# THE CHEMISTRY OF QUATERNIZED HYDRAZINE COMPOUNDS

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## I. INTRODUCTION

### A. Scope of review

The great increase in interest shown in hydrazine and its derivatives during and since World War II (8, 14) has not yet been extended to those organic substitution products in which one of the nitrogens is quaternized, as in 1,1,1-trimethylhydrazinium chloride (I).

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$$\begin{bmatrix} CH_3 \\ | \\ CH_3NNH_2 \\ | \\ CH_3 \end{bmatrix}^+ \ Cl^-$$

I
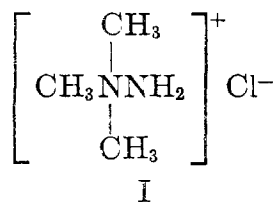
1,1,1-Trimethylhydrazinium chloride

Although such compounds have been known for eighty years (22), the study of their chemistry has been haphazard and incomplete. This review presents a survey of the known chemistry of quaternary hydrazinium compounds, including tho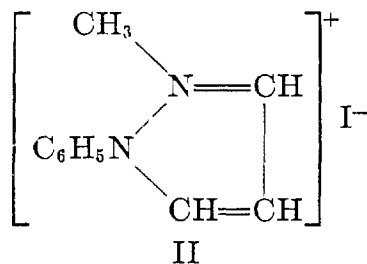se in the chemical literature of 1954. It covers the preparation and properties of those quaternary hydrazinium salts which are stable as such. Quaternized hydrazines in which both nitrogens are part of the same heterocyclic ring, as in II, will be omitted.

$$\begin{bmatrix} CH_3 \\ \diagdown \\ N{=\!=}CH \\ \diagup \quad | \\ C_6H_5N \\ \diagdown \\ CH{=}CH \end{bmatrix}^+ \ I^-$$

II

2-Methyl-1-phenylpyrazolium iodide

In addition, the novel triphenylmethane dye ions (15),



IIIa



IIIb
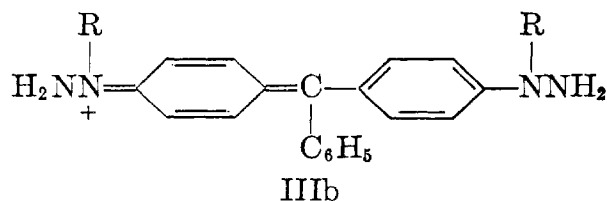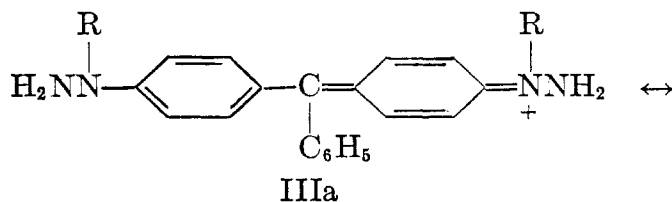
will be excluded. Adducts of polyarylhydrazines, although referred to in *Chemical Abstracts* and Sidgwick's *Organic Chemistry of Nitrogen* as "hydrazinium compounds," will not be discussed here.

### B. Nomenclature

The cation having the formula $R_3\overset{+}{N}NR_2$ has been given many names. Emil Fischer called the first known representative of this type a "hydrazonium bromide" (22) but later referred to the same compound as an "azonium bromide" (23). *Chemical Abstracts* has used the names "azinium," "azonium," "hydrazinium," and, most commonly of late, "hydrazonium" for the same type (5). As a logical extension of the recommendations recently made (45) for naming

$[H_3NNH_2]^+$, it is suggested that the name "hydrazinium" be adopted. Quaternization of a nitrogen is often indicated by conversion of its "ine" suffix to "inium" (see International Union of Chemistry rule No. 33, second paragraph). This is partially true of aliphatic amines, and especially true of aromatic and heterocyclic amines. Accordingly, it is suggested here that the name "hydrazonium" be restricted to salts of hydrazones (including quaternary salts). Since the term "azine" is now being properly restricted to the acyclic difunctional derivative of hydrazine containing the —C=N—N=C— chain, "azinium" should similarly be restricted to the salts of this grouping. Use of these names as proper subgeneric terms for different types of hydrazinium compounds would permit a more flexible, yet less ambiguous system of nomenclature. Examples of such names are given below:
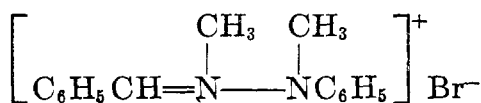
$$\left[ \begin{array}{c} \quad CH_3 \quad CH_3 \\ C_6H_5 N\text{———} NC_6H_5 \\ \quad CH_3 \end{array} \right]^+ Br^-$$
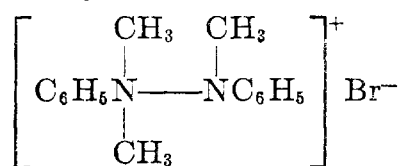
IV

1,1,2-Trimethyl-1,2-diphenyl-
hydrazinium bromide

$$\left[ \begin{array}{c} \quad\quad CH_3 \\ C_6H_5CH=N\text{—}NC_6H_5 \\ \quad\quad CH_3 \end{array} \right]^+ Br^-$$
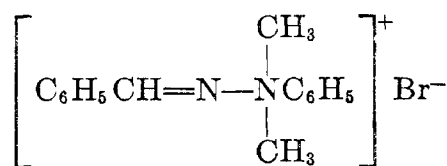
V

2-Benzylidene-1,1-dimethyl-
1-phenylhydrazonium bromide

$$\left[ \begin{array}{c} \quad CH_3 \quad CH_3 \\ C_6H_5CH=N\text{———}NC_6H_5 \end{array} \right]^+ Br^-$$

VI

1-Benzylidene-1,2-dimethyl-2-
phenylhydrazonium bromide

$$\left[ \begin{array}{c} \quad\quad CH_3 \\ C_6H_5CH=N\text{—}N=CHC_6H_5 \end{array} \right]^+ Br^-$$
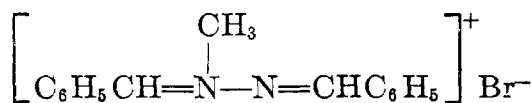
VII

1,2-Bis(benzylidene)-1-
methylazinium bromide

$$\left[ \begin{array}{c} \quad\quad CH_3 \\ C_6H_5N=NC_6H_5 \end{array} \right]^+ Br^-$$
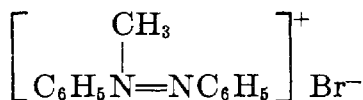
VIII

1-Methyl-1,2-diphenylazonium bromide

Cations in this review will be named in accordance with these examples.

### C. History of hydrazinium compounds

The first hydrazinium compounds were prepared in 1876 by Emil Fischer, who observed that phenylhydrazine reacts readily with ethyl bromide to form a crystalline, water-soluble, alkali-stable salt. The preparative reaction and the physical and chemical properties of the product showed it to be the first of a new family of compounds, analogous to the quaternary ammonium salts. The first purely aliphatic hydrazinium compound (IX) was prepared three years later (24), and the first heterocyclic hydrazinium product (X) in 1883 (36):

$$\left[ \begin{array}{c} \quad\quad CH_2CH_3 \\ CH_3CH_2NCH_2CH_3 \\ \quad\quad NH_2 \end{array} \right]^+ I^-$$

IX

Triethylhydrazinium iodide

$$\left[ \begin{array}{c} \quad CH_2CH_2 \quad\quad CH_3 \\ H_2C \quad\quad\quad N \\ \quad CH_2CH_2 \quad\quad NH_2 \end{array} \right]^+ I^-$$
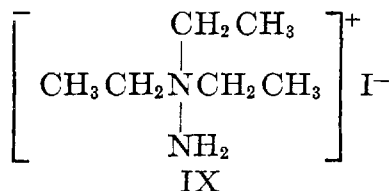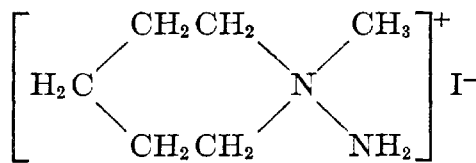
X

1-Amino-1-methylpiperidinium iodide

The first hydrazinium salt in which both nitrogens were substituted was reported in 1894 (32), and in the same year the first hydrazinium ion containing an oxygen function (26) was also described. Although Fischer reported the ethylmethyl-phenylhydrazinium cation (XI) in 1878 (23), it was not until 1913 that it was

$$
\left[
\begin{array}{c}
CH_3 \\
| \\
C_6H_5\overset{\cdot}{N}NH_2 \\
| \\
CH_2CH_3
\end{array}
\right]^+
$$

XI

shown to be resolvable (57) into optical isomers. The first purely aromatic hydrazinium compound (XII) was prepared about eight years later and, with it, the first "ylide" type hydrazinium betaine (XIII) (54):
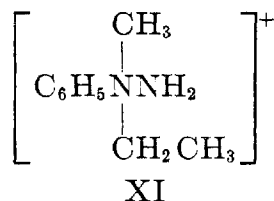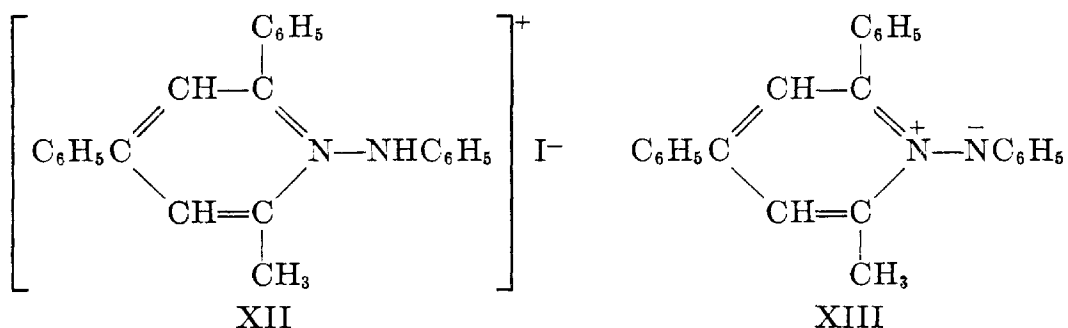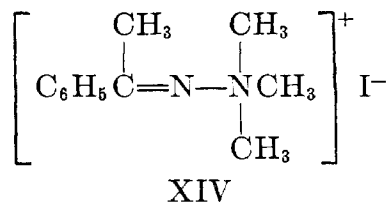
$$
\left[
\begin{array}{c}
C_6H_5 \\
| \\
CH-C \\
C_6H_5C \qquad N-NHC_6H_5 \\
CH=C \\
| \\
CH_3
\end{array}
\right]^+ I^-
\qquad
\begin{array}{c}
C_6H_5 \\
| \\
CH-C \\
C_6H_5C \qquad \overset{+}{N}-\overset{-}{N}C_6H_5 \\
CH=C \\
| \\
CH_3
\end{array}
$$

| XII | XIII |
|---|---|
| 1-Anilino-2-methyl-4,6-diphenyl-pyridinium iodide | 2-Methyl-4,6-diphenyl-pyridine-1-phenylimide |

The first hydrazonium salts were described by Theilacker and Leichtle (63):

$$
\left[
\begin{array}{c}
CH_3 \qquad CH_3 \\
| \qquad\qquad | \\
C_6H_5\overset{}{C}=N-\overset{}{N}CH_3 \\
| \\
CH_3
\end{array}
\right]^+ I^-
$$

XIV

1,1,1-Trimethyl-2-(1-phenylethylidene-1)hydrazonium iodide

The azinium compounds, e.g., VII, were prepared much earlier (64).

## II. Properties

### A. hydrazinium hydroxides

Quaternary hydrazinium compounds are, as would be expected, similar in many ways to quaternary ammonium salts. This analogy is in agreement with the lack of reactivity of the amino group of the hydrazinium ion.

