THE HOFMANN-BECKMANN-CURTIUS-LOSSEN REARRANGEMENTS

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Received March 14, 1933

INTRODUCTION

In this paper the attempt is made to show that the Hofmann, Beckmann, Curtius, and Lossen rearrangements involve the augmentation[1] (1) of primary alcohols to aldehydes, (2) of secondary and tertiary alcohols to ketones, (3) of aldehydes and ketones to carbylic acids,[2] and (4) of carbylic acids to carbonic acids. The augmenting agents which bring about these rearrangements are hypochlorous acid chlorine, hypobromous acid bromine, nitric acid nitrogen, hydrogen peroxide oxygen, the hydroxylamine NO group, and hydrazine nitrogen.

Alcohols

The mono- and di-alkyl amines are ammono alcohols, which is to say that they are alcohols belonging to a nitrogen system of compounds in the same sense that the aquo alcohols may be said to belong to an oxygen system (24, 27).

The formulas RCH_2OH, RCH_2NH_2, and RCH_2NHCH_2R represent primary alcohols; R_2CHOH, R_2CHNH_2, and $R_2CHNHCHR_2$ secondary alcohols; R_3COH, R_3CNH_2, and R_3CNHCR_3, tertiary alcohols; RCH_2NHCHR_2, mixed primary secondary alcohols; RCH_2NHCR_3, primary tertiary alcohols; and $R_2CHNHCR_3$, secondary tertiary alcohols.

In support of our assumption that the amines represented by these formulas are just as truly alcohols as are their oxygen analogs, it will suffice present purposes to emphasize the fact that they closely resemble the aquo alcohols in their behavior toward augmenting agents. For example, Chuck (14) found that benzamidine is formed in good yields when a liquid ammonia solution containing benzylamine and ammonium

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[1] The terms "augment" and "augmentation" will be used instead of "oxidize" and "oxidation" as understood in the broad general sense (28).

[2] The carboxylic acids, the carbazylic acids or acid amidines, and the carboxazylic acid or acid amides.

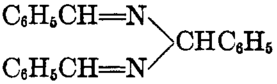
azide is heated at 60°C. for a time; and Strain (71) prepared benzylideneimine by the ammonolytic action of liquid ammonia on aquobenzaldehyde

$$C_6H_5CH{=}O + NH_3 = C_6H_5CH{=}NH + H_2O$$

and found furthermore that benzylideneimine, under the action of iodine in liquid ammonia solution, is readily nitridized to benzamidine.

Aldehydes and ketones

Contingent upon the trivalency of nitrogen in contrast with the divalency of oxygen, strict nitrogen analogs of the aquo aldehydes and aquo ketones are a theoretical impossibility. Approximate analogs of benzaldehyde, for example, are benzylideneimine, $C_6H_5CH{=}NH$, phenylbenzylideneimine, $C_6H_5CH{=}NC_6H_5$, and hydrobenzamide,



$$\left.\begin{matrix}C_6H_5CH{=}N\\C_6H_5CH{=}N\end{matrix}\right\rangle CHC_6H_5$$

all three of which closely resemble ordinary benzaldehyde in their aldehydic behavior. All three compounds are aldehydes in so far as the carbon to nitrogen double bonds are concerned. Somewhat arbitrarily perhaps we have chosen to call the first compound a benzaldehyde-alcohol, the second, a benzaldehyde-ether, and the third, a benzaldehyde-acetal. The formulas, $R_2C{=}NH$ and $R_2C{=}NR'$, represent ketone-alcohols and ketone-ethers which are the approximate analogs of the aquo ketones. Without forgetting that ethylideneimine and benzylideneimine, by virtue of the presence of the imino hydrogen, are something more than aldehydes, we shall on occasion speak of the former as an ammonoacetaldehyde and of the latter as an ammonobenzaldehyde.

Carbylic acids

Acetic acid, CH_3COOH, acetamide, CH_3CONH_2, and acetamidine, $CH_3C(NH)NH_2$, are, respectively, an aquoacetic acid, an aquo-ammonoacetic acid and an ammonoacetic acid. With acetic acid and other acids containing the carboxyl group, long familiarly known as carboxylic acids, we have adopted the practice in this laboratory of referring to the acid amides as carboxazylic acids, the acid amidines as carbazylic acids, and of including the carboxylic acids, the carboxazylic acids, and the carbazylic acids under the general designation of carbylic acids.

Carbonic acids

The formula $OC(OH)_2$ represents an aquocarbonic acid which is assumed to exist in water solution. Cyanamide, H_2NCN, and guanidine,

$HNC(NH_2)_2$, are examples of ammonocarbonic acids. Cyanic acid, $HNCO$, carbamic acid, H_2NCOOH, and urea, $OC(NH_2)_2$, are aquo-ammonocarbonic acids (26).

Plus and minus signs

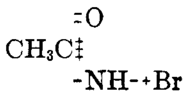
It is fair to assume that all covalent bonds between unlike atoms are more or less polar, which is to say that the one atom of a bonded pair is positive, augmented, de-electronized, with respect to the other. On this assumption we shall on occasion find it convenient to represent this polarity[3] by means of small plus and minus signs, as for example in the formulas, $CH_3{}^{+}{-}OH$ and $CH_3{}^{+}{-}NH_2$, for methyl alcohol and methylamine. The plus signs are to be read as indicating that the carbon atom in the methyl group is more or less augmented in respect to the hydroxyl and amino groups; the minus sign, conversely, that the oxygen and nitrogen atoms are in a corresponding state of reduction.

Whether belonging to the oxygen system or to the nitrogen system, the primary, secondary, and tertiary alcohols are characterized by the respective groups, $RCH_2{}^{+}$, R_2CH^{+}, and R_3C^{+}, the aldehydes by the group, $RCH\substack{+\\+}$, the ketones by $R_2C\substack{+\\+}$, and the carbylic acids by $RC\substack{+\\+\\+}$. We shall therefore on occasion speak of the augmentation of an alcohol to an aldehyde when, under the action of an augmenting agent, an $RCH_2{}^{+}$ group passes over into an $RCH\substack{+\\+}$ group, of the augmentation of an aldehyde to a carbylic acid when an $RCH\substack{+\\+}$ group is converted into an $RC\substack{+\\+\\+}$ group, and of the augmentation of a carbylic acid to a carbonic acid when the carbon atom of an $RC\substack{+\\+\\+}$ group is converted into a carbonic acid carbon atom, $\substack{+\\+}C\substack{+\\+}$.

In general, the carbylic acids are decidedly stable toward augmenting agents. Even so we shall find as we proceed that certain intramolecular rearrangements are to be explained on the assumption that they involve augmentation of carbylic acids to carbonic acids.

