **79**, 21; Malbot, *Ann. chim. phys.*, [6] **13**, 504; Berg, *Ibid.*, [7] **3**, 305.

[4] Scholl and Escales, *Ber.*, **30**, 3134; Menschutkin, *J. Russ. Physik. Chem. Ges.*, **30**, 252.

122° and yielding 24.79% of chlorine, were obtained. Calculated for $C_6H_5(CH_3)NH.HCl$: Cl, 24.70. On concentrating the ether solution and letting stand, large transparent plates melting at 100° were obtained. That these were acetylmethylaniline[1] was further evidenced by the formation of *acetylmethylaniline hydrochloride* when treated in anhydrous ether solution with hydrogen chloride—transparent prisms and rhombic plates melting at 71°.

Calculated for $C_6H_5(CH_3)(CH_3CO)N.HCl$: Cl, 19.11. Found: Cl, 19.00.

Acetylmethylaniline, or methylacetanilide, floats on water and hydrolyzes slowly with most curious spinning and darting motions, yielding an acid solution.

Ethylaniline.—The precipitate first formed contained 21.29% of chlorine; after recrystallizing[2] from chloroform, 17.85%. Calculated for $C_6H_5(C_2H_5)(CH_3CO)N.HCl$: Cl, 17.77; $C_6H_5(C_2H_5)NH.HCl$: Cl, 22.50. The ether solution contained acetethylaniline.[3]

Piperidine.—From 2.9 grams of piperidine and 2.6 grams of acetyl chloride,[4] 2 grams of nearly pure piperidine hydrochloride,[5] melting at 230° and containing 28.88% of chlorine, were obtained. Calculated for $C_5H_{11}N.HCl$: Cl, 29.17. The ether solution yielded acetylpiperidine.[6]

Tertiary Bases.

Triethylamine.—Owing to the presence of water, only triethylamine hydrochloride[7] melting at 256° was obtained.

Tripropylamine.—Transparent hexagonal and rectangular plates and needles were obtained, melting below 80°

Calculated for $(C_3H_7)_3N.CH_3COCl$:		Cl, 15.99.
Calculated for $(C_3H_7)_3N.HCl$:		19.74.
Found (different samples):	Cl, 19.27, 18.36, 17.73,	17.23.

Evidently these were mixtures of *tripropylamine acetyl chloride* and *tripropylamine hydrochloride.* The latter, long hygroscopic needles, melts at 90°.

Dimethylaniline.—Equimolecular quantities of dimethylaniline and acetyl chloride in anhydrous ether gave at first only an oily precipitate. After standing for a number of days this solidified and thin transparent flakes, subliming to the neck of the flask, were obtained.

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[1] Hepp, *Ber.*, 10, 328; Duparc, *Jsb. Chem.*, 1888, 683; Hofmann, *Ber.*, 10, 599; Pictet and Crépieux, *Ber.*, 21, 1108; Wallach, *Ann.*, 214, 236; Pawlewski, *Ber.*, 31, 662; Wedekind, *Ber.*, 32, 514.

[2] Ethylaniline hydrochloride melts at 172–176°; Reynolds, *J. Chem. Soc.*, 61, 355; Bischoff, *Ber.*, 30, 3178.

[3] Ethylacetanilide melts at 54.5°; Elsbach, *Ber.*, 15, 690; 20, 3423; 16, 30; 21, 1108.

[4] Schotten, *Ber.*, 15, 426.

[5] Needles melting at 237°; Ladenburg, *Ann.*, 247, 55

[6] Schotten, *Ber.*, 15, 426; Wallach, *Ann.*, 214, 238.

[7] Schiff and Monsacchi, *Z. physik. Chem.*, 24, 516.

Calculated for $C_6H_5(CH_3)_2N.CH_3COCl$: Cl, 17.77.
Calculated for $C_6H_5(CH_3)_2N.HCl$: Cl, 22.50.
Found (different samples): 20.23, 18.50, 18.05.

Dimethylaniline acetyl chloride is very hygroscopic and melts[1] at 60–70°.

Diethylaniline.—Transparent monosymmetric crystals and prismatic needles were observed under the microscope, melting at 156°.

Calculated for $C_6H_5(C_2H_5)_2N.CH_3COCl$: Cl, 15.59.
Calculated for $C_6H_5(C_2H_5)_2N.HCl$: Cl, 19.10.
Found: Cl, 17.45, 18.38.

This was nearly an equimolecular mixture of *diethylaniline acetyl chloride* and diethylaniline hydrochloride,[2] transparent prismatic needles, melting at 145°.

Diethyl-p-toluidine.—A heavy amber oil was formed at once. After a number of days it solidified to white needles melting at 125°.

Calculated for $CH_3C_6H_4(C_2H_5)_2N.CH_3COCl$: Cl, 14.69.
Calculated for $CH_3C_6H_4(C_2H_5)_2N.HCl$: Cl, 17.76.
Found: Cl, 16.88.

