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.

with organic bases in a similar manner and forms molecular compounds of the types:

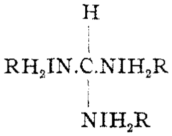
$$\text{I.}\quad RNH_2.CHI_3$$
$$\text{II.}\quad (RNH_2)_2.CHI_3$$
$$\text{III.}\quad (RNH_2)_3.CHI_3$$

that is, one molecule of iodoform unites with one, two or three molecules of the base. The compounds thus resulting resemble, in many respects, hydrated salts. They are, for instance, quite unstable; the more complex ones yield with hot chloroform or absolute alcohol the less complex derivatives.

The mechanism of formation of these types of compounds is simple, as is indicated by the following formulas and equations:

$$\text{IV.}\quad CHI_2I :: NH_2R \longrightarrow CHI_2.NIH_2R$$
$$\text{V.}\quad (CHI.NIH_2R)I :: NH_2R \longrightarrow CHI(NIH_2R)_2$$
$$\text{VI.}\quad CH(NIH_2R)_2I :: NH_2R \longrightarrow CH(NIH_2R)_3$$

The structure of the end product of VI may be shown as follows:

VII. 

$$RH_2IN.\overset{\displaystyle H}{\underset{\displaystyle NIH_2R}{C}}.NIH_2R$$

The reactions of organic bases with iodoform, as with carbon tetrabromide,[1] diiodoacetylene,[2] tetrabromoethane,[3] and tetraiodoethylene,[4] are all promoted by direct sunlight. This influence of direct sunlight is especially marked with iodoform. Clear solutions yield immediate precipitates in direct sunlight and in most cases the precipitates coat the glass where the light meets it.

The molecular compounds shown above are readily decomposed (1) by an excess of the base, (2) by water, (3) by heat, and (4) by hot organic solvents.

The influence of an *excess of the base*[5] is indicated by the equation:

$$\text{VIII.}\quad RNH_2.CHI_3 + RNH_2 \longrightarrow RNH_2.HI + RNH.CHI_2.$$

Here the hydriodide and the diiodomethyl derivatives of the base are obtained. The hydriodides were frequently isolated, in fact often they were the only crystallin product. The diiodomethyl derivatives are hypothetical; their probable formation was indicated by the colored solutions almost invariably formed.

With water the compounds may be resolved into iodoform and the base in accordance with the simple equation:

$$\text{IX.}\quad RNH_2.CHI_3 \longrightarrow RNH_2 + CHI_3.$$

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[1] THIS JOURNAL, **33**, 1588.

[2] *Ibid.*, **33**, 1594.

[3] *Ibid.*, **34**, 286.

[4] *Ibid.*, **34**, 290.

[5] Cf. *Ibid.*, **34**, 1401.

Since hydriodides and formates of the respective bases, as well as iodoform, are obtained, other equations are necessary, and this for the further reason that the solutions may be acid, neutral or alkalin in reaction. Such equations are as follows:

X. $3RNH_2.CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + HCOOH + 2CHI_3$
XI. $4RNH_2.CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + RNH_2.HCOOH + 3CHI_3$
XII. $5RNH_2.CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + RNH_2.HCOOH + RNH_2 + 4CHI_3$
XIII. $(RNH_2)_2.CHI_3 + 2H_2O \longrightarrow 2RNH_2.HI + HCOOH + HI$
XIV. $2(RNH_2)_2.CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + RNH_2.HCOOH + CHI_3$
XV. $3(RNH_2)_2.CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + RNH_2.HCOOH + 2RNH_2 + 2CHI_3$
XVI. $(RNH_2)_3.CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + HCOOH$
XVII. $4(RNH_2)_3.CHI_3 + 6H_2O \longrightarrow 9RNH_2.HI + 3RNH_2.HCOOH + CHI_3$
XVIII. $2(RNH_2)_3CHI_3 + 2H_2O \longrightarrow 3RNH_2.HI + RNH_2.HCOOH + 2RNH_2 + CHI_3$

It will be observed that equations X, XIII and XVI give acid reactions; equations XI, XIV and XVII give neutral reactions; equations XII, XV, and XVIII give alkalin reactions. Since aqueous decompositions typified by IX are often more extensive than X to XVIII, the end product may be alkalin even when X, XIII, or XVI are involved.

Decomposition by water is so easy that moist air must be avoided while preparing and studying these compounds. Complete avoidance of water, however, is almost impossible, hence there is great difficulty in preparing and analyzing these compounds. Usually the crystallin products become yellow on exposure to air, owing to the separation of iodoform. This property of separating iodoform with water enables one to distinguish between compounds such as $(RNH_2)_3.CHI_3$ and $RNH_2.HI$, which have nearly the same percentages of composition. Of course, the melting points of these compounds are different and when one, such as the hydriodide of the base, is known, additional information of the composition of the original crystallin product is derived from taking such melting points.