Hypohalous acids

Chloramine, $H_2N{-}{+}Cl$, and dichloramine, $HN\substack{-\\-}\substack{+\\+}Cl_2$, as nitrogen analogs of aquohypochlorous acid, $HO{-}{+}Cl$, are ammonohypochlorous acids which, like the aquo acid, are effective augmenting agents. Ethylchloramine, $C_2H_5NH{-}{+}Cl$, diethylchloramine, $(C_2H_5)_2N{-}{+}Cl$, and ethyldichloramine, $C_2H_5N\substack{-\\-}\substack{+\\+}Cl_2$, are ethyl esters of the two ammonohypochlorous acids. Acetbromamide, represented by the formula



$$CH_3C\substack{+\\+\\+}\begin{matrix}\substack{-\\-}O\\ \\ -NH{-}{+}Br\end{matrix}$$

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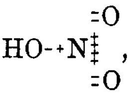
[3] Potential polarity according to W. A. Noyes (51).

is a mixed compound which is at the same time an aquo-ammonoacetic acid and an ammonohypobromous acid.

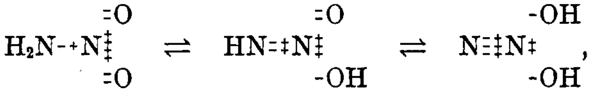
Nitric acids

Ordinary nitric acid,



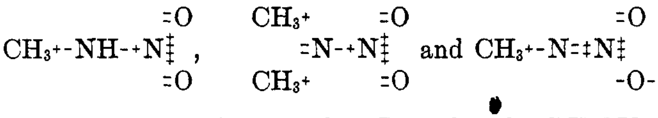
$$\begin{array}{rl} & {=}O \\ HO{-}{+} & N\ddagger \\ & {=}O \end{array},$$

nitramide,



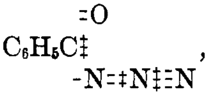
$$\begin{array}{rl} & {=}O \\ H_2N{-}{+} & N\ddagger \\ & {=}O \end{array} \rightleftharpoons \begin{array}{rl} & {=}O \\ HN{=}{+} & N\ddagger \\ & {-}OH \end{array} \rightleftharpoons \begin{array}{rl} & {-}OH \\ N{\equiv}{\ddagger} & N{+} \\ & {-}OH \end{array},$$

and hydrazoic acid, $HN{=}{\ddagger}N{\ddagger}{\equiv}N$, are respectively an aquonitric acid, an aquo-ammononitric acid, and an ammononitric acid. The formulas



$$\begin{array}{rl} & {=}O \\ CH_3{+}{-}NH{-}{+} & N\ddagger \\ & {=}O \end{array}, \quad \begin{array}{l} CH_3{+} \\ \quad {=}N{-}{+} \\ CH_3{+} \end{array}\begin{array}{l} {=}O \\ N\ddagger \\ {=}O \end{array} \text{ and } \begin{array}{rl} & {=}O \\ CH_3{+}{-}N{=}{+} & N\ddagger \\ & {-}O{-}{+}CH_3 \end{array}$$

represent known esters of nitramide. Benzyl azide, $C_6H_5CH_2{+}{-}N{=}{\ddagger}N{\ddagger}{\equiv}N$ is a benzyl ammononitrate. Benzoyl azide,



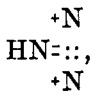
$$\begin{array}{rl} & {=}O \\ C_6H_5 & C\ddagger \\ & {-}N{=}{\ddagger}N{\ddagger}{\equiv}N \end{array},$$

is a compound which is at the same time a mixed benzoic anhydride-anammonide and a nitric acid anammonide, the acid anammonides being the nitrogen analogs of the acid anhydrides.

Hydrazoic acid in all probability is a tautomeric compound to which either of the formulas, $HN{=}{\ddagger}N{\ddagger}{\equiv}N$ or

$$\begin{array}{c} HN{\ddagger}N \\ {}^{-}{}^{+}{}^{+}{}^{+}{}^{-}{}^{-} \\ N \end{array}$$

, may be ascribed. The first formula represents an ammononitric acid, the second a cyclic nitrous acid hydrazide. The formula,



$$\begin{array}{rl} & {+}N \\ HN{=} & {::}, \\ & {+}N \end{array}$$

represents hydrazoic acid, an ammonohyponitrous acid.

Nitrous acids

The following formulas, $HO{-}{+}N{\ddagger}{=}O$, $HO{-}{+}N{\ddagger}{=}NH \rightleftharpoons O{=}{\ddagger}N{+}{-}NH_2$, and $H_2N{-}{+}N{\ddagger}{=}NH$, represent an aquonitrous acid, an aquo-ammononitrous acid and an ammononitrous acid. The first acid is known in solution and in the form of salts and esters; the second and third in the form of esters and ester salts. Diazobenzene, $C_6H_5{+}{-}N{=}{\ddagger}N{+}{-}OH$ and dimethylnitrosoamine, $(CH_3)_2{\ddagger}{=}N{-}{+}N{\ddagger}{=}O$, are esters; diazobenzene potassium, $C_6H_5{+}{-}N{=}{\ddagger}N{+}{-}OK$, is an ester salt of an aquo-ammononitrous acid. Diazoaminobenzene, $C_6H_5{+}{-}N{=}{\ddagger}N{+}{-}NH{-}{+}C_6H_5$, and diazoaminobenzene sodium, $C_6H_5{+}{-}N{=}{\ddagger}N{+}{-}N(Na)C_6H_5$, are respectively an ester and an ester salt of an ammononitrous acid.

Hydrogen peroxide, hydroxylamine, and hydrazine

For representing these compounds we shall make use of the formulas, $HO{:}OH$, $H_2N{:}OH$ and $H_2N{:}NH_2$, in which the colons indicate non-polar unions or unions concerning the polarity of which no opinion is expressed. The especial reason for adopting these formulas is that the colon will serve as a label, which will enable us to follow the peroxide oxygen, the hydroxylamine nitrogen and oxygen, and the hydrazine nitrogen in certain reactions we shall discuss later.

Hydrogen peroxide is a powerful augmentor, hydroxylamine is less actively so, while hydrazine only now and then acts as an augmenting agent. Hydrazine may be looked upon as the nitrogen analog of hydrogen peroxide. Hydroxylamine is a mixed compound derived at the same time from water and ammonia.

INTRAMOLECULAR AUGMENTATION OF ALCOHOLS TO ALDEHYDES AND KETONES

The alkyl chloramines

The compounds $RCH_2NH{-}{+}Cl$ and $(RCH_2)_2N{-}{+}Cl$, containing augmentable alcohol groups and an augmentor in the form of hypochlorous acid chlorine, undergo intramolecular augmentation and reduction reactions which in principle are Hofmann rearrangements.