In general, the hydrazinium hydroxides are highly hygroscopic, frequently deliquescent solids, often difficult to obtain in the crystalline state. Thus tri-methylhydrazinium hydroxide has been described (33) as a strongly alkaline, deliquescent, white mass, which readily absorbs carbon dioxide from the atmos-

phere. These hydrazinium hydroxides are probably slightly less basic than the corresponding quaternary ammonium hydroxides. They are very soluble in water and insoluble in nonpolar solvents. Hydrazonium and azinium hydroxides are unknown.

### B. HYDRAZINIUM HALIDES AND OTHER SALTS

Hydrazinium halides are easier to handle than the hydroxides, since they are, for the most part, crystalline, relatively nonhygroscopic solids. The expected analogies to quaternary ammonium halides are generally valid; the salts undergo metathesis, and they form insoluble picrates, tetrachloroaurates, hexachloroplatinates, and ferrocyanides (26). They also form complexes of very low solubility with mercuric iodide. They are soluble in water and many of them are soluble in chloroform; they are generally insoluble in nonpolar solvents. The crystallographic habits and the solubilities of certain hydrazinium halides have been studied (62). Most of the salts studied showed a lower molecular weight, as determined ebullioscopically, in ethanol than in water; this is contrary to the Nernst–Thompson rule (65). In water, but not in alcohol, the degree of association of these compounds is an inverse function of their formula weights. Many of the optically active hydrazinium compounds undergo mutarotation, the extent of which is a function of both the solvent and the nature of the substituents on the quaternary nitrogen atom.

### C. HYDRAZONIUM SALTS

Hydrazonium salts are colorless and crystalline, and generally similar to the hydrazinium salts. The absorption spectra of a number of the hydrazonium iodides, e.g., XIV, have been studied (41). Examination of Nujol mulls of these substances showed that the band at 6.08–6.28 $\mu$, characteristic of ketimines, is strengthened but not shifted by the addition of the quaternized nitrogen to the doubly bonded nitrogen. The ultraviolet spectra showed more marked changes, where the hydrazonium double bond is conjugated with an aromatic ring. Thus, in the spectrum of 1,1,1-trimethyl-2-(1-phenylethylidene-1-) hydrazonium iodide (XIV) the characteristic peaks are shifted toward longer wavelengths. The same compounds give high exaltations, increasing with molecular weight, in determinations of molecular refraction. Azinium salts are similar to the hydrazonium salts in properties, although they are generally more intensely colored and more easily hydrolyzed (39).
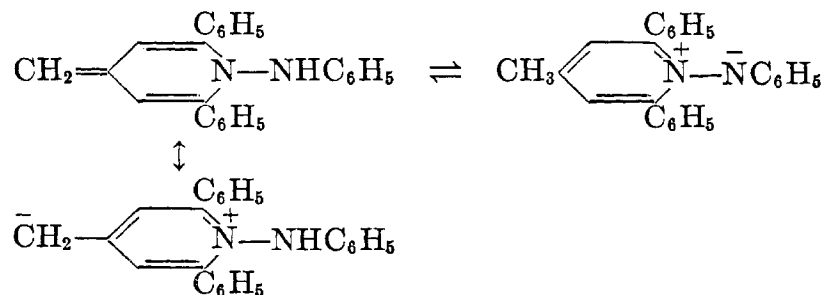
### D. AMINE IMIDES

Quaternized hydrazines of the general formula $R_4\overset{+}{N}\overset{-}{N}R$ have been referred to previously as "ylides," "aminimides" (66c), and "azeniates" (53), and are frequently written as dipolar ionic derivatives of an acidic imine, e.g.:

$$p\text{-}CH_3C_6H_4SO_2\overset{-}{N}\overset{+}{N}(CH_3)_3$$

XV
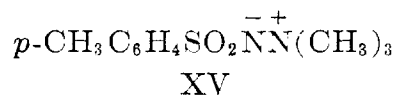
Trimethylamine $p$-toluenesulfonylimide

Their properties are in agreement with a covalent rather than an ionic structure, since they are generally crystalline solids of relative low melting point and are soluble in common nonpolar solvents. They are, for the most part, either colorless or light yellow in color. However, the first known representatives of the type, anhydro bases of 1-anilino-2,6-diaryl-4-alkylpyridinium salts, have intense blue to blue-black colors (54). The intense color of these so-called "azeniates" may be due to the following structures:
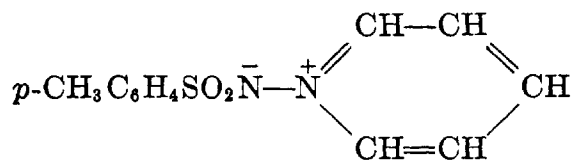
$$CH_2=\underset{C_6H_5}{\overset{C_6H_5}{\diamond}}N-NHC_6H_5 \quad \rightleftharpoons \quad CH_3\underset{C_6H_5}{\overset{C_6H_5}{\diamond}}\overset{+}{N}-\overset{-}{N}C_6H_5$$

$$\updownarrow$$

$$\overset{-}{C}H_2-\underset{C_6H_5}{\overset{C_6H_5}{\diamond}}\overset{+}{N}-NHC_6H_5$$

The intensely blue anhydro bases of analogous 1-alkyl-2-(4-nitrobenzyl)pyridinium salts are believed to have the following structure:

$$p\text{-}O_2NC_6H_4CH=\underset{R}{\overset{}{\diamond}}_{N}$$
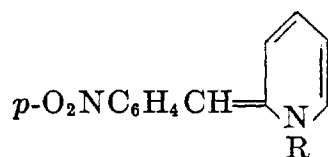
XVI

Tosylated pyridine 1-imides are colorless and apparently have the following structure (6):

$$p\text{-}CH_3C_6H_4SO_2\overset{-}{N}-\overset{+}{N}\begin{array}{c} CH-CH \\ \diamond \quad \diamond \\ CH=CH \end{array}CH$$

XVII

Pyridine 1-p-toluenesulfonylimide

The ultraviolet absorption spectra of these compounds have been reported (6).

## III. PREPARATION

### A. HYDRAZINIUM HYDROXIDES

Hydrazinium hydroxides have been prepared almost invariably by the reaction of quaternary hydrazinium halides with silver oxide:

$$2[C_6H_5(CH_3)_2NNH_2]^+Br^- + Ag_2O + H_2O \rightarrow$$

XVIII                                    $2[C_6H_5(CH_3)_2NNH_2]^+OH^- + 2AgBr$
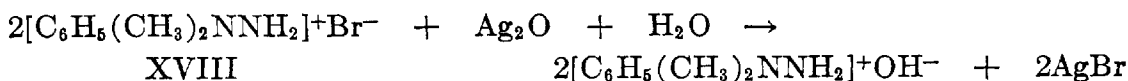
1,1-Dimethyl-1-phenyl-
hydrazinium bromide

Neither alkali nor alkaline earth hydroxides will convert halides of the type $(RR_2'NNH_2)X$ to the hydroxide (24), but a combination of barium hydroxide and thallous sulfate was found useful in forming the readily oxidized 1,1,1,2-tetramethylhydrazinium hydroxide (35). There are indications that dilute caustic is sufficient to convert 1-aminopyridinium chloride to its unstable hydroxide, but no product has been isolated (6).
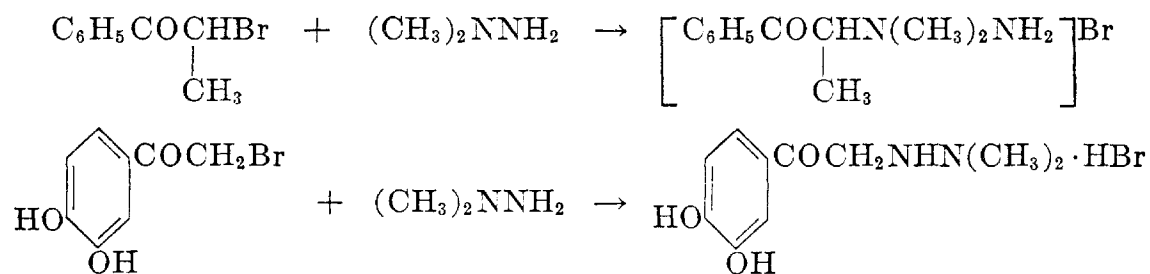
### B. HYDRAZINIUM HALIDES AND OTHER SALTS

Hydrazinium halides are the common intermediates for other hydrazinium compounds, because of the relative availability of the quaternizing halides. By far the most common method for preparing the halides is by alkylation of hydrazine or a substituted hydrazine. A fairly detailed review of such alkylations is believed warranted before turning to the other methods of preparation (metathesis, neutralization, and condensation).
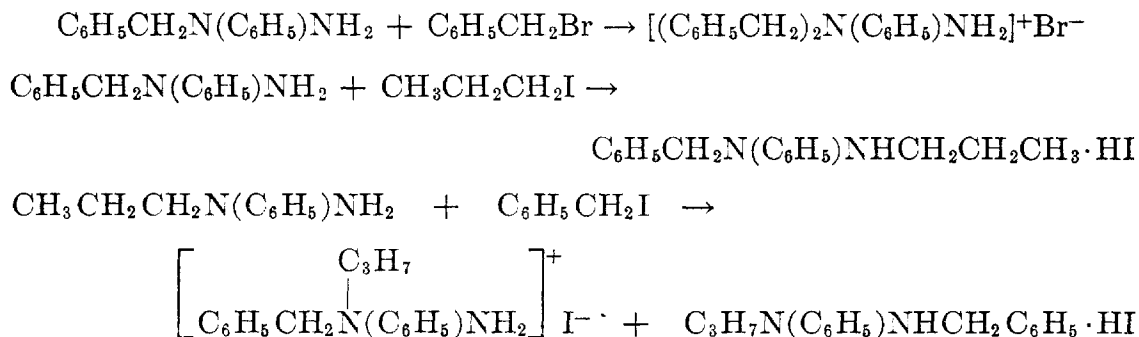
### 1. Alkylation

Alkylation of an alkylhydrazine occurs at the substituted nitrogen provided steric effects do not interfere (67). When an alkyl halide free of electron acceptor or bulky groups is used, the hydrazine becomes more basic on substitution and undergoes further alkylation more readily. For this reason, alkylation of a lower normal aliphatic hydrazine (or hydrazine itself) with a lower normal alkyl halide gives good yields only of the trialkylated quaternary hydrazinium halide, and the procedure is not recommended for preparation of a lower mono- or dialkyl-hydrazine (24). Beyond this point, the analogy to the alkylation of ammonia or simple amines fails. Use of a bulky alkyl chloride favors the formation of a 1,1,2-trialkyl- and a 1,1,2,2-tetraalkylhydrazine rather than a 1,1,1-trialkylhydrazinium salt (67). In general, alkylation of the second nitrogen atom does not occur after quaternization of the first. Methyl iodide, for example, converts 1,2-dimethylhydrazine to 1,1,1,2-tetramethylhydrazinium iodide (68).