A mixture of *diethyl-p-toluidineacetylchloride* and diethyl-*p*-toluidine hydrochloride.[3]

Pyridine.—When 4 grams of pyridine and 3.96 grams of acetyl chloride were brought together in anhydrous ether, much heat was developed and 5.5 grams of hygroscopic crystals separated at once. From an alcohol or chloroform solution, ether precipitated rhombic plates, melting at 118°.

Calculated for $C_5H_5N.CH_3COCl$: Cl, 22.51.
Found: Cl, 22.72.

Evaporated on the water bath with water, *pyridine acetyl chloride* yielded needles melting at 71°. Their alcohol solution with ether yielded needles melting at 128°, *pyridine hydrochloride.*

Calculated for $C_5H_5N.HCl$: Cl, 30.69.
Found: Cl, 30.60.

Quinoline.—A hygroscopic mass of needles melting at 88–90° was obtained.

Calculated for $C_9H_7N.CH_3COCl$: Cl, 17.08.
Calculated for $C_9H_7N.HCl$: Cl, 21.42.
Found (different samples): 20.27, 19.66, 18.29.

Evidently the crystals represented a mixture of *quinoline acetyl chloride* and quinoline hydrochloride.

Quinaldine.—White prismatic needles were obtained.

Calculated for $C_{10}H_9N.CH_3COCl$: Cl, 16.00.
Calculated for $C_{10}H_9N.HCl$: Cl, 19.75.
Found: 18.56, 18.23, 19.01.

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[1] Dimethylaniline melts at 85–95°. Scholl and Escales, *Ber.*, **30**, 3134; Menschutkin, *J. Russ. Physik. Chem. Ges.*, 30, 252; Perkins, *J. Chem. Soc.*, **69**, 1235; Bredig, *Ber.*, **30**, 673.

[2] Reynolds, *J. Chem. Soc.*, 61, 457.

[3] Schmidt, *J. prakt. Chem.*, [2] **48**, 49.

Evidently only a little *quinaldine acetyl chloride* with much *quinaldine hydrochloride*. After purifying, the latter was obtained as needles softening at 125° and melting at 179°.

Acridine.—A bright yellow precipitate of rhombic plates and prismatic needles was formed immediately.

Calculated for $C_{13}H_7N.CH_3COCl$: Cl, 13.87.
Found: Cl, 13.77.

Acridine acetyl chloride is powerfully sneeze-producing and melts at 236°.

Miscellaneous Bases.

Quinine.—An immediate precipitate of crystals which soften at 125° and melt at 200°.

Calculated for $C_{20}H_{24}O_2N_2.2CH_3COCl$: Cl, 14.74.
Calculated for $C_{20}H_{24}O_2N_2.CH_3COCl$: Cl, 8.80.
Calculated for $C_{20}H_{24}O_2N_2.2HCl$: Cl, 17.86.
Calculated for $C_{20}H_{24}O_2N_2.HCl$: Cl, 9.83.
Found (different samples): 16.25, 15.24, 15.01, 14.92.

Evidently the crystals were nearly pure *quinine diacetyl chloride.*[1]

α,α-Lutidine.—The precipitate was first white, then yellow, and finally dirty green in color.

Calculated for $C_7H_9N.CH_3COCl$: Cl, 19.11.
Calculated for $C_7H_9N.HCl$: Cl, 24.70.
Found: Cl, 20.49.

m-Nitroaniline.—An immediate yellow mixture of *m*-nitroaniline hydrochloride[2] and acet-*m*-nitroaniline hydrochloride.[3]

Caffeine.—A little caffeine hydrochloride was precipitated.

Urea.—A semi-solid sticky mass was formed.

Dimethylarsine.—No effect was observed.

Analogous reactions with benzoyl chloride are being studied.

SEATTLE, WASH.

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

THE ACTION OF IODOFORM ON ORGANIC BASES.

BY WILLIAM M. DEHN AND RAY B. CONNER.

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In previous contributions[4] it was shown that certain polyhalogenated derivatives of methane and ethane unite with organic bases in anhydrous ether solution to form molecular compounds or derivatives of these molecular compounds. In this paper it will be shown that iodoform unites

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[1] An acetylquinine melting at 108° is given. Hesse, *Ann.*, 205, 317; Beckett and Wright, *Jsb. Fortschr. Chem.*, 1876, 613.

[2] Städel, *Ber.*, 16, 28.

[3] Meyer and Stüber, *Ann.*, 165, 183; Salmon and Mendola, *J. Chem. Soc.*, 53, 778; Pawlewski, *Ber.*, 31, 661; Tassinari, *Gazz. chim. ital.*, 24, I, 446.

[4] THIS JOURNAL, 33, 1588, 1598; 34, 286, 290.