Ethylchloramine, ethyl ammonohypochlorite, $CH_3CH_2NH{-}{+}Cl$. Unfortunately all that is definitely known concerning the decomposition of this compound is that aldehydes, presumably formaldehyde and acetaldehyde, are obtained by warming the chloramine with alcoholic potassium hydroxide and heating the resulting solution with hydrochloric acid (6). However, in view of Berg's discussion of his observations, it is reasonable to say that the decomposition of ethylchloramine takes place partly in accordance with the equation

$$CH_3CH_2NH{-}{+}Cl \xrightarrow[-HCl]{} CH_3CH{=}NH \xrightarrow[-NH_2]{+H_2O} CH_3CHO$$

which represents the intramolecular augmentation of an ethyl alcohol group to an acetaldehyde group and the concomitant reduction of hypochlorous acid chlorine to hydrochloric acid chlorine, followed by the hydrolysis of ethylideneimine to aquoacetaldehyde and ammonia.

Since methylamine was found among the decomposition products, it may be further assumed that ethylchloramine decomposes in part in accordance with the equation

$$CH_3CH_2NH^{-+}Cl \rightarrow CH_3N{=}CH_2 + HCl$$

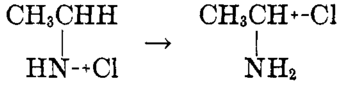
and that the methylmethyleneimine thus formed is hydrolyzed to aquoformaldehyde and methylamine

$$CH_2{=}NCH_3 + H_2O = CH_2O + CH_3NH_2$$

Following Stieglitz (62) these results are to be explained on the assumption that ethylchloramine breaks down directly to form hydrochloric acid and the unstable univalent nitrogen compound, $CH_3CH_2{-}N$ and that the two-thirds free nitrogen in the ephemeral compound thus formed nitridizes the ethyl alcohol group, $CH_3CH_2^{+}$ to the acetaldehyde group, $CH_3CH^{\ddagger}$, the univalent nitrogen itself simultaneously undergoing reduction to ammonia nitrogen, with the result that ethylideneimine is formed. At the same time another portion of the ephemeral compound is converted into methylmethyleneimine as the result of the augmentation of carbon to carbon union in the ethyl alcohol group.

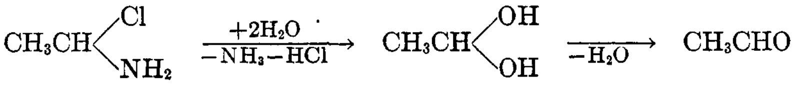
$$CH_3CH_2{-}N \rightarrow CH_3N{=}CH_2$$

Quite as legitimately, however, it may be assumed that the first step in the decomposition of ethylchloramine to form acetaldehyde takes place as represented by the equation



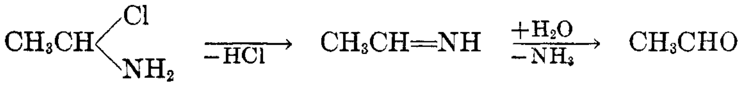
$$\begin{matrix} CH_3CHH \\ | \\ HN^{-+}Cl \end{matrix} \rightarrow \begin{matrix} CH_3CH^{+-}Cl \\ | \\ NH_2 \end{matrix}$$

in accordance with which a Beckmann-like rearrangement, involving an exchange of positions of the chlorine atom of the hypochlorous acid group and one of the hydrogen atoms of the CH_2 group, brings about the augmentation of the ethyl alcohol group to an aldehyde group and the concomitant reduction of hypochlorous acid chlorine to hydrochloric acid chlorine. The unknown aldehyde amide-chloride thus formed may either undergo hydrolysis



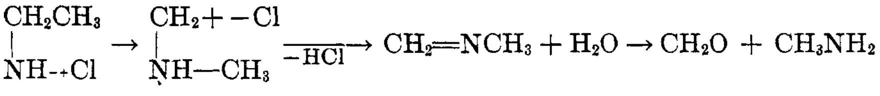
$$CH_3CH\left\langle\begin{matrix} Cl \\ NH_2 \end{matrix}\right. \xrightarrow[-NH_3-HCl]{+2H_2O} CH_3CH\left\langle\begin{matrix} OH \\ OH \end{matrix}\right. \xrightarrow[-H_2O]{} CH_3CHO$$

or it may lose hydrochloric acid directly, thereby passing over into ethylideneimine, which in turn is hydrolyzed to aquoacetaldehyde and ammonia.



$$CH_3CH\genfrac{}{}{0pt}{}{\diagup Cl}{\diagdown NH_2} \xrightarrow[-HCl]{} CH_3CH{=}NH \xrightarrow[-NH_3]{+H_2O} CH_3CHO$$

In a similar manner as represented herewith

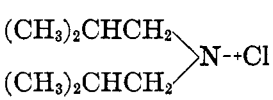


$$\begin{array}{l} CH_2CH_3 \\ | \\ NH\text{-+}Cl \end{array} \rightarrow \begin{array}{l} CH_2{+}\,{-}Cl \\ | \\ NH{-}CH_3 \end{array} \xrightarrow[-HCl]{} CH_2{=}NCH_3 + H_2O \rightarrow CH_2O + CH_3NH_2$$

aquoformaldehyde and methylamine are formed. It is to be noted that here it is the methyl group and the chlorine atom which change places, with the result that the carbon to carbon union in the ethyl group is augmented.

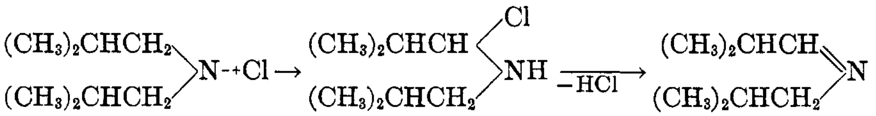
It is clear from the preceding discussion that it is scarcely possible to say which of the described mechanisms constitutes the first step in the conversion of ethylchloramine into acetaldehyde. Moreover, for many of the rearrangements to be considered later, similar alternative explanations are possible. We shall find as we proceed that certain rearrangements are simply explained on the assumption of the primary formation of a univalent nitrogen compound, while in others the formation of such compounds is scarcely possible. Finally it will appear that all the Hofmann-Beckmann-Curtius-Lossen rearrangements, without exception, may be explained on the assumption of the primary formation of rearrangement products after the pattern of the conversion of ethylchloramine into acetaldehyde chloride-amide.