The following conflicting reactions have been reported (10):

$$C_6H_5COCHBr \underset{CH_3}{|} \; + \; (CH_3)_2NNH_2 \; \rightarrow \; \left[ C_6H_5COCHN(CH_3)_2NH_2 \underset{CH_3}{|} \right]Br$$

$$HO\!\!\bigotimes\!\!\begin{matrix}COCH_2Br\\OH\end{matrix} \; + \; (CH_3)_2NNH_2 \; \rightarrow \; HO\!\!\bigotimes\!\!\begin{matrix}COCH_2NHN(CH_3)_2 \cdot HBr\\OH\end{matrix}$$

The difference may be the result of the formation of a salt between the acidic hydroxyl groups and the more basic nitrogen. Hydrazine itself, presumably less basic than dimethylhydrazine, forms salts with phenols (56). The directing effect of basicity may be less predictable than that of steric repulsions. Ethyl iodide has been reported to convert 1-acetylphenylhydrazine to 1-acetyl-1-phenyl-hydrazinium iodide (27), but no proof of the structure of the product has been given. The observed effect of solvent polarity on the quaternization of amines
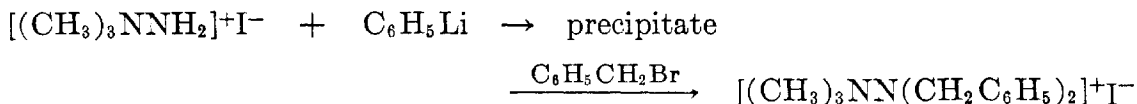
has not been tested in hydrazinium salt formation. Higher alkylation temperatures favor the formation of tri- and tetraalkylhydrazines, rather than hydrazinium salts (35, 67). Methyl $p$-toluenesulfonate, with 1,2-dimethylhydrazine, gives 1,1,1,2-tetramethylhydrazinium tosylate in good yields. The same hydrazine gives, on isopropylation, only the tri- and tetrasubstituted hydrazines. The following reactions have been reported (58):

$$C_6H_5CH_2N(C_6H_5)NH_2 + C_6H_5CH_2Br \rightarrow [(C_6H_5CH_2)_2N(C_6H_5)NH_2]^+Br^-$$

$$C_6H_5CH_2N(C_6H_5)NH_2 + CH_3CH_2CH_2I \rightarrow$$

$$C_6H_5CH_2N(C_6H_5)NHCH_2CH_2CH_3 \cdot HI$$

$$CH_3CH_2CH_2N(C_6H_5)NH_2 + C_6H_5CH_2I \rightarrow$$

$$\left[ \begin{array}{c} C_3H_7 \\ | \\ C_6H_5CH_2N(C_6H_5)NH_2 \end{array} \right]^+ I^- \cdot + C_3H_7N(C_6H_5)NHCH_2C_6H_5 \cdot HI$$

Benzylation of 1-methyl-1-phenylhydrazine gives the expected hydrazinium iodide and possibly some benzyldimethylhydrazinium iodide. Analogous displacements have been reported in the preparation of quaternary ammonium halides. Quaternizations of hydrazines by lower alkyl bromides and iodides are readily completed, even in cold ether. Chlorides frequently require heating or long standing. Other quaternizing agents have also been used, e.g., cyanogen bromide (67), trimethyl phosphite, trimethyl phosphate, and ethyl nitrate (35), dimethyl sulfate (67), methyl $p$-toluenesulfonate (35), and many polyfunctional alkyl halides such as ethyl bromoacetate, 2-bromoethyl acetate (50), and benzhydryloxyethyl chloride (48).

Alkylene dihalides have also been used to form alkylene-bis-hydrazinium halides (51). The reaction of hydrazine hydrate with 1,3-dibromopropane was found to yield pyrazolidine, pyrazolidinopyrazolidine, and unidentified hydrazinium bromides (13).

The following probably general preparation of highly substituted hydrazinium salts has been reported (70):

$$[(CH_3)_3NNH_2]^+I^- + C_6H_5Li \rightarrow \text{precipitate}$$

$$\xrightarrow{C_6H_5CH_2Br} [(CH_3)_3NN(CH_2C_6H_5)_2]^+I^-$$

Azines (40, 64) and $N,N$-disubstituted hydrazones (41) have been alkylated to yield azinium and hydrazonium salts, respectively (e.g., compounds VII and V).

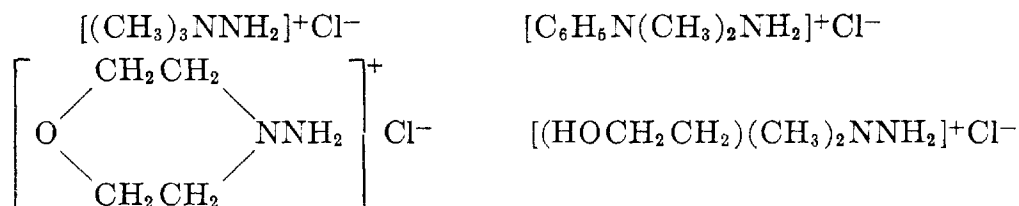### 2. Addition of chloramine to a tertiary amine

A new synthesis of 1,1,1-trisubstituted hydrazinium chlorides has been reported (44a) by two of the authors of this paper. In this process a mixture of chloramine and ammonia gas, produced by the gas-phase reaction of chlorine and an excess of ammonia, is passed into an excess of the liquid tertiary amine or a solution of the amine in an inert solvent. In many instances the correspond-

ing trisubstituted hydrazinium salt crystallizes in a fair degree of purity and almost quantitative yield, in accordance with the following equation:

$$R_3N + NH_2Cl \rightarrow [R_3NNH_2]^+Cl^-$$
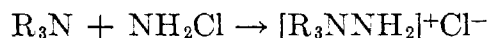
This method has been successfully tested on more than a score of tertiary amines. Representative examples of the hydrazinium salts prepared in this way include the following:

$$[(CH_3)_3NNH_2]^+Cl^- \qquad\qquad [C_6H_5N(CH_3)_2NH_2]^+Cl^-$$
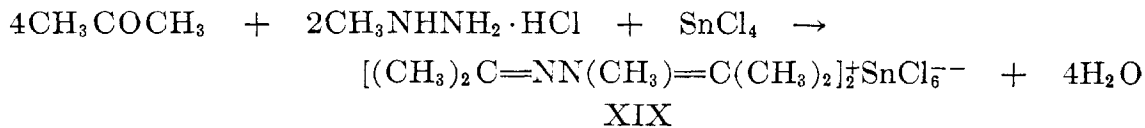
$$\left[\begin{array}{c} CH_2CH_2 \\ O \diagup \diagdown NNH_2 \\ \diagdown CH_2CH_2 \diagup \end{array}\right]^+ Cl^- \qquad\qquad [(HOCH_2CH_2)(CH_3)_2NNH_2]^+Cl^-$$

### 3. Metathesis and neutralization

Metathesis is, as expected, a useful way of preparing halides and other hydrazinium salts:

$$(R_3NNH_2)^+X^- + MA \rightarrow MX + (R_3NNH_2)^+A^-$$
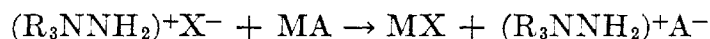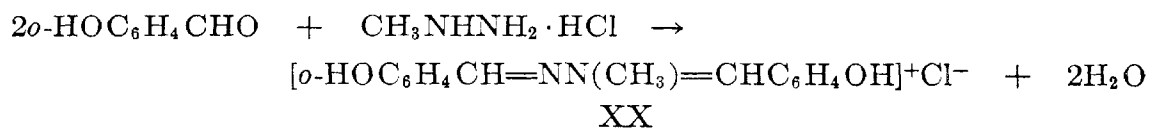
The reaction dates back to the first work on hydrazinium salts. In a typical case, aqueous trimethylhydrazinium iodide is digested with an excess of silver chloride, and the filtrate is evaporated to dryness to give the hygroscopic trimethylhydrazinium chloride (33). The tetrachloroaurates, the hexachloroplatinates, the picrates, and other water-insoluble salts have frequently been prepared by the action of the proper acid on the soluble hydrazinium halides. Shaking aqueous trimethylhydrazinium hydroxide with methyl iodide and potassium hydroxide gives an almost quantitative yield of the hydrazinium iodide (33). Hydrazinium salts have also been formed by neutralization of the corresponding hydroxides (71).

### 4. Condensation

A few condensations have been used in the preparation of quaternized hydrazine derivatives. Such compounds have been those containing a carbon atom doubly bonded to the quaternized nitrogen. Azinium chlorides have been prepared from the acidic condensation of aldehydes or ketones with methylhydrazine (38, 39):
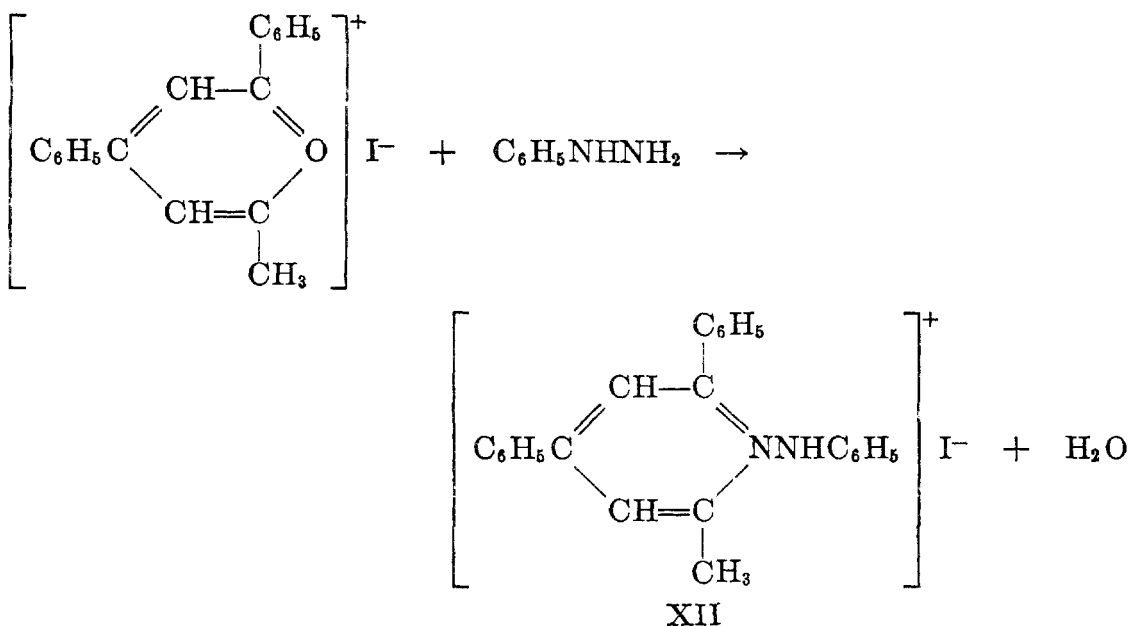
$$4CH_3COCH_3 + 2CH_3NHNH_2\cdot HCl + SnCl_4 \rightarrow$$

$$[(CH_3)_2C\!=\!NN(CH_3)\!=\!C(CH_3)_2]_2^+ SnCl_6^{--} + 4H_2O$$

<div align="center">

XIX

1-Methyl-1,2-bis(isopropylidene)-
azinium hexachlorostannate

</div>

$$2o\text{-}HOC_6H_4CHO + CH_3NHNH_2\cdot HCl \rightarrow$$

$$[o\text{-}HOC_6H_4CH\!=\!NN(CH_3)\!=\!CHC_6H_4OH]^+Cl^- + 2H_2O$$

<div align="center">

XX

1-Methyl-1,2-bis(salicylidene)-
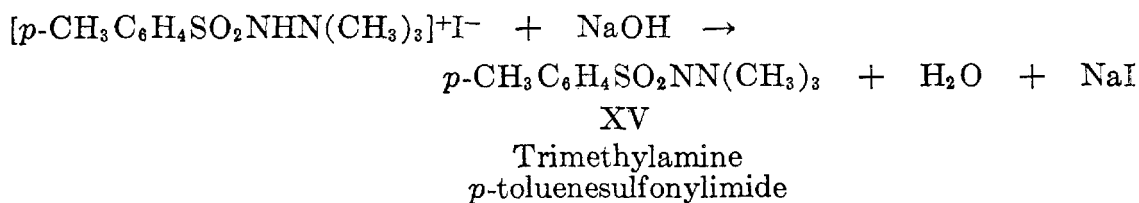azinium chloride

</div>

The products formed in the above reactions closely resemble those obtained by direct alkylation of an azine (40).