Decomposition by heat is indicated while taking melting points. Though heated in sealed capillaries, the substances invariably soften some ten degrees below the definit melting points.

Decompositions by organic solvents were observed while recrystallizing from hot chloroform or hot absolute alcohol. With the compound of pyridine, $(C_5H_5N)_3.CHI_3$, hot chloroform yielded $C_5H_5N.CHI_3$. This decomposition is similar to the dehydrating effect of alcohol on salts containing water of crystallization.

Ethylamine.—When equimolecular quantities of iodoform and ethylamine were dissolved in anhydrous ether and the solution was preserved in the dark, little or no precipitate was formed. In the direct sunlight white or light yellow clusters of needles continued to form during a number of days. Finally a dark brown-red crystallin mass resulted. The crystals first formed melted at 102° and were soluble in absolute alcohol and chloroform; from the latter white needles were obtained.

Calculated for $(C_2H_5NH_2)_2.CHI_3$: I, 78.69; found, I, 79.23, 79.00, 78.44.

On standing in moist air or when treated with water,[1] *ethylamineiodoform* yields iodoform and an alkalin solution of ethylamine hydriodide[2] and formate.

Diethylamine.—An immediate precipitate was formed. Direct sunlight, after some hours, yielded a dark brown solution and granular white prisms. From chloroform crystals melting at 124° were obtained:

Calculated for $(C_2H_5)_2NH.CHI_3$: I, 81.55; found: I, 81.63, 81.48.

With water *diethylamineiodoform* yields iodoform and a neutral solution of the hydriodide.[3]

Triethylamine.—An immediate precipitate was formed.

Calculated for $(C_2H_5)_3N.CHI_3$: I, 76.96; found, I, 78.25.

Dipropylamine.—In diffused sunlight an immediate yellow precipitate and in direct sunlight a dark brown crystallin mass were obtained. From chloroform flakes melting at 144° were obtained.

Calculated for $(C_3H_7)_2NH.CHI_3$: I, 76.94, found, I, 76.93.

With water *dipropylamineiodoform* yielded iodoform and pearly flakes of dipropylamine hydriodide.[4] The latter was also formed when a chloroform solution was permitted to stand in moist air.

Diamylamine.—One sample yielded prismatic needles melting at 221°.

Calculated for $(C_5H_{11})_2NH.CHI_3$: I, 69.11; found, I, 68.88.

This was *diamylamineiodoform*. Another sample yielded only pearly flakes, which did not melt at 310°.

Calculated for $(C_5H_{11})_2NH.HI$: I, 44.51; found, I, 44.41.

This was dimethylamine hydriodide.[5]

Other aliphatic Bases.—Isopropylamine gave only a dark brown oil. Isobutylamine gave transparent needles of the hydriodide[6] and a heavy brown oil. Isoamylamine gave the hydriodide[7] and a heavy brown oil. Allylamine gave a heavy brown oil from which no crystallin product could be separated.

Benzylamine.—A heavy red-brown oil was slowly formed in direct sunlight. After a number of days it was replaced by long, yellow, prismatic needles, which on dissolving in alcohol and reprecipitating with ether, melted at 158°.

Calculated for $(C_6H_5CH_2NH_2)_2.CHI_3$: I, 62.65; found, I, 62.98.

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[1] See equations IX and XI above.

[2] THIS JOURNAL, **34**, 292.

[3] *Ibid.*, **34**, 293.

[4] *Ibid*, **34**, 293.

[5] Malbot, *Ann. chim. phys.*, [6] **13**, 504.

[6] Rudnew, *J. prakt. Chem.*, [2] **46**, 312.

[7] Rudnew, *Ibid.*, [2] **46**, 314.

With water *benzylamineiodoform* yields benzylamine hydriodide[1] and iodoform.

Dibenzylamine.—Sunlight promoted the precipitation of transparent rectangular plates, soluble in water and alcohol and melting at 224°.

Calculated for $(C_6H_5CH_2)_2NH.HI$: I, 39.01; found, I, 39.12.

Evidently this dibenzylamine hydriodide[2] resulted from the presence of water.

Phenylhydrazine.—When equimolecular quantities of the substances were used, much unchanged iodoform was recovered; a crystallin mass and a deep red solution were obtained. The crystals, transparent prismatic needles not melting at 310°, were identified as phenylhydrazine hydriodide.[3]

Calculated for $C_6H_5NHNH_2.HI$: I, 53.79; found, I, 53.97.