Diisobutylchloramine,



$$\begin{array}{l}(CH_3)_2CHCH_2\diagdown \\ (CH_3)_2CHCH_2\diagup \end{array} N\text{-+}Cl$$

In the presence of a warm alcoholic solution of sodium hydroxide, diisobutyl ammonohypochlorite decomposes to form isobutylisobutylideneimine and hydrochloric acid, say, in accordance with the equation,



$$\begin{array}{l}(CH_3)_2CHCH_2\diagdown \\ (CH_3)_2CHCH_2\diagup \end{array} N\text{-+}Cl \rightarrow \begin{array}{l}(CH_3)_2CHCH\genfrac{}{}{0pt}{}{\diagup Cl}{} \\ (CH_3)_2CHCH_2\diagup \end{array} NH \xrightarrow[-HCl]{} \begin{array}{l}(CH_3)_2CHCH\diagdown\!\diagdown \\ (CH_3)_2CHCH_2\diagup \end{array} N$$

The acetal represented by the intermediate formula,[4] which has not been isolated, loses hydrochloric acid to form isobutylisobutylideneimine. By

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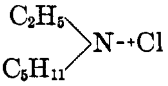
[4] An isobutyraldehyde amide-chloride in which amido hydrogen is replaced by an isobutyl alcohol group.

the action of dilute hydrochloric acid, Berg (8) hydrolyzed this acetal to aquoisobutyraldehyde and isobutylamine,

$$(CH_3)_2CHCH{=}NCH_2CH(CH_3)_2 + H_2O = (CH_3)_2CHCH{=}O + (CH_3)_2CHCH{-}NH_2$$

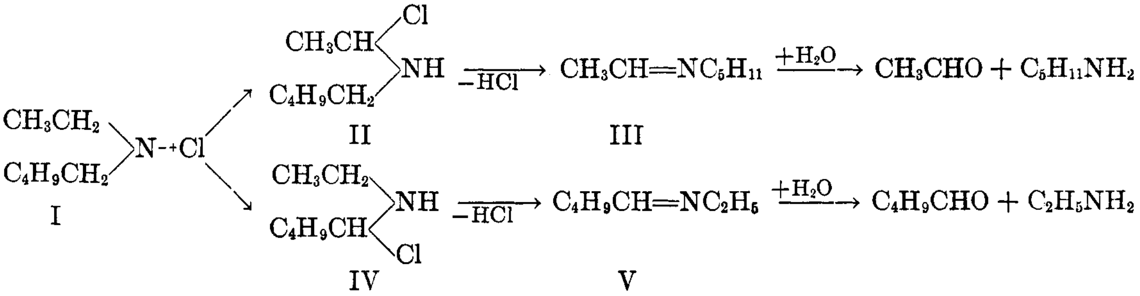
Certainly a univalent nitrogen compound is not formed when diisobutylchloramine loses hydrochloric acid.

Ethylisoamylchloramine,



$$\begin{matrix} C_2H_5 \\ C_5H_{11} \end{matrix} \!\!> N{-}{+}Cl$$

Berg (9) obtained acetaldehyde, isovaleraldehyde, ethylamine, and isoamylamine by treating ethylisoamylchloramine with alcoholic sodium hydroxide and adding to the reaction mixture an excess of aqueous hydrochloric acid. The manner of formation of these compounds is clear. As summarized by the scheme,

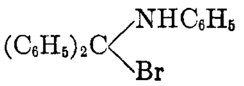


ethylisoamylchloramine rearranges partly to II and partly to IV. These hypothetical compounds readily lose hydrochloric acid to form the aldehyde-acetals III and V, which under the action of aqueous hydrochloric acid are hydrolyzed, the one to aquoacetaldehyde and isoamylamine, the other to isovaleraldehyde and ethylamine.

Triphenylmethylbromamine, $(C_6H_5)_3CNH{-}{+}Br$. Miss Vosburgh (64, 70, 75) found that this triphenylmethyl ester of an ammonohypobromous acid when heated with soda lime is decomposed into phenylbenzophenoneimine and hydrobromic acid.

$$(C_6H_5)_3CNH{-}{+}Br = (C_6H_5)_2C{=}NC_6H_5 + HBr$$

Independent of the question as to whether the formation of a univalent nitrogen compound, $(C_6H_5)_3CN$, or of a mixed ketone-acetal,



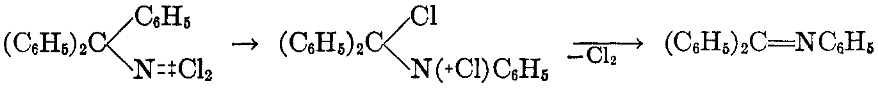
$$(C_6H_5)_2C \!\!< \begin{matrix} NHC_6H_5 \\ Br \end{matrix}$$

constitutes the initial step in the reaction, it is clear that what Miss Vosburgh accomplished was the augmentation of a tertiary alcohol to a ketone-acetal, using bromine as the primary augmenting agent.

Miss Vosburgh found also that triphenylmethyldichloramine when heated with soda lime yields chlorine and phenylbenzophenoneimine. The reactions involved may be explained as taking place with the intermediate formation of univalent nitrogen,

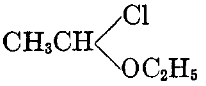
$$(C_6H_5)_3CN{=}{\ddagger}C \xrightarrow[-Cl_2]{} (C_6H_5)_3C{-}N \rightarrow (C_6H_5)_2C \quad NC_6H_5$$

or it may be assumed that one of the hypochlorous acid chlorine atoms augments a paraffin carbon to phenyl carbon union,



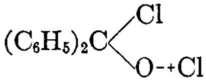
$$(C_6H_5)_2C\begin{matrix}\nearrow C_6H_5 \\ \searrow N{=}{\ddagger}Cl_2\end{matrix} \rightarrow (C_6H_5)_2C\begin{matrix}\nearrow Cl \\ \searrow N(^+Cl)C_6H_5\end{matrix} \xrightarrow[-Cl_2]{} (C_6H_5)_2C{=}NC_6H_5$$

following which the positive and negative chlorine are eliminated as elementary chlorine, leaving phenylbenzophenoneimine. The hypothetical intermediate compound is a ketone-acetal which may be compared with the aldehyde-acetal,



$$CH_3CH\begin{matrix}\nearrow Cl \\ \searrow OC_2H_5\end{matrix}$$

known as monochlorodiethyl ether, or better with the unknown acetal of the formula,



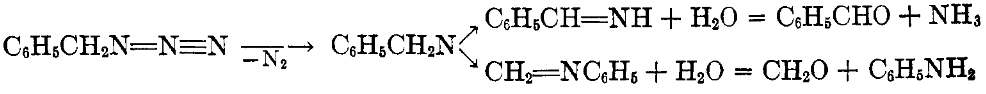
$$(C_6H_5)_2C\begin{matrix}\nearrow Cl \\ \searrow O{-}{^+}Cl\end{matrix}$$

The alkyl azides, esters of ammononitric acid

Since hydrazoic acid is an active nitridizing agent, it is reasonable to expect that the alkyl azides will be found to undergo intramolecular nitridation–reduction reactions closely similar to those involved in the transformations of the chloramines. Little or nothing is known of the manner of decomposition of methyl azide or ethyl azide.