Condensation of a cyclic oxonium iodide with phenylhydrazine has been shown to yield a cyclic hydrazinium salt (52);
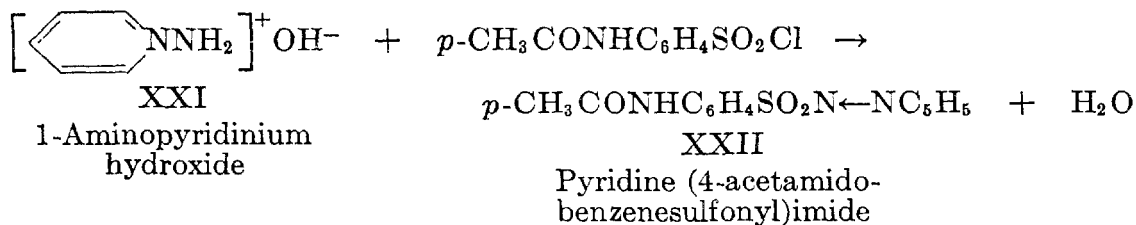
$$
\left[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{CH—C} \\
\text{C}_6\text{H}_5\text{C} \qquad \text{O} \\
\text{CH=C} \\
\text{CH}_3
\end{array}
\right]^+ \text{I}^- \;+\; \text{C}_6\text{H}_5\text{NHNH}_2 \;\rightarrow
$$

$$
\left[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{CH—C} \\
\text{C}_6\text{H}_5\text{C} \qquad \text{NNHC}_6\text{H}_5 \\
\text{CH=C} \\
\text{CH}_3
\end{array}
\right]^+ \text{I}^- \;+\; \text{H}_2\text{O}
$$

XII

### C. AMINE IMIDES
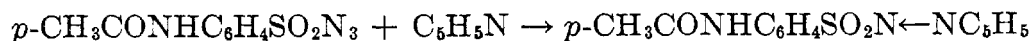
Reference has been made earlier to hydrazinium "ylides," quaternized hydrazines of the general formula $\text{R}_3\text{N}\rightarrow\text{NR}$. Their properties indicate the absence of ionic bonds. Some of these compounds have been prepared by the reaction of specially substituted hydrazinium salts with a base (6, 55, 66):

$$[p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHN(CH}_3)_3]^+\text{I}^- \;+\; \text{NaOH} \;\rightarrow$$

$$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NN(CH}_3)_3 \;+\; \text{H}_2\text{O} \;+\; \text{NaI}$$

XV

Trimethylamine
$p$-toluenesulfonylimide

A similar product was prepared in an attempt to form a derivative of a hydrazinium hydroxide (6):

$$\left[\bigcirc\!\!-\!\text{NNH}_2\right]^+\text{OH}^- \;+\; p\text{-CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{Cl} \;\rightarrow$$

XXI
1-Aminopyridinium
hydroxide

$$p\text{-CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{N}\leftarrow\text{NC}_5\text{H}_5 \;+\; \text{H}_2\text{O}$$

XXII
Pyridine (4-acetamido-
benzenesulfonyl)imide

XXII was initially made by the following condensation (6):

$$p\text{-CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{N}_3 \;+\; \text{C}_5\text{H}_5\text{N} \;\rightarrow\; p\text{-CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{N}\leftarrow\text{NC}_5\text{H}_5$$

The precipitate obtained on adding a solution of phenyllithium in ether to trimethylhydrazinium iodide (70) may be an "ylide," as indicated by the following equation:

$$[(CH_3)_3NNH_2]^+I^- + C_6H_5Li \rightarrow C_6H_6 + LiI + (CH_3)_3N{\rightarrow}NH$$
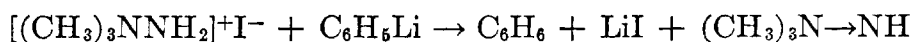
## IV. REACTIONS

This summary of the known chemistry of hydrazinium compounds will be arranged according to reactions as listed in the table of contents. Under each reaction subdivisions will be made of the different types of anion, e.g., $OH^-$ and $X^-$. Each reaction is applied first to hydrazinium compounds, then to hydrazonium compounds, and finally to azinium compounds.

### A. HYDRATION AND HYDROLYSIS

The hydrazinium hydroxides, like their ammonium analogs, are readily decomposed in hot or boiling water (22):

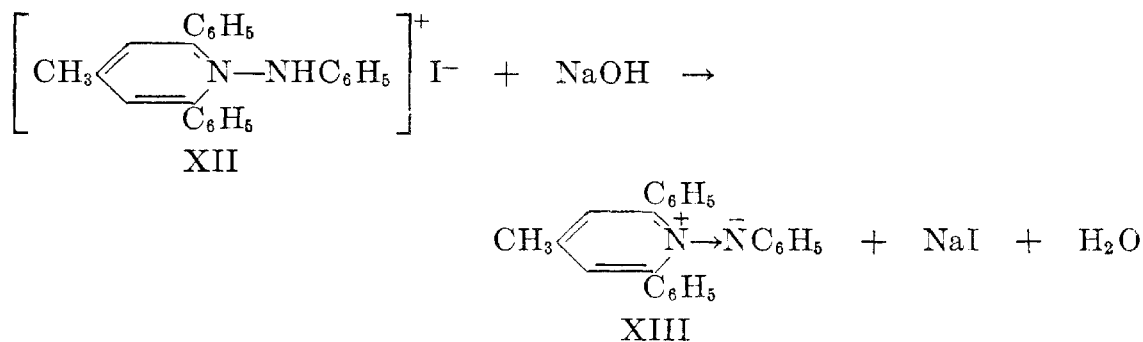$$(R_3NNH_2)^+OH^- \xrightarrow{\ H_2O\ } R_2NNH_2 + ROH$$
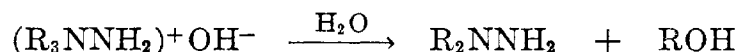
Distinction has been made here between hydrolysis and pyrolysis because of the difference in mechanisms and products. Although not required by the equation for the above reaction, the presence of water is necessary. The reaction is not as simple or consistent as the equation might imply. A few generalizations can be made about the aqueous decomposition of hydrazinium hydroxides. The most apparent of these is that the course of the reaction, including products, follows pretty closely the Hoffmann and Emde degradations (20), with the $NH_2$ group being considered as its isosteric $—CH_3$ analog (51). Thus, although triethylhydrazinium hydroxide in boiling water gives ethylene and 1,1-diethylhydrazine (24), diethylphenylhydrazinium hydroxide yields ethanol and ethyl-1-phenyl-1-hydrazine (25). Trimethylhydrazinium hydroxide strongly resists aqueous decomposition (for its pyrolysis see Section IV,B). However, 1-amino-1-methylpiperidinium hydroxide is converted by boiling water to ammonia, piperidine, and an unidentified hydrazine (36), as contrasted to the Hofmann conversion of $N$-alkylated piperidinium hydroxides. Hydrolysis of hydrazinium hydroxides is usually independent of the presence of caustic (acid, of course, neutralizes the hydroxide). Tetrasubstituted hydrazinium hydroxides apparently are split at the nitrogen–nitrogen bond (32):

$$[(CH_3)_3NNHCH_3]^+OH^- + H_2O \rightarrow (CH_3)_3N + CH_2O + NH_4OH$$
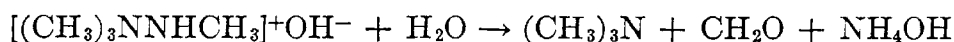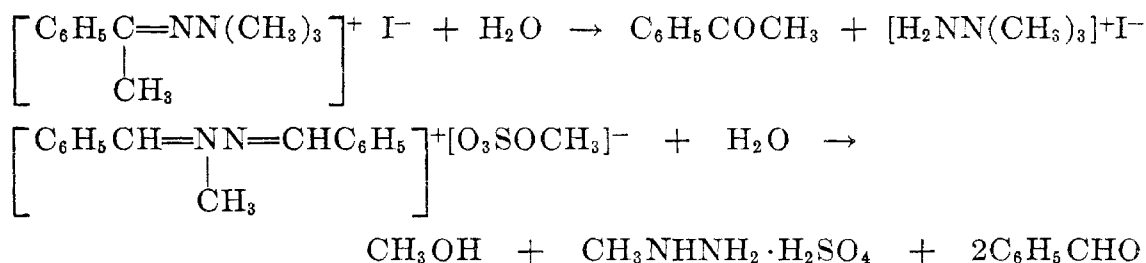
Hydrazonium, azinium, and 1-aminopyridinium hydroxides are unstable in aqueous solution and unknown in the pure state.

Hydrazinium salts, especially those of strong mineral acids, are not attacked by water save under pyrolytic conditions. The hydrazinium halides resist attack by hot caustic more strongly than do, in general, the corresponding quaternary ammonium salts. Many of the hydrazinium chlorides can be recovered unchanged after being refluxed with 10 per cent sodium hydroxide or potassium

hydroxide solution (35). Hydrazinium halides are similarly unaffected by prolonged treatment with hot acids (the second nitrogen of these compounds is nonbasic). However, hydrazinium halides in which one of the nitrogens is negatively substituted undergo dehydrohalogenation with caustic (54):
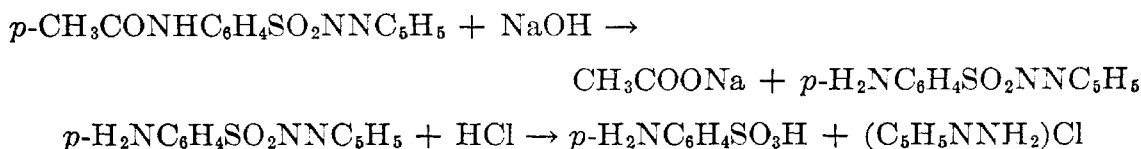
$$\left[ CH_3 \diagup\!\!\!\diagdown \begin{array}{c} C_6H_5 \\ N\!-\!NHC_6H_5 \\ C_6H_5 \end{array} \right]^+ I^- \;+\; NaOH \;\rightarrow$$

XII

$$CH_3 \diagup\!\!\!\diagdown \begin{array}{c} C_6H_5 \\ \overset{+}{N}\!\rightarrow\!\overset{-}{N}C_6H_5 \\ C_6H_5 \end{array} \;+\; NaI \;+\; H_2O$$

XIII

Both hydrazonium and azinium salts are readily hydrolyzed to carbonyl compounds and hydrazinium salts or hydrazines (38, 41):

$$\left[ \begin{array}{c} C_6H_5C\!=\!NN(CH_3)_3 \\ | \\ CH_3 \end{array} \right]^+ I^- \;+\; H_2O \;\rightarrow\; C_6H_5COCH_3 \;+\; [H_2NN(CH_3)_3]^+I^-$$

$$\left[ \begin{array}{c} C_6H_5CH\!=\!NN\!=\!CHC_6H_5 \\ | \\ CH_3 \end{array} \right]^+ [O_3SOCH_3]^- \;+\; H_2O \;\rightarrow$$

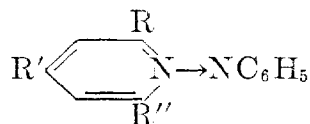$$CH_3OH \;+\; CH_3NHNH_2\cdot H_2SO_4 \;+\; 2C_6H_5CHO$$

The hydrazonium iodides which have been studied are, for the most part, more readily hydrolyzed by alkali than by acid. 1,1,1-Trimethyl-2-(1-phenylethylidene-1-)hydrazonium iodide on being refluxed with strong hydriodic acid for 5 hr. gave 85 per cent of the theoretical quantity of 1,1,1-trimethylhydrazinium iodide and 76.5 per cent of the theoretical quantity of acetophenone. After refluxing with a solution of sodium ethoxide in wet ethyl alcohol for 2 hr., the same ketone derivative gave the same percentage yield of the hydrazinium iodide, a trace of trimethylamine, and a quantitative yield of the ketone (41).