The bright red ether solution yielded phenyl iodide,[4] a trace of phenyl isocyanide, and unchanged phenylhydrazine. An equation largely accounting for these facts is as follows:

XIX. $3C_6H_5NHNH_2 + CHI_3 \longrightarrow 2C_6H_5I + C_6H_5NHNH_2.HI + N_2 + CH_4 + H_2.$

Piperidine.—An immediate precipitate of white clusters of needles began to form in diffused sunlight and was rapidly increased by direct sunlight. The dark colored crystallin mass clung to the walls of the flask with great tenacity. After a number of days the ether was decanted; the residue was dissolved in warm absolute alcohol and was reprecipitated by absolute ether. Thus obtained the crystals were long, white or light yellow needles, melting at 107°.

Calculated for $C_5H_{11}N.CHI_3$: I, 79.51; found, I, 79.60.

When distilled with steam, *piperidineiodoform* yielded an acid distillate containing formic acid and a trace of diiodoacetylene. The aqueous solution contained piperidine hydriodide and a precipitate of iodoform. Equations accounting for these facts are as follows:

XX. $C_5H_{11}N.CHI_3 \longrightarrow C_5H_{11}N + CHI_3$

XXI. $2C_5H_{11}N.CHI_3 + 2H_2O \longrightarrow 2C_5H_{11}N.HI + HCOOH + 2HI + C_2I_2$

When treated with cold water, the substance yielded iodoform and piperidine hydriodide in the proportions of 0.29 g. to 0.55 g., or nearly equimolecular proportions. An equation accounting for this is as follows:

XXII. $4C_5H_{11}N.CHI_3 + 2H_2O \longrightarrow 3C_5H_{11}N.HI + C_5H_{11}N.HCOOH + 3CHI_3$

Pyridine.—A precipitate was formed only slowly in direct sunlight. After recrystallizing from absolute alcohol, white needles melting at 183° were obtained.

Calculated for $(C_5H_5N)_3.CHI_3$: I, 60.35; found, I, 60.52.

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[1] THIS JOURNAL, **34**, 294.

[2] Spica, Carrara, *Gazz. chim. ital.*, **19**, 428.

[3] THIS JOURNAL, **33**, 1600.

[4] Cf. *J. prakt. Chem.*, [2] **36**, 115; THIS JOURNAL, **33**, 1601.

This *pyridineiodoform* quickly turns yellow in moist air owing to the separation of iodoform. From hot chloroform it yielded a compound:

Calculated for $C_5H_5N.CHI_3$: I, 80.53; found, I, 80.52.

With water this pyridineiodoform yielded an acid solution, iodoform, iodic acid,[1] and pyridine hydriodide.[2]

α-Picoline.—In direct sunlight a gummy mass almost black in color was obtained. By dissolving in absolute alcohol and reprecipitating with absolute ether, a bright red, gummy mass was obtained.

Calculated for $(CH_3C_5H_4N)_2.CHI_3$: I, 65.66; found, I, 65.47.

When heated with water, *α-picolineiodoform* yielded iodine, iodoform and picoline hydriodide.[3]

Lutidine.—A dark brown oil was obtained.

Collidine.—A dark brown oil and long transparent needles were obtained.

Quinoline.—Small reddish brown needles were slowly precipitated by direct sunlight. After recrystallizing from alcohol and ether they melted sharply at 132°.

Calculated for $(C_9H_7N)_2.CHI_3$: I, 58.46; found, I, 58.60.

Caffeine.—The solution remained clear in the dark and in direct sunlight precipitated a dark brown, fluffy substance, which after extracting with a large quantity of chloroform to remove a trace of caffeine, melted not sharply at 154°.

Calculated for $(C_8H_{10}N_4O_2)_2.CHI_3$: I, 48.69; found, I, 49.07.

With water, *caffeineiodoform* yields iodoform.

Triphenylphosphine.—A gummy mass followed by an amorphous yellow substance, melting at 129°, was obtained.

Calculated for $[(C_6H_5)_3P]_2.CHI_3$: I, 41.47; found, I, 41.90.

Triphenylphosphineiodoform yields iodoform with water.

Strychnine.—The mixture remained clear in the dark; in direct sunlight a voluminous brown precipitate was formed.

Morphine.—A fluffy brown precipitate softening at 215° and melting at 248° was obtained.

Nicotine.—A brown-black, gummy mass.

Other Bases.—Aniline, dimethylaniline, diethylaniline, the naphthylamines, diphenylamine, acetamide, etc., gave dark precipitates but were not investigated closely. These will be reported on at some future time.

SEATTLE, WASH.

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[1] THIS JOURNAL, **34**, 291.

[2] Trowbridge, *Ibid.*, **19**, 326.

[3] Merrill, *Ibid.*, **21**, 831.