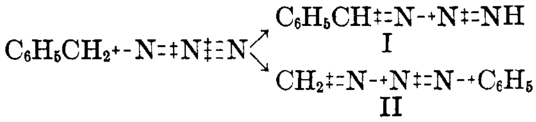
Benzyl azide, benzyl ammononitrate, $C_6H_5CH_2{^+}{-}N{=}{\ddagger}N{\ddagger}{=}N$. This azide, which is remarkably stable toward alkalies, gives abundant yields of benzaldehyde, ammonia, formaldehyde, nitrogen, and aniline when heated with dilute sulfuric acid (16, 17).

The reactions involved in the formation of these compounds have been explained as taking place by way of a univalent nitrogen compound as follows,



$$C_6H_5CH_2N{=}N{\equiv}N \xrightarrow[-N_2]{} C_6H_5CH_2N\begin{array}{l} \nearrow C_6H_5CH{=}NH + H_2O = C_6H_5CHO + NH_3 \\ \searrow CH_2{=}NC_6H_5 + H_2O = CH_2O + C_6H_5NH_2 \end{array}$$

However it may well be that the first step in the decomposition of benzyl azide consists of a Beckmann-like rearrangement,



$$C_6H_5CH_2{+}{-}N{=}{\ddagger}N{\ddagger}{\equiv}N\begin{array}{l} \nearrow \underset{\text{I}}{C_6H_5CH{\ddagger}{=}N{-}{+}N{\ddagger}{=}NH} \\ \searrow \underset{\text{II}}{CH_2{\ddagger}{=}N{-}{+}N{\ddagger}{=}N{-}{+}C_6H_5} \end{array}$$

in accordance with which benzyl ammononitrate, by intramolecular augmentation and reduction, rearranges partly into the benzaldehyde nitrous acid acetal (I) and partly into the formaldehyde acetal (II). Neither of these compounds is known.[5] Compound I would be expected to lose nitrous anammonide (nitrogen) to form benzylideneimine, which in the presence of water is hydrolyzed to aquobenzaldehyde and ammonia. The second compound, losing nitrogen, would form phenylmethyleneimine, $CH_2NC_6H_5$, which readily hydrolyzes to aquoformaldehyde and aniline. Whether in these rearrangements the primary reaction involves the formation of an ephemeral univalent nitrogen compound or the unstable nitrous acid acetals, it does not seem possible in the present state of our knowledge to say. Whatever the details of the reactions concerned may be, it is clear that a benzyl alcohol group is augmented partly to a benzaldehyde group and partly to a formaldehyde group, while at the same time nitric acid nitrogen is reduced to nitrous acid nitrogen.

Triphenylmethyl azide, $(C_6H_5)_3C{+}{-}N{=}{\ddagger}N{\ddagger}{\equiv}N$. Senior (60) has shown that triphenylmethyl azide under the action of heat alone gives a good yield of phenylbenzophenoneimine. As represented by the equation,

$$(C_6H_5)_3C{+}{-}N{=}{\ddagger}N{\ddagger}{\equiv}N = (C_6H_5)_2C{=}NC_6H_5 + N_2$$

the reactions involved consist in the augmentation of a tertiary alcohol, in the form of its ammononitric acid ester, to a ketone-ether, and the simultaneous reduction of nitric acid nitrogen to nitrous acid nitrogen.

An intermediate step in the conversion of triphenylmethyl azide into phenylbenzophenoneimine and nitrogen may be the formation of the

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[5] It is interesting to note that an unstable compound closely related to the hypothetical compound (II) above has been obtained by the interaction of formaldehyde and the ethyl ester of triazenobenzoic acid in cold ether solution (22).

$$CH_2O + 2H_2{-}{+}N{\ddagger}{=}N{-}{+}C_6H_4COOC_2H_5 = CH_2{\ddagger}({-}NH{-}{+}N{\ddagger}{=}N{-}{+}C_6H_4COOC_2H_5)_2 + H_2O$$

univalent nitrogen compound, $(C_6H_5)_3CN$, or possibly, after the manner indicated above for the decomposition of benzyl azide, of the ketone nitrous acid acetal, $(C_6H_5)_2C\ddagger{=}N{-}{+}N\ddagger{=}N{-}{+}C_6H_5$.

Alkyl nitramides, esters of aquo-ammononitric acid

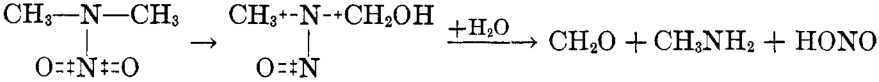
Certain N,N-dialkyl derivatives of nitramide have been found to undergo decomposition in a manner closely resembling that of the azides discussed above. Dimethylnitramide, for example, when warmed with potassium hydroxide yields methylamine, formaldehyde, and nitrous acid (74), perhaps by direct scission into nitrous acid and methylmethyleneimine,

$$(CH_3)_2N{-}NO_2 = CH_2{=}NCH_3 + HONO$$

followed by the hydrolysis of the formaldehyde-ether to formaldehyde and methylamine,

$$CH_2{=}NCH_3 + H_2O = CH_2O + CH_3NH_2$$

but more probably in accordance with the scheme,



$$\begin{array}{c}\mathrm{CH_3{-}N{-}CH_3}\\ | \\ \mathrm{O{=}\ddagger N\ddagger{=}O}\end{array} \rightarrow \begin{array}{c}\mathrm{CH_3{+}{-}N{-}{+}CH_2OH}\\ | \\ \mathrm{O{=}\ddagger N}\end{array} \xrightarrow{+H_2O} CH_2O + CH_3NH_2 + HONO$$

which represents first, the intramolecular oxidation of one of the methyl groups of an ammono methyl alcohol to a formaldehyde group and second, the hydrolysis of the formaldehyde methyl nitrous acid acetal thus formed to aquoformaldehyde, methylamine, and aquonitrous acid.

Alkyl aquonitrates

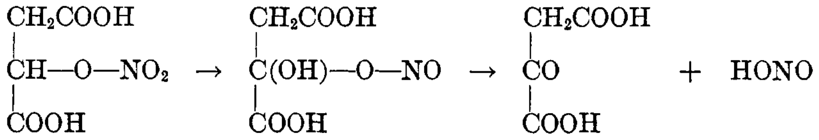
Certain alkyl nitrates appear to undergo intramolecular oxidation and reduction in a similar manner. For example, it has been found that benzyl nitrate decomposes quantitatively into nitrous acid and benzaldehyde when gently heated with alcoholic potassium hydroxide (12, 50).