Azinium salts are hydrolyzed more readily, e.g., addition of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid to 1,2-bis(isopropylidene)-1-methylazinium hexachlorostannate gives an immediate precipitate of acetone 2,4-dinitrophenylhydrazone. Phenylhydrazine behaved similarly to its dinitro derivative (36). Water alone converts 1,2-bis(benzylidene)-1-methylazinium methosulfate rapidly to methylhydrazine (64).
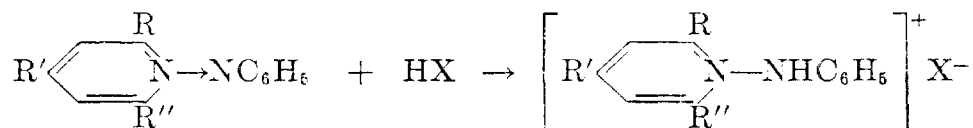
The amine imides resist hydrolysis. Refluxing in 20 per cent aqueous sodium hydroxide converts pyridine (4-acetamidobenzenesulfonyl)imide (XXII) to a fair yield of the deacetylated product; this with refluxing 1:1 hydrochloric acid gives 1-aminopyridinium chloride (6):

$$p\text{-}CH_3CONHC_6H_4SO_2NNC_5H_5 \;+\; NaOH \;\rightarrow$$

$$CH_3COONa \;+\; p\text{-}H_2NC_6H_4SO_2NNC_5H_5$$

$$p\text{-}H_2NC_6H_4SO_2NNC_5H_5 \;+\; HCl \;\rightarrow\; p\text{-}H_2NC_6H_4SO_3H \;+\; (C_5H_5NNH_2)Cl$$

Schneider's "azeniates," the pyridine $N$-arylimides,

$$R'\underset{R''}{\overset{R}{\diagdown}}N{\rightarrow}NC_6H_5$$

are similarly resistant to attack by water or alkali. Acid is reported to convert them, like other representatives of the type, to the anilinopyridinium salts (52):

$$R'\underset{R''}{\overset{R}{\diagdown}}N{\rightarrow}NC_6H_5 \;+\; HX \;\rightarrow\; \left[R'\underset{R''}{\overset{R}{\diagdown}}N{-}NHC_6H_5\right]^+ X^-$$

One might expect an amine imide to form, by addition of water, the corresponding hydrazinium hydroxide:

$$p\text{-}CH_3C_6H_4SO_2NN(CH_3)_3 + H_2O \rightarrow [p\text{-}CH_3C_6H_4SO_2NHN(CH_3)_3]OH$$
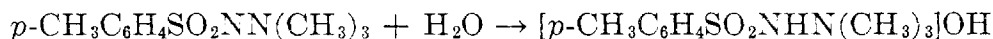
It has been shown by conductometric measurements, however, that this reaction goes to less than 0.1 per cent of the theoretical (66c). Although the ylide forms a stable monohydrate (isomeric with 1,1,1-trimethyl-2-$p$-toluenesulfonylhydrazinium hydroxide) on recrystallization from water, the product is undissociated in water, and the water of crystallization is lost on recrystallization from alcohol. Recrystallization of XV from alcohol does not yield an alcoholate. This behavior contrasts with that of the formally similar amine oxides $R_3N{\rightarrow}O$, which form weakly basic, dissociated hydrates and alcoholates.

### B. PYROLYSIS

Thermal decomposition of hydrazinium hydroxides follows a course roughly parallel to that of the quaternary ammonium hydroxides. Dry distillation of 1,1,1-trimethylhydrazinium hydroxide at 150 mm. pressure was reported to give a 20 per cent yield of 1,1-dimethylhydrazine, plus dimethylamine, ammonia, and at least one other unisolated substance (32). Forty years later, a detailed study showed that pyrolysis of the sesquihydrated trimethylhydrazinium hydroxide gives nitrogen, water, ammonia, methyl alcohol, dimethylamine, trimethylamine, 1,1-dimethylhydrazine, tetramethyldiaminomethane, and a solid residue (34). Distillation from a caustic solution at about 170°C. gives a similar mixture.

The hydrazinium halides are more resistant to thermal decomposition than are the hydroxides. In fact, many of the halides melt at temperatures above those used to decompose the corresponding hydroxides. Gas evolution has frequently been reported as part of the decomposition occurring on melting a hydrazinium salt. However, no study has been made of the products formed.

Pyrolysis of XV at 185–195°C. gives ammonia, a trace of formaldehyde, trimethylamine, $p$-toluenesulfonamide, and sulfonamide-formaldehyde condensation polymers (66c):

$$p\text{-}CH_3C_6H_4SO_2NN(CH_3)_3 \rightarrow NH_3 + HCHO + (CH_3)_3N$$
$$+ (p\text{-}CH_3C_6H_4SO_2NCH_2{-})_n$$
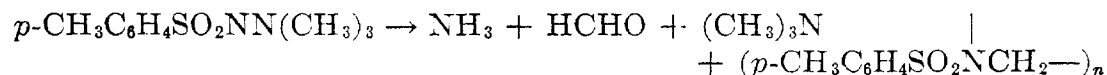
The nitrogen–nitrogen bond appears to be, as would be expected, less stable in the amine imides than in the salts or hydroxides.

## C. OXIDATION

Very little has been reported on the oxidation of quaternized hydrazines. In contrast to the mono- and disubstituted hydrazines, quaternary hydrazinium hydroxides in general do not reduce Fehling's solution (33). Formylalkylhydrazinium hydroxides do, of course, reduce Fehling's solution (26). Even less has been reported on the oxidizability of hydrazinium salts. Nitrous acid gives, with trimethylhydrazinium iodide, a green solution and an unidentified gas (32). Hydrogen peroxide (30 per cent) reacts with trimethylamine $p$-toluenesulfonylimide, forming a small amount of $p$-toluenesulfonamide (66). Presumably trimethylamine oxide is also formed, but this has not been established.

## D. REDUCTION

Although several attempts have been made to reduce quaternary hydrazinium salts to 1,1-disubstituted hydrazines, only one has been successful. Hydrogenation of 1-acetamidopyridinium chloride over platinum gives a fair yield of acetamidopiperidine (6). The unacetylated salt gives, as do other hydrazinium salts, cleavage of the nitrogen–nitrogen bond on hydrogenation. Catalytic hydrogenation of a ketoalkylhydrazinium salt has been shown to yield first a ketoalkyldialkylamine and then a hydroxyalkyl derivative (10). Other reductants listed in other reports include zinc plus acid (24, 40), sodium or its amalgam in alcohol (71), magnesium (59), and hydrogen sulfide (35). Trimethylamine $p$-toluenesulfonylimide (XV) is readily reduced by zinc in aqueous acetic acid. The pyridine $N$-arylimides are also readily cleaved by either zinc and caustic or by hydrogen over platinum (55).

$$R\langle\!=\!\rangle\overset{R}{\underset{R'}{N}}\!\to\!NC_6H_5 \xrightarrow{\ H_2\ } R\langle\!=\!\rangle\overset{R}{\underset{R'}{N}} + C_6H_5NH_2$$
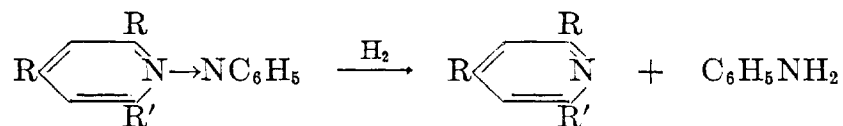
## E. ALKYLATION AND ACYLATION

It has been noted in Section III that quaternized hydrazines in general resist further alkylation. Some exceptions to this generalization were also pointed out. This appears to be typical of the reaction of alkyl iodides with hydrazinium hydroxides. Although the hydroxide is converted to the iodide by the action of methyl iodide, the same reagent, in ethanol at 125–130°C., converts trimethylhydrazinium iodide to tetramethylammonium iodide. Iodine, nitrogen, and hydrogen [sic] were indicated as other products, which established the general route of the reaction (33). Methyl iodide is reported to convert 2-hydroxyethyl-1,1-dimethylhydrazine to 2-hydroxyethyl-1,1,1,2,2-pentamethylhydrazinium diiodide; no proof of structure or analytical data are given (10). Trimethylhydrazinium iodide, with ethereal phenyllithium, gave an unidentified precipitate which was capable of ready benzylation (70).

Acetic anhydride converts 1-aminopyridinium chloride to 1-acetamidopyridinium chloride (6). Although 1-aminopyridinium hydroxide has not been isolated, it readily undergoes acylation in aqueous solution (6):

$$\left[\underset{\phantom{x}}{\bigodot}NNH_2\right]^+ OH^- + CH_3CONH\bigodot SO_2Cl \xrightarrow{NaOH}$$

$$\bigodot NNSO_2\bigodot NHCOCH_3 + NaCl + H_2O$$

Alkylation of amine imides has also been reported. The benzylation described at the end of Section III,B,1 may have been a reaction of trimethylamine imide or its lithium derivative. A similar benzylation has been reported recently (66c):

$$p\text{-}CH_3C_6H_4SO_2NN(CH_3)_3 + C_6H_5CH_2Cl \rightarrow$$

$$\left[\underset{CH_2C_6H_5}{\overset{p\text{-}CH_3C_6H_4SO_2NN(CH_3)_3}{|}}\right]^+ Cl^-$$

The yield was poor, and the structure of the product was not established. The same authors reported that the same amine imide gives, with either methyl iodide or ethyl iodide, only low yields of 1,1,1-trimethyl-2-$p$-tolylsulfonyl-hydrazinium iodide. The same product is formed in much better yield by the action of hydriodic acid:

$$p\text{-}CH_3C_6H_4SO_2NN(CH_3)_3 \xrightarrow{RI} [p\text{-}CH_3C_6H_4SO_2NHN(CH_3)_3]^+I^- + ?$$

$$p\text{-}CH_3C_6H_4SO_2NN(CH_3)_3 \xrightarrow{HI} [p\text{-}CH_3C_6H_4SO_2NHN(CH_3)_3]^+I^-$$

## F. CARBONYL CONDENSATIONS

It has been stated before that the amino group of a 1,1,1-trisubstituted hydrazinium compound behaves more like the isosteric —CH₃ group than the —NH₂ group of an amine or a hydrazine. Attempts to prepare hydrazonium compounds by direct condensation of a hydrazinium compound with an aldehyde or ketone have been almost completely unsuccessful. The only successful reaction of this type that has been reported (71) is given below:

$$[H_2NN(CH_3)_2CH_2CH_2CH(OC_2H_5)_2]_2C_2O_4 \xrightarrow{H_2O, H_2C_2O_4}$$

$$\left[\begin{array}{c} NCH_3 \\ CH_3N \diagup \diagdown CH_2 \\ \phantom{x} \| \phantom{xxx} | \\ HC\text{——}CH_2 \end{array}\right]_2 C_2O_4$$

$$[H_2NN(CH_3)_2CH_2CH_2CHO]_2PtCl_6 \xrightarrow[\text{acetone}]{\text{heat}} \left[\begin{array}{c} NCH_3 \\ CH_3N \diagup \diagdown CH_2 \\ \phantom{x} \| \phantom{xxx} | \\ HC\text{——}CH_2 \end{array}\right]_2 PtCl_6$$