Nef explains the reaction as consisting in the dissociation of benzyl nitrate into the benzylidene group and nitric acid, followed by the oxidation of the free benzylidene group to benzaldehyde and the reduction of nitric acid to nitrous acid. It would seem more reasonable to say that the reactions take place in accordance with the scheme,

$$\begin{array}{l}\mathrm{C_6H_5CH_2}\\ | \\ \mathrm{O{-}NO_2}\end{array} \rightarrow \begin{array}{l}\mathrm{C_6H_5CH{-}OH}\\ | \\ \mathrm{O{-}NO}\end{array} \rightarrow C_6H_5CHO + HONO$$

which represents the nitric acid ester as undergoing rearrangement to a nitrous acid half-acetal, followed by the decomposition of this hypothetical compound to form benzaldehyde and nitrous acid (potassium nitrite).

According to Lachman (40) nitromalic acid under the action of potassium hydroxide gives a fair yield of oxalacetic acid,



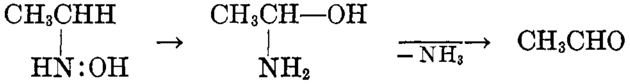
$$\begin{array}{l}CH_2COOH\\|\\CH—O—NO_2\\|\\COOH\end{array}\rightarrow\begin{array}{l}CH_2COOH\\|\\C(OH)—O—NO\\|\\COOH\end{array}\rightarrow\begin{array}{l}CH_2COOH\\|\\CO\\|\\COOH\end{array}+\ HONO$$

By intramolecular rearrangement the secondary alcohol nitric acid ester part of the nitromalic acid molecule is converted into a ketone nitrous acid acetal, which decomposes to form oxalacetic acid and nitrous acid.

The alkylhydroxylamines

Many derivatives of hydroxylamine undergo intramolecular rearrangements which clearly consist in the augmentation of alcohols to aldehydes or ketones, and since the oxime part of the molecule may act as a purveyor of either oxygen or nitrogen, the resulting aldehydes and ketones may belong either to the oxygen or to the nitrogen system.

N-Ethylhydroxylamine, $C_2H_5NH{:}OH$. When this compound is heated with dilute hydrochloric acid, acetaldehyde and ammonia are formed (39). The reactions involved may be explained as taking place by way of the univalent nitrogen compound, CH_3CH_2N, or in accordance with the scheme,



$$\begin{array}{c}CH_3CHH\\|\\HN{:}OH\end{array}\rightarrow\begin{array}{c}CH_3CH—OH\\|\\NH_2\end{array}\xrightarrow[-NH_3]{}CH_3CHO$$

which represents first the augmentation of an ethyl alcohol group to an acetaldehyde group and the simultaneous reduction of the hydroxylamine group to form aldehyde ammonia, and second, the deammonation of this product of the rearrangement to acetaldehyde.[6]

$$CH_3CH(NH_2)OH = CH_3CH{=}NH + H_2O$$

N-Isopropylhydroxylamine, $(CH_3)_2CH—NH{:}OH$. Kjellin found also that acetone and ammonium chloride are formed when *N*-isopropylhydroxylamine hydrochloride is heated in the dry state. After the manner of the conversion of a primary alcohol hydroxylamine into an aldehyde and ammonia as explained above, so here a secondary alcohol oxime rearranges to form a ketone and ammonia.

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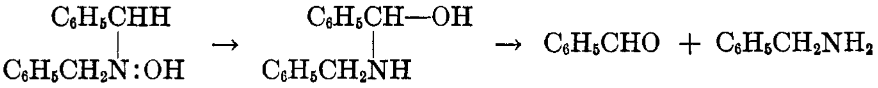
[6] It is interesting in this connection to recall that aldehyde ammonia is deammonated to acetaldehyde in the presence of acids in water solution as represented by the above equation and that in liquid ammonia solution in the presence of calcium amide it is dehydrated to ethylideneimine.

$$CH_3CH(NH_2)OH = CH_3CH{=}NH + H_2O$$

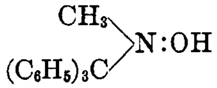
N,N-Dibenzylhydroxylamine, $(C_6H_5CH_2)_2N{:}OH$. When this primary alcohol derivative of hydroxylamine is heated with acetic acid saturated with hydrochloric acid gas, it is converted practically quantitatively into benzaldehyde and benzylamine (76). It may be assumed that the reactions involved take the course



$$\begin{array}{c} C_6H_5CHH \\ | \\ C_6H_5CH_2N{:}OH \end{array} \rightarrow \begin{array}{c} C_6H_5CH{-}OH \\ | \\ C_6H_5CH_2NH \end{array} \rightarrow C_6H_5CHO + C_6H_5CH_2NH_2$$

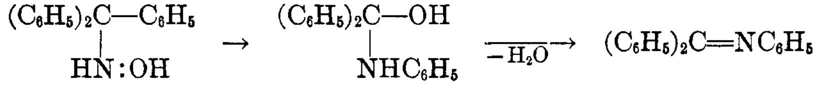
The first step consists in a Beckmann-like rearrangement of dibenzylhydroxylamine to form a benzaldehyde-acetal; the second in the breaking down of this acetal to form an aldehyde and an alcohol after the familiar manner of acetals in the presence of mineral acids.

N-Triphenylmethylhydroxylamine, $(C_6H_5)_3C{-}NH{:}OH$ *and N-triphenylmethyl-N-methylhydroxylamine,*



When the first compound, in ether solution, is treated with phosphorus pentachloride, a practically quantitative yield of phenylbenzophenone is obtained (68). Whether the reactions involved take place in accordance with the one or the other of the schemes,

$$(C_6H_5)_3CNH{:}OH \xrightarrow[-H_2O]{} (C_6H_5)_3C{-}N \rightarrow (C_6H_5)_2C{=}NC_6H_5$$

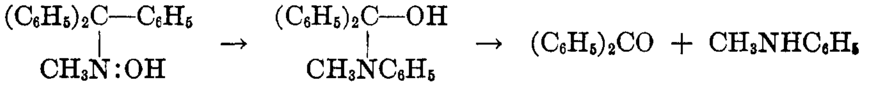


$$\begin{array}{c} (C_6H_5)_2C{-}C_6H_5 \\ | \\ HN{:}OH \end{array} \rightarrow \begin{array}{c} (C_6H_5)_2C{-}OH \\ | \\ NHC_6H_5 \end{array} \xrightarrow[-H_2O]{} (C_6H_5)_2C{=}NC_6H_5$$

it is difficult to say. In any event a tertiary alcohol undergoes augmentation to form a ketone-ether, hydroxylamine simultaneously undergoing reduction to ammonia and water.

Under similar treatment the second compound gives moderate yields of methylaniline and benzophenone (69).

While the decomposition of the first compound has been represented as following either of the familiar routes as indicated above, it is not so easy to explain the decomposition of the second compound on the assumption of the formation of an intermediate compound containing univalent nitrogen (68, 69). The reactions may, however, be represented as follows:



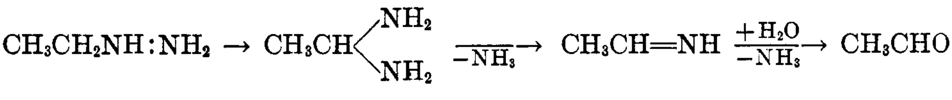
$$\begin{array}{c} (C_6H_5)_2C{-}C_6H_5 \\ | \\ CH_3N{:}OH \end{array} \rightarrow \begin{array}{c} (C_6H_5)_2C{-}OH \\ | \\ CH_3NC_6H_5 \end{array} \rightarrow (C_6H_5)_2CO + CH_3NHC_6H_5$$

N-triphenylmethyl-*N*-methylhydroxylamine undergoes in effect a Beckmann rearrangement to form a ketone-acetal, which decomposes to form an aquo ketone and an ammono alcohol.

Triphenylmethylmethylchloramine, $(C_6H_5)_3C-NCl-CH_3$, according to Miss Vosburgh (65) does not undergo rearrangement.

Alkylhydrazines

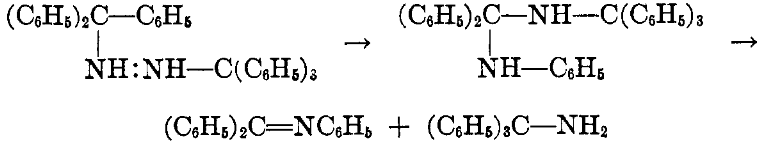
Since hydrazine may be looked upon as a nitrogen analog of hydrogen peroxide, it is reasonable to assume that it possesses nitridizing properties, and that in particular certain of its derivatives will be found to undergo intramolecular reactions similar to those which have been shown to characterize the alkyl derivatives of hydroxylamine and the esters of the ammonohypochlorous acids and of hydrazoic acid. For example, ethylhydrazine might be expected to undergo intramolecular nitridation and reduction as represented by the scheme,



$$CH_3CH_2NH{:}NH_2 \rightarrow CH_3CH\left\langle\begin{matrix}NH_2\\ NH_2\end{matrix}\right. \xrightarrow[-NH_3]{} CH_3CH{=}NH \xrightarrow[-NH_3]{+H_2O} CH_3CHO$$

to form aquoacetaldehyde and ammonia. As a matter of fact, however, none of the simpler alkyl derivatives of hydrazine has been observed to undergo such reactions, and this presumably for the reason that hydrazine behaves generally as a powerful reducing agent and only now and then as an augmenting agent.

Symmetrical bis-triphenylmethylhydrazine, $(C_6H_5)_3C-NH-NH-C(C_6H_5)_3$. However, Stieglitz and Brown (67) have shown that one of the reactions taking place when symmetrical bis-triphenylmethylhydrazine is heated with zinc chloride results in the formation of phenylbenzophenoneimine and triphenylmethylamine. The reactions, whether involving the formation of a univalent nitrogen compound, $(C_6H_5)_3CN$, or following the course,



$$\begin{matrix}(C_6H_5)_2C-C_6H_5\\ |\\ NH{:}NH-C(C_6H_5)_3\end{matrix} \rightarrow \begin{matrix}(C_6H_5)_2C-NH-C(C_6H_5)_3\\ |\\ NH-C_6H_5\end{matrix} \rightarrow$$

$$(C_6H_5)_2C{=}NC_6H_5 + (C_6H_5)_3C-NH_2$$

consist in the intramolecular nitridation of a tertiary alcohol to a ketone-acetal and the simultaneous reduction of hydrazine nitrogen to ammonia nitrogen.

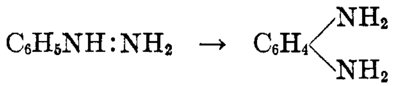
It is interesting furthermore to recall that Stieglitz and Brown found that bis-triphenylmethylhydrazine at its melting point decomposes practically quantitatively into triphenylmethane and nitrogen. This observation is in harmony with experience to the effect that hydrazine and its derivatives generally act as powerful reducing agents. The equation

$$(C_6H_5)_3C—NH:NH—C(C_6H_5)_3 = 2(C_6H_5)_3CH + N_2$$

represents the reduction of the tertiary alcohol groups, $(C_6H_5)_3C^+$, to a hydrocarbon, $(C_6H_5)_3CH$, and the augmentation (dehydrogenation) of hydrazine to elementary nitrogen.

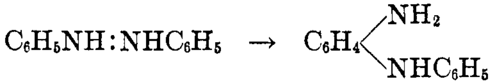
Aryl hydrazides

The well-known rearrangements of phenylhydrazine to *p*-phenylenediamine,



$$C_6H_5NH:NH_2 \rightarrow C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$$

and of hydrazobenzene to *p*-semidine,



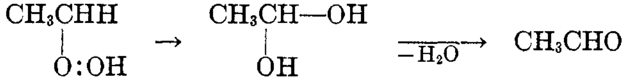
$$C_6H_5NH:NHC_6H_5 \rightarrow C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NHC_6H_5\end{matrix}$$

involve the nitridation of a phenyl group to a phenylene group and the reduction of hydrazine nitrogen to ammonia nitrogen. When hydrazobenzene is converted into benzidine, the hydrazine group may be said to nitridize the two phenyl groups to form a diphenyl group, the hydrazine nitrogen at the same time undergoing reduction to ammonia nitrogen.

Alkyl derivatives of hydrogen peroxide

Recalling again the many similarities in the behavior of hydrogen peroxide, hydrazine, and hydroxylamine, it is interesting to find that certain alkyl hydroperoxides have been observed to undergo rearrangements which are clearly analogous to the intramolecular augmentation–reduction reactions discussed above.