## TABLE 1
### *1,1,1-Trisubstituted hydrazinium compounds*
### $[RR'R''NNH_2]^+A^-$

| R | R' | R'' | A⁻ or Anion | Melting Point | References |
|---|---|---|---|---|---|
| | | | | °C. | |
| $CH_3$— | $CH_3$— | $CH_3$— | $OH^-$ | | (35) |
| | | | $Cl^-$ | | (33) |
| | | | $I^-$ | ca. 235 (d.)* | (33, 41) |
| | | | $(CH_3)_2PO_3^-$ | | (35) |
| | | | $(CH_3)_2PO_4^-$ | | (35) |
| $HCOCH_2$— | $CH_3$— | $CH_3$— | $OH^-$ | Not iso-lated | |
| | | | $Cl^-$ | | (26) |
| | | | $I^-$ | | |
| | | | $PtCl_6^{--}$ | | (26) |
| $C_2H_5$— | $CH_3$— | $CH_3$— | $OH^-$ | | (35) |
| | | | $Cl^-$ | | (49) |
| | | | $Br^-$ | | (49) |
| | | | $I^-$ | | (49) |
| | | | $NO_2^-$ | | (35) |
| | | | $PtCl_6^{--}$ | | (49) |
| $HCOCH_2CH_2$— | $CH_3$— | $CH_3$— | $Cl^-$ | | (71) |
| | | | $PtCl_6^{--}$ | 197-198 | (71) |
| $HOC_2H_4$— | $CH_3$— | $CH_3$— | $Cl^-$ | | (44a) |
| $CH_3COCH_2CH_2$— | $CH_3$— | $CH_3$— | $Br^-$ | | (50) |
| | | | $AuCl_4^-$ | 125-126 | (50) |
| $CH_3OCOCH_2CH_2$— | $CH_3$— | $CH_3$— | $Br^-$ | 132-133 | (50) |
| $C_6H_5$— | $CH_3$— | $CH_3$— | $Cl^-$ | 187-188 (d.) | (58) |
| | | | $I^-$ | 126 (d.) | (59) |
| | | | $AuCl_4^-$ | 123-124 (d.) | (1, 2, 3) |
| | | | $PtCl_6^{--}$ | 158-159 (d.) | (1, 2, 3) |
| $p$-$CH_3C_6H_4$— | $CH_3$— | $CH_3$— | $Cl^-$ | 165-166 | (44a) |
| $(C_2H_5O)_2CHCH_2$— | $CH_3$— | $CH_3$— | $Cl^-$ | Oil | (26) |
| | | | $I^-$ | Oil | (26) |
| | | | $PtCl_6^{--}$ | 165 (d.) | (26) |
| | | | $Fe(CN)_6^{---}$ | | (26) |
| | | | 2,4,6-$(NO_2)_3$-$C_6H_2O^-$ | Oil | (26) |
| $C_6H_5CH_2$— | $CH_3$— | $CH_3$— | $I^-$ | 125 (d.) | (58) |
| $(C_2H_5O)_2CHCH_2CH_2$— | $CH_3$— | $CH_3$— | $OH^-$ | | (71) |
| | | | $Cl^-$ | | (71) |
| | | | $I^-$ | 91 | (71) |
| | | | $PtCl_6^{--}$ | | (71) |
| | | | $HC_2O_4^-$ | 102 | (71) |
| $C_6H_5COCH(CH_3)$— | $CH_3$— | $CH_3$— | $Br^-$ | 200 | (10) |
| $n$-$C_{12}H_{25}$— | $CH_3$— | $CH_3$— | $I^-$ | 126 | (68) |
| $(CH_3)_2N(CH_2)_{10}$—<br>$\quad\mid$<br>$\quad NH_2$ | $CH_3$— | $CH_3$— | $2Br^-$ | 114-115 | (51) |
| $(C_6H_5)(n$-$C_3H_7)CHCOOC_2H_4$— | $CH_3$— | $CH_3$— | $Cl^-$ | 96 | (48) |
| $(C_6H_5)_2CHOCH_2CH_2$— | $CH_3$— | $CH_3$— | $Cl^-$ | 127 | (48) |
| | | | $I^-$ | 159 | (48) |
| $(C_6H_5)_2CHCOOCH_2CH_2$— | $CH_3$— | $CH_3$— | $Cl^-$ | 146 | (48) |
| $(p$-$C_7H_7)(C_6H_5)CHOC_2H_4$— | $CH_3$— | $CH_3$— | $Cl^-$ | 132-133 | (48) |
| $(C_6H_5)(C_6H_{11})CHCOOC_2H_4$— | $CH_3$— | $CH_3$— | $Cl^-$ | 127-128 | (48) |
| $n$-$C_{18}H_{37}$— | $CH_3$— | $CH_3$— | $I^-$ | 163-164.5 (d.) | (68) |
| | | | $(CH_3)SO_4^-$ | 99-100 | (68) |
| $n$-$C_{12}H_{25}$— | $CN$— | $CH_3$— | $Br^-$ | 71-72 | (68) |
| $C_6H_5$— | $C_2H_5$— | $CH_3$— | $OH^-$ | Syrup | (34, 57) |
| | | | $Br^-$ | | (23) |
| | | | $I^-$ | 119 (d.) | (23, 34, 59) |
| | | | $I^-$·$2H_2NCSNH_2$ | 192-193 | (61) |
| | | | 2,4,6-$(NO_2)_3$-$C_6H_2O^-$ | 110-111 | (60) |

TABLE 1—*Continued*

| R | R' | R'' | A⁻ or Anion | Melting Point | References |
|---|---|---|---|---|---|
| | | | | °C. | |
| d-C₆H₅— | C₂H₅— | CH₃— | I⁻ | 115–116 (d.) | (52) |
| | | | AuCl₄⁻ | 97 (d.) | (52) |
| | | | PtCl₆⁻⁻ | 159 (d.) | (52) |
| | | | C₄H₅O₆⁻·H₂O | ca. 80 | (52) |
| | | | C₁₀H₁₅O₄⁻ | 178–179 | (52) |
| | | | C₁₀H₁₅O₄S⁻ | 134–135 | (52) |
| | | | C₁₀H₁₄BrO₄S⁻ | 152–153 | (60) |
| l-C₆H₅— | C₂H₅— | CH₃— | 2,4,6-(NO₂)₃-C₆H₂O⁻ | 114–115 (d.) | (60) |
| n-C₁₂H₂₅— | C₂H₅— | CH₃— | Br⁻ | 82 | (68) |
| n-C₁₆H₃₃— | C₂H₅— | CH₃— | Br⁻ | 94 | (68) |
| n-C₁₂H₂₅— | C₃H₅— | CH₃— | Cl⁻ | Oil | (68) |
| | | | Br⁻ | Oil | (68) |
| C₆H₅— | n-C₃H₇— | CH₃— | I⁻ | 106–107 (d.) | (59, 60) |
| n-C₁₆H₃₃— | C₂H₅OCOCH₂— | CH₃— | Br⁻ | 68–69 | (68) |
| C₆H₅CH₂— | C₆H₅— | CH₃— | OH⁻ | Oil | (58) |
| | | | Cl⁻ | 158–159 (d.) | (58) |
| | | | I⁻ | 122 (d.) | (58, 59) |
| | | | I⁻·2H₂NCSNH₂ | 211 | (59) |
| | | | HgI₃⁻ | 128–129 (d.) | (58) |
| | | | HgI₄⁻⁻ | 135–136 (d.) | (58) |
| | | | AuCl₄⁻ | 134 (d.) | (58) |
| | | | PtCl₆⁻⁻ | 162 (d.) | (58) |
| | | | HFe(CN)₆⁻⁻ | 140 (d.) | (58) |
| | | | H₅Fe₂(CN)₁₂⁻⁻ | (d.) | (58) |
| | | | 2,4,6-(NO₂)₃-C₆H₂O⁻ | 152 (d.) | (58) |
| | | | C₁₀H₁₄BrO₄S⁻ | 173–175 | (58) |
| l-C₆H₅CH₂— | C₆H₅— | CH₃— | I⁻ | 123–124 (d.) | (58) |
| d-C₆H₅CH₂— | C₆H₅— | CH₃— | I⁻ | 114 (d.) | (58) |
| | | | HgI₃⁻ | 124 (d.) | (58) |
| | | | HgI₄⁻⁻ | 128–129 (d.) | (58) |
| | | | AuCl₄⁻ | 128–129 (d.) | (58) |
| | | | PtCl₆⁻⁻ | 154 (d.) | (58) |
| | | | 2,4,6-(NO₂)₃-C₆H₂O⁻ | 146–147 (d.) | (58) |
| | | | C₁₀H₁₅O₄S⁻ | 176–177 (d.) | (58) |
| | | | C₁₀H₁₄BrO₄S⁻ | 197 | (58) |
| C₆H₅— | CH₃CO— | C₂H₅— | I⁻ | 201 | (27) |
| HOC₂H₄— | C₂H₅— | C₂H₅— | Cl⁻ | | (44a) |
| C₂H₅— | C₂H₅— | C₂H₅— | OH⁻ | | (24) |
| | | | Cl⁻ | | (24) |
| | | | I⁻ | | (24) |
| | | | NO₃⁻ | | (24) |
| | | | PtCl₆⁻⁻ | | (24) |
| HOC₂H₅— | C₂H₅— | C₂H₅— | Cl⁻ | | (44a) |
| C₆H₅— | C₂H₅— | C₂H₅— | OH⁻ | Not isolated | (24) |
| | | | Cl⁻ | 197–198 (d.) | (23, 46) |
| | | | Br⁻ | ca. 193 (d.) | (25) |
| | | | I⁻ | 145 (d.) | (1) |
| | | | PtCl₆⁻⁻ | | (23) |
| | | | H₅Fe₂(CN)₁₂⁻ | | (23) |

TABLE 1—*Concluded*

| R | R' | R'' | A⁻ or Anion | Melting Point °C. | References |
|---|----|-----|-------------|-------------------|------------|
| $C_6H_{11}$— | $C_2H_5$— | $C_2H_5$— | Cl⁻ | | (44a) |
| $C_6H_5$— | $C_2H_5$— | $C_2H_5$— | I⁻ | 107–108 (d.) | (34) |
| | | | PtCl₆⁻⁻ | 151 (d.) | (34) |
| $C_6H_5$— | $C_6H_5CO$— | $C_2H_5$— | I⁻ | Oil | (68) |
| 2,4,5-$(CH_3)_3C_6H_2CH_2$— | 2,4,5-$(CH_3)_3C_6H_2CH_2$— | $C_2H_5$— | I⁻ | 160 | (17) |
| $C_6H_5CH_2$— | $C_6H_5$— | $C_2H_5$— | I⁻ | 116–117 (d.) | (34) |
| | | | $C_{10}H_{15}O_4S$⁻ | 187–188 | (34) |
| | | | I⁻·$H_2NCSNH_2$ | | (59) |
| d-$C_6H_5CH_2$— | $C_6H_5$— | $C_2H_5$— | $C_{10}H_{15}O_4S$⁻ | 147–148 | (34) |
| n-$C_3H_7$— | n-$C_3H_7$— | n-$C_3H_7$— | Cl⁻ | 156 | (67) |
| $C_4H_5$— | n-$C_3H_7$— | n-$C_3H_7$— | Br⁻ | 85 | (1) |
| | | | I⁻ | 110 | (2, 3) |
| $C_6H_5$— | i-$C_3H_7$— | i-$C_3H_7$— | I⁻ | | (1, 60) |
| $C_6H_5CH_2$— | $C_6H_5$— | n-$C_3H_7$— | Cl⁻ | 145–146 (d.) | (60) |
| | | | I⁻ | 125–126 (d.) | (59) |
| | | | AuCl₄⁻ | 132–133 (Unstable) | (60) |
| | | | PtCl₆⁻⁻ | 151 (d.) | (60) |
| | | | $C_{10}H_{15}O_4S$⁻ | | (60) |
| | | | I⁻·$2H_2NCSNH_2$ | 180–181 | (60) |
| | | | $C_{10}H_{14}BrO_4S$⁻ | 144–148 | (60) |
| l-$C_6H_5CH_2$— | $C_6H_5$— | n-$C_3H_7$— | $C_{10}H_{15}O_4S$⁻ | 191 | (60) |
| | | | $C_{10}H_{14}BrO_4S$⁻ | 178–179 | (60) |
| d-$C_6H_5CH_2$— | $C_6H_5$— | n-$C_3H_7$— | $C_{10}H_{15}O_4S$⁻ | 190 | (60) |
| n-$C_4H_9$— | n-$C_4H_9$— | n-$C_4H_9$— | Cl⁻ | | (67) |
| $C_6H_5$— | n-$C_4H_9$— | n-$C_4H_5$— | Br⁻ | 148 | (2) |
| | | | I⁻ | 95 | (2) |
| $C_6H_5$— | i-$C_4H_9$— | i-$C_4H_9$— | I⁻ | | (1, 2) |
| $C_6H_5$— | i-$C_5H_{11}$— | i-$C_5H_{11}$— | Br⁻ | | (1) |
| | | | I⁻ | | (2, 3) |
| $C_6H_5CH_2$— | $C_6H_5CH_2$— | $C_6H_5$— | OH⁻ | | (46) |
| | | | Cl⁻ | 153–154 | (46) |
| | | | Br⁻ | 143 | (46) |
| | | | I⁻ | 133–134 (d.) | (58) |
| | | | AuCl₄⁻ | 147–148 (d.) | (58) |
| | | | PtCl₆⁻⁻ | 151 (d.) | (58) |
| n-$C_6H_{13}$— | n-$C_6H_{13}$— | n-$C_6H_{13}$— | Cl⁻ | 65 | (67, 68) |
| n-$C_7H_{15}$— | n-$C_7H_{15}$— | n-$C_5H_{15}$— | Cl⁻ | 65.5–66.5 | (44a) |

* d. = decomposes.

The most recently described route to azinium salts (39) may possibly involve a carbonyl condensation of a hydrazonium salt (reaction 2) instead of the more readily acceptable quaternization through condensation of a preformed hydrazone (reaction 1):
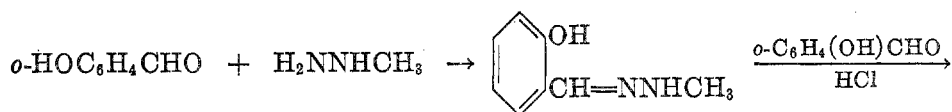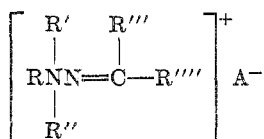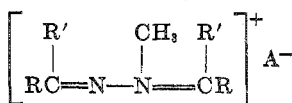
o-$\overset{\cdot}{H}OC_6H_4CHO$ + $H_2NNHCH_3$ → [structure: benzene ring with OH and CH=NNHCH₃ substituents] $\xrightarrow[HCl]{o\text{-}C_6H_4(OH)CHO}$

$$\left[\begin{array}{c} \text{OH} \qquad \text{HO} \\ \text{CH}=\text{NN}=\text{CH} \\ | \\ \text{CH}_3 \end{array}\right]^+ \text{Cl}^- \qquad (1)$$

$$o\text{-HOC}_6\text{H}_4\text{CHO} + \text{H}_2\text{NNHCH}_3 \xrightarrow{\text{HCl}}$$

$$\left[\begin{array}{c} \text{OH} \\ \text{CH}=\text{NNH}_2 \\ | \\ \text{CH}_3 \end{array}\right]^+ \text{Cl}^- \quad o\text{-C}_6\text{H}_4(\text{OH})\text{CHO} \qquad (2)$$

Most (41) found that it is easier to prepare hydrazonium salts by quaternization of a hydrazone than by reaction of a ketone with 1,1,1-trimethylhydrazinium iodide. In addition, Todd (66a) has prepared authentic samples of $N$-alkyl- and $N,N$-dialkylhydrazones

$$\text{CH}_3\text{NHNH}_2 + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{CH}_3\text{NHN}=\text{CHC}_6\text{H}_5 + \text{H}_2\text{O}$$

## TABLE 2

*Tetra- and pentasubstituted hydrazinium compounds*

$(\text{RR}'\text{R}''\text{NNR}'''\text{R}'''')^+\text{A}^-$

| R | R' | R'' | R''' | R'''' | A⁻ | Melting Point | References |
|---|---|---|---|---|---|---|---|
| | | | | | | °C. | |
| CH₃— | CH₃— | CH₃— | CH₃— | H— | OH⁻ | (d.) | (35) |
| | | | | | I⁻ | 226.5 | (69) |
| | | | | | PtCl₆⁻⁻ | 220 | (60) |
| | | | | | p-C₇H₇SO₃⁻ | | (35) |
| CH₃— | CH₃— | CH₃— | H— | HCO— | I⁻ | 166–167 | (9a) |
| CH₃— | CH₃— | CH₃— | ClC₂H₄OCO— | H— | I⁻ | 185 (d.) | (18) |
| CH₃— | CH₃— | CH₃— | HOC₂H₄OCO— | H— | I⁻ | 105 | (18) |
| CH₃— | CH₃— | CH₃— | p-C₇H₇SO₂⁻ | H— | I⁻ | 155–157(d.) | (66) |
| | | | | | — | 175–176 | (66) |
| | | | | | —·H₂O | 171–172 | (66) |
| C₆H₅— | CH₃— | CH₃— | CH₃— | H— | OH⁻ | | (31) |
| | | | | | I⁻ | 145 | (31) |
| | | | | | PtCl₆⁻⁻ | | (31) |
| | | | | | 2,4,6-(O₂N)₃C₆H₂O⁻ | | (31) |
| C₆H₅— | CH₃C(=NH)— | CH₃— | CH₃— | H— | I⁻ | 210 (d.) | (12) |
| CH₃— | CH₃— | CH₃— | CH₃— | CH₃— | OH⁻ | | (9a) |
| | | | | | Br⁻ | 223–224 (d.) | (9a) |
| | | | | | I⁻ | 222–223 (d.) | (9a) |
| CH₃— | CH₃— | CH₃— | CH₃— | HCO— | I⁻ | 180–181 | (9a) |
| CH₃— | CH₃— | CH₃— | —COOCH₂CH₃— | | I⁻ | 208 (subl.) | (18) |
| CH₃— | CH₃— | CH₃— | C₇H₇— | C₇H₇— | I⁻ | 170–174 (d.) | (70) |
| CH₃— | CH₃— | CH₃— | p-C₇H₇SO₂— | C₇H₇— | Cl⁻ | 171–173 (d.) | (66) |

TABLE 3

*Hydrazonium compounds*

$$\left[\begin{array}{c} R' \quad R''' \\ | \quad | \\ RN\!N\!\!=\!\!C\!-\!R'''' \\ | \\ R'' \end{array}\right]^{+} A^{-}$$

| R | R' | R'' | R''' | R'''' | A⁻ | Melting Point | References |
|---|----|-----|------|-------|-----|-----|------------|
| | | | | | | °C. | |
| CH₃— | CH₃— | CH₃— | C₄H₉— | CH₃— | I⁻ | 168–169 | (41) |
| CH₃— | CH₃— | CH₃— | C₆H₅— | CH₃— | I⁻ | 147 (d.) | (41, 63) |
| | | | | | ClO₄⁻ | 145 | (41) |
| | | | | | 2,4,6-(O₂N)₃C₆H₂O⁻ | 121 | (41) |
| CH₃— | CH₃— | CH₃— | C₆H₅CH₂— | CH₃— | I⁻ | | (63) |
| CH₃— | CH₃— | CH₃— | 2,4-(O₂N)₂C₆H₃CH₂— | CH₃— | I⁻ | 160 (d.) | (63) |
| CH₃— | CH₃— | CH₃— | (CH₃)₂CHCH₂— | (CH₃)₂CHCH₂— | I⁻ | 60–80 | (63) |
| CH₃— | CH₃— | CH₃— | C₆H₅— | C₆H₅— | I⁻ | 171–172.5 | (63) |
| CH₃— | CH₃— | CH₃— | C₆H₅CH₂— | C₆H₅CH₂— | I⁻ | 147 | (63) |
| CH₃— | CH₃— | CH₃— | p-CH₃OC₆H₄— | p-CH₃OC₆H₄— | I⁻ | 177–180 (d.) | (63) |

TABLE 4

*Azinium compounds*

$$\left[\begin{array}{c} R' \quad\quad CH_3 \; R' \\ | \quad\quad\;\; | \quad | \\ RC\!\!=\!\!N\!-\!N\!\!=\!\!CR \end{array}\right]^{+} A^{-}$$

| R | R' | A⁻ | Melting Point | Remarks | Reference |
|---|----|-----|---------------|---------|-----------|
| | | | °C. | | |
| C₆H₅— | H— | SnCl₆⁻⁻ | 205–206 | Microcrystalline, pale yellow | (39) |
| | | CH₃OSO₃⁻ | 128 | | (40) |
| o-HOC₆H₄— | H— | Cl⁻ | 204 | Red in concentrated NaOH | (38) |
| 2,4-(HO)₂C₆H₃— | H— | SnCl₆⁻⁻ | ca. 230 | Microcrystalline, deep yellow | (38) |
| p-CH₃OC₆H₄— | H— | SnCl₆⁻⁻ | 215–216 | Microcrystalline, bright yellow | (38) |
| 3,4-(CH₃O)(HO)C₆H₃— | H— | SnCl₆⁻⁻ | ca. 180 | Yellow powder | (38) |
| C₆H₅CH=CH— | H— | SnCl₆⁻⁻ | 197 (d.) | Microcrystalline, vermillion | (38) |
| 3,4-(CH₃O)₂C₆H₃— | H— | SnCl₆⁻⁻ | 225 (d.) | Yellow powder | (38) |
| CH₃— | CH₃— | SnCl₆⁻⁻ | 200–203 (d.) | Clear rhombs | (39) |
| C₂H₅— | CH₃— | SnCl₆⁻⁻ | 138–139 | Colorless prisms | (39) |

and has studied the action of alkalies on these compounds in connection with the Wolff–Kishner reduction (66b). The earlier work of Harries and Haga (33) on the action of aldehydes with alkylhydrazines gave high-melting condensation products and not the simple hydrazones (66a, 66b). These findings suggest that quaternization is the second step of the Lamchen–Pugh–Stephen preparation of azinium salts.

### G. METATHESIS; SALT AND ADDUCT FORMATION

Hydrazinium salts do not add an additional mole of acid to form $(R_3NNH_3)X_2$ (57). The inertness of the amino group and its lack of basicity have been discussed earlier. Certain hydrazinium iodides do, however, form adducts with thiourea having the general formula $(R_3NNH_2)I \cdot 2H_2NCSNH_2$. Alkylbenzylphenyl-hydrazinium iodide forms a 1:1 adduct, and the dimethylphenyl and diethyl-phenyl compounds none at all (61). Both hydrazinium iodide, $N_2H_5I$, and quaternary ammonium iodides form similar adducts (7). Metathesis of hydrazinium halides is probably the most commonly reported reaction of these compounds. It has been discussed briefly in Section III,B.

The "azeniates" of Schneider are reported to form stable, colored adducts with carbon disulfide, phenyl isocyanate, and phenyl isothiocyanate (52). Although the structures of the products were not elucidated, they were believed to be derived from the 1-anilino-2-methylene-1,2-dihydropyridines, rather than the 2-picoline phenylimides:



### H. REARRANGEMENTS

In view of the reported rearrangements of hydrazones (63), one might expect the hydrazonium salts to undergo a similar reaction. The expectation is realized, although not as anticipated. In completely anhydrous solutions 2-hydrazonium iodides having a methylene group alpha to the $-C{=}N-$ undergo an alkali-catalyzed rearrangement to $\alpha$-aminoketones (41). The mechanism given is as follows:



This parallels the mechanism given for the Neber reaction (42), the Baumgarten-Bower rearrangement of dichloroamines (9), and the Favorskii reaction (21). In the presence of traces of water the rearrangement does not occur, but hydrolysis does.

## TABLE 5
### *Cyclic compounds*
#### A. 1-Aminopyridinium compounds

$$\left[ \begin{array}{c} \overset{3}{\underset{4}{\bigcirc}}\overset{2}{\underset{5}{\phantom{.}}}\overset{7}{\underset{6}{N}}-\overset{7}{N}-8 \end{array} \right]^{+} X^{-}$$

| 2 | 3 | 4 | 5 | 6 | 7 | 8 | X⁻ | Melting Point °C. | Reference |
|---|---|---|---|---|---|---|---|---|---|
| H— | H— | H— | H— | H— | H— | H— | Cl⁻ | 160 | (8) |
| H— | H— | H— | H— | H— | CH₃CO— | H— | 2,4,6-(O₂N)₃-C₆H₂O⁻ | 154–155 | (8) |
| H— | H— | H— | H— | H— | p-H₂NC₆H₄SO₂— | — | Cl⁻ | 222 | (6) |
| H— | H— | H— | H— | H— | p-CH₃CONHC₆H₄SO₂— | — | — | 295–300 (d.) | (8) |
| H— | O— | CH₃— | C₆H₅— | H— | H— | H— | — | 235–236 | (8) |
| H— | HO— | CH₃— | C₆H₅— | H— | H— | H— | Cl⁻ | 192–195 | (6) |
| H— | CH₃O— | CH₃— | C₆H₅— | H— | H— | H— | (O₂N)₃C₆H₂O⁻ | 195–200 (d.) | (40a) |
| H— | CH₃COO— | CH₃— | H— | H— | H— | H— | Cl⁻ | 149–151 | (40a) |
| H— | H— | H— | H— | H— | H— | H— | Cl⁻ | 216 | (40a) |
| H— | H— | H— | H— | H— | CH₃CO— | H— | (O₂N)₃C₆H₂O⁻ | 160 | (40a) |
| H— | H— | H— | H— | H— | p-H₂NC₆H₄SO₂— | — | Cl⁻ | 154–155 | (6) |
| H— | H— | H— | H— | H— | p-CH₃CONHC₆H₄SO₂— | — | — | 222 | (8) |
| CH₃— | H— | C₆H₅— | H— | C₆H₅— | CH₃— | H— | — | 295–300 (d.) | (6) |
| CH₃— | H— | C₆H₅— | H— | C₆H₅— | C₆H₅— | H— | I⁻ | 235–236 | (6) |
| CH₃— | H— | C₆H₅— | H— | C₆H₅— | C₆H₅— | CH₃ | — | 185 | (55) |
| CH₃— | H— | C₆H₅— | H— | C₆H₅— | C₆H₅— | H— | I⁻ | | (55) |
| CH₃— | H— | C₆H₅— | H— | C₆H₅— | C₆H₅— | — | — | | (55) |
| CH₃— | H— | m-BrC₆H₄— | H— | m-BrC₆H₄— | C₆H₅— | H— | I⁻ | 196.5 | (53) |
| CH₃— | H— | p-BrC₆H₄— | H— | p-BrC₆H₄— | p-BrC₆H₄— | H— | I⁻ | 150 | (53) |
| CH₃— | H— | p-BrC₆H₄— | H— | p-BrC₆H₄— | p-CH₃C₆H₄— | H— | I⁻ | 151 | (53) |
| CH₃— | H— | m-ClC₆H₄— | H— | m-ClC₆H₄— | C₆H₅— | — | I⁻ | 181 | (53) |

Substituents

| A | | | | | | | Melting Point | Reference |
|---|---|---|---|---|---|---|---|---|
| CH₃-- | H-- | m-ClC₆H₄-- | H-- | m-ClC₆H₄-- | H-- | I-- | 183.5 | (53) |
| CH₃-- | H-- | p-ClC₆H₄-- | H-- | C₆H₅-- | H-- | I-- | 150.5 | (53) |
| CH₃-- | H-- | p-ClC₆H₄-- | H-- | m-CH₃C₆H₄-- | | I-- | 170 | (53) |
| CH₃-- | H-- | p-ClC₆H₄-- | H-- | p-CH₃C₆H₄-- | H-- | I-- | 131 | (53) |
| CH₃-- | H-- | m-CH₃C₆H₄-- | H-- | C₆H₅-- | | I-- | 190.5 | (53) |
| CH₃-- | H-- | m-CH₃C₆H₄-- | H-- | p-CH₃C₆H₄-- | H-- | I-- | 154.5 | (53) |
| CH₃-- | H-- | p-CH₃C₆H₄-- | H-- | C₆H₅-- | | I-- | 166 | (53) |
| CH₃-- | H-- | p-CH₃C₆H₄-- | H-- | p-BrC₆H₅-- | H-- | I-- | 192 (d.) | (53) |
| CH₃-- | H-- | p-CH₃C₆H₄-- | H-- | m-CH₃C₆H₄-- | | I-- | 164 | (53) |
| CH₃-- | H-- | p-CH₃C₆H₄-- | H-- | p-CH₃C₆H₄-- | | I-- | 154.5 | (53) |
| CH₃-- | H-- | p-CH₃OC₆H₄-- | H-- | C₆H₅-- | H-- | I-- | 155 | (53) |
| CH₃-- | H-- | p-CH₃OC₆H₄-- | H-- | p-BrC₆H₄-- | | I-- | 152 | (53) |
| CH₃-- | H-- | p-CH₃OC₆H₄-- | H-- | p-CH₃OC₆H₄-- | H-- | I-- | 134 | (53) |
| C₂H₅-- | H-- | C₆H₅-- | C₆H₅-- | | H-- | I-- | 145 | (53) |
| C₃H₅-- | H-- | p-CH₃C₆H₄-- | H-- | p-CH₃C₆H₄-- | H-- | I-- | 147.5 | (53) |

B. Miscellaneous heterocyclic derivatives

$$\left[ \begin{array}{c} R \\ \text{AN} \end{array} {+\atop} {\atop NH_2} \right] X^-$$
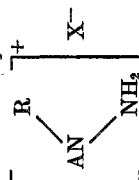
| A | R | X- | Melting Point °C. | Reference |
|---|---|---|---|---|
| --CH₂CH₂OCH₂CH₃-- | CH₃-- | OH- | | (37) |
| | | Cl- | 235 (d.) | (44a.) |
| | | I- | 170-171 | (37) |
| --CH₂CH₂CH₂CH₂CH₂-- | CH₃-- | I- | 215 | (36) |

The 4,6-diaryl-2-picoline phenylimides, e.g., compound XXIII, were found to undergo a different rearrangement in boiling alcohol (55):
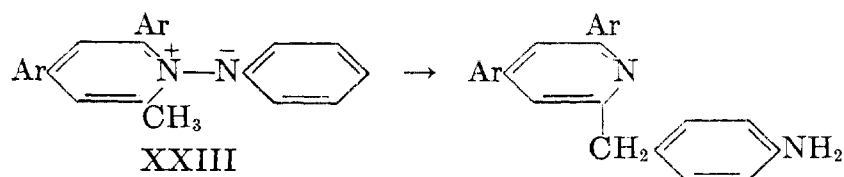


The reaction can be followed by the eye, since the intense blue to blue-violet of the amide rapidly fades to colorless. While the overall result suggests an ortho-semidine rearrangement, the mechanisms are probably dissimilar. The kinetics of this reaction have been studied.

## V. USES

Relatively few commercial or potentially commercial applications of quaternized hydrazines have been studied. An azinium methosulfate has been mentioned as the preferred intermediate in the preparation of methylhydrazine (11). The direct reaction of chloramine and methylamine now appears to offer a better route (44). The rearrangement of picoline phenylimides gives a primary aromatic amine, which was shown to undergo diazotization. No report has been made on the value of azo dyes from 4-($\alpha$-picolyl)aniline and miscellaneous phenols (55). Since the cumene hydroperoxide process for making phenol yields acetophenone as a by-product, Schneider's work assumes a potential industrial significance.

The pharmacological effects of hydrazinium salts have been studied in some detail. Hydrazinium analogs of the "invert soaps" have been reported as effective bacteriostats, e.g., 1-hexadecyl-1,1-dimethylhydrazinium methosulfate stops the growth of lactic bacteria at 1:500,000 dilution (68). The corresponding bromide was slightly less effective. The surfactant properties of these compounds were mentioned in the same report. In partial contrast, pyridine (4-acetylsul-fanilyl)imide is reported to be inactive against $S.$ $aureus$ (6).

Hydrazinium salts analogous to common antihistaminics and antispasmodics have been described as more powerful than the amines now used medicinally (48). The three analogs of Benadryl prepared were two to four times more active (by aerosol test) antihistamines than Benadryl. In order of decreasing activity, these compounds were 1,1-dimethyl-1-$\beta$-benzhydryloxyethylhydrazinium chloride, its mono $p$-tolyl homolog, and its corresponding iodide. Of the three antispasmodic esters prepared, only one, 1,1-dimethyl-1-[2-(phenylcyclohexyl-acetoxy)ethyl]hydrazinium chloride, was interesting. When tested against acetylcholine-induced spasms, this salt was seventy-five times more effective than Propivan.

The only bis-hydrazinium salt of established structure, 1,10-decamethylene-bis(1,1-dimethylhydrazinium bromide), was prepared by Scheuler and Hanna (51) as an analog of the known curarimimetic, $C_{10}$. The therapeutic index of this compound, i.e., the ratio of head drop dose to $LD_{50}$ in rabbits, was approximately the same as that of $C_{10}$. The same authors had earlier compared 1,1-dimethyl-1-

β-acetoxyethylhydrazinium bromide, 1,1-dimethyl-1-β-carbomethoxyethylhydrazinium bromide, trimethylhydrazinium iodide, and triethylhydrazinium iodide (50) with acetylcholine and tetramethylammonium bromide. Of the four compounds investigated, the propionyl ester was the most toxic (by a factor of at least five), having a $LD_{50}$ (in mice) of 52 mg./kg. The two esters exhibited the same general physiological effects as did acetylcholine, but to a lesser degree. The same relationship was shown between the simpler hydrazinium salts and tetramethylammonium salts.

Hydrazinium compounds have been mentioned or claimed in patents as effective catalysts and initiators of olefin polymerization (29, 30, 43). Where the class has been claimed, 1,1,1-trimethylhydrazinium iodide has usually been cited. It may be significant that such patents do not give specific examples using the hydrazinium salts. In the light of the known value of hydrazines, azines, and hydrazides as sources of free radicals (16), the hydrazinium compounds should show some initiator effect. One patent specification puts trimethylhydrazinium iodide with hydrazine sulfate and dibenzoylhydrazine in "a preferred class of catalysts" (29). Quaternary ammonium compounds do not appear to be capable of such uses.

The paucity of information on the uses of hydrazinium compounds may well be due to the current uneconomical and tedious processes for their preparation. A simpler synthesis is as much to be desired as is a more intensive study of the chemistry of the quaternized hydrazines. The recently reported synthesis (44a) with chloramine provides a possible answer to this problem.

## VI. TABLES OF KNOWN HYDRAZINIUM COMPOUNDS

Tables 1 to 5 contain most of the quaternized hydrazine compounds reported in the available literature through December, 1955. Within each table the compounds are listed in order of increasing complexity of the cation, using the system of the Formula Index of *Chemical Abstracts*. The known salts of each cation are listed under the cation. Amine imides are listed under the proper cationic structure and are indicated by a dash in the anion column. Although the references include all those known to deal with hydrazinium compounds, the references listed in the tables are not all of the references pertaining to any one compound.

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