Ethyl hydroperoxide, $C_2H_5O:OH$. Concerning rearrangements of this compound it is known only that in the presence of molecular silver it gives small yields of acetaldehyde and acetic acid (1a). The acetaldehyde is probably formed in accordance with the equation,

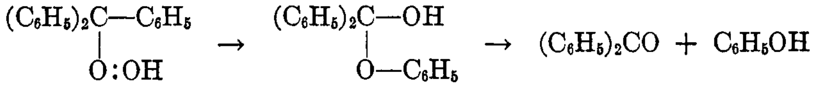


$$\begin{matrix}CH_3CHH\\ |\\ O:OH\end{matrix} \rightarrow \begin{matrix}CH_3CH—OH\\ |\\ OH\end{matrix} \xrightarrow[-H_2O]{} CH_3CHO$$

which represents a reaction analogous to that involved in the conversion of ethylhydroxylamine into acetaldehyde and ammonia (p. 230) and of bis-triphenylmethylhydrazine into phenylbenzophenoneimine and triphenylmethylamine (p. 232).

Since the formation of acetaldehyde from ethylhydroxylamine and from ethyl hydroperoxide almost certainly involve similar reactions, it follows that the formation of a univalent nitrogen compound as the first step in the rearrangement of ethylhydroxylamine is highly improbable.

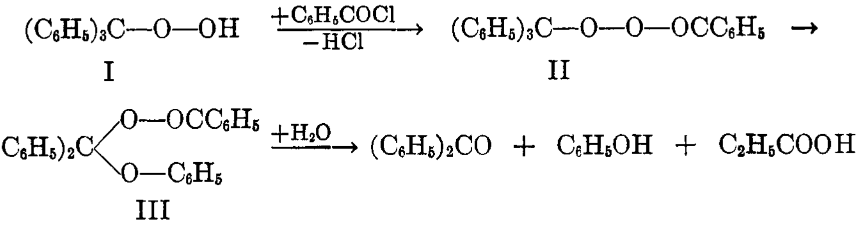
Triphenylmethyl hydroperoxide, $(C_6H_5)_3CO{:}OH$, when heated above its melting point decomposes to form benzophenone and phenol (78). While it may be that the compound breaks down directly, it seems more reasonable to assume that a rearrangement takes place and that the resulting ketone-acetal decomposes to form benzophenone and phenol



$$\begin{array}{l}(C_6H_5)_2C—C_6H_5\\ \quad|\\ \quad O{:}OH\end{array} \rightarrow \begin{array}{l}(C_6H_5)_2C—OH\\ \quad|\\ \quad O—C_6H_5\end{array} \rightarrow (C_6H_5)_2CO + C_6H_5OH$$

When triphenylmethyl hydroperoxide together with benzoyl chloride is treated with a strong solution of potassium hydroxide a benzophenone-acetal of the formula III below is formed, which under the action of hot alcoholic potassium hydroxide is hydrolyzed to benzophenone, phenol, and benzoic acid.

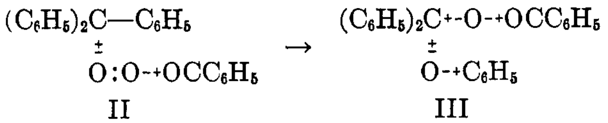
According to Wieland and Maier the reactions involved take place as follows:



$$\underset{\text{I}}{(C_6H_5)_3C—O—OH} \xrightarrow[-HCl]{+C_6H_5COCl} \underset{\text{II}}{(C_6H_5)_3C—O—O—OCC_6H_5} \rightarrow$$

$$\underset{\text{III}}{(C_6H_5)_2C\begin{array}{l}\diagup O—OCC_6H_5\\ \diagdown O—C_6H_5\end{array}} \xrightarrow{+H_2O} (C_6H_5)_2CO + C_6H_5OH + C_2H_5COOH$$

The nature of the transformation of II into III may perhaps be made clearer by writing the equation,

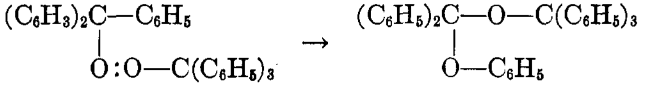


$$\underset{\text{II}}{\begin{array}{l}(C_6H_5)_2C—C_6H_5\\ \quad\pm\\ \quad O{:}O^{-+}OCC_6H_5\end{array}} \rightarrow \underset{\text{III}}{\begin{array}{l}(C_6H_5)_2C^{+-}O^{-+}OCC_6H_5\\ \quad\pm\\ \quad O^{-+}C_6H_5\end{array}}$$

and noting that the exchange of positions of the phenyl and C_6H_5COO groups, in principle a Beckmann rearrangement, involves the augmentation of a tertiary alcohol group to a ketone group and the simultaneous reduction of hydrogen peroxide oxygen. Compound III is a ketone-acetal which should of course readily hydrolyze to benzophenone, phenol, and benzoic acid.

The isolation and identification of the intermediate ketone-acetal (III) in this conversion of triphenylmethyl hydroperoxide into benzophenone and phenol, lends substantial support to our earlier assumptions that similar intermediate compounds are formed in the analogous transformations of the derivatives of chloramine, hydrazoic acid, hydroxylamine, and hydrazine.

Bis-triphenylmethyl peroxide, $(C_6H_5)_3C^{+}\text{-}O{:}O\text{-}^{+}C(C_6H_5)_3$. When this compound is heated with xylene in an atmosphere of carbon dioxide, limited amounts of benzophenone, phenol, and triphenylcarbinol are formed (77). The appearance of these compounds among the reaction products is reasonably accounted for on the assumption that a portion of the bis-triphenylmethyl peroxide undergoes rearrangement,



$$\begin{array}{l}(C_6H_3)_2C\text{—}C_6H_5\\ \quad\vert\\ \quad O{:}O\text{—}C(C_6H_5)_3\end{array} \rightarrow \begin{array}{l}(C_6H_5)_2C\text{—}O\text{—}C(C_6H_5)_3\\ \quad\vert\\ \quad O\text{—}C_6H_5\end{array}$$

to form a ketone-acetal which should in turn be hydrolyzable to benzophenone, phenol, and triphenylcarbinol. However, if this explanation of the formation of these compounds is to hold it is necessary to assume that small quantities of water were adventitiously present in Wieland's reaction mixtures. Much the greater portion (75 per cent) of the peroxide undergoes a benzidene-like transformation to form a diethyl ester of benzpinacone with which we do not concern ourselves here.

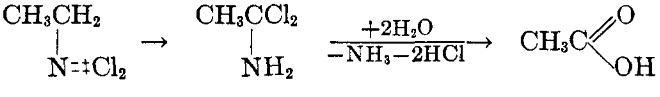
INTRAMOLECULAR AUGMENTATION OF ALCOHOLS TO CARBYLIC ACIDS

Alkyldichloramines

It will be recalled that the alkyl monochloramines yield aldehydes and hydrochloric acid as decomposition products, the one atom of hypochlorous acid chlorine contained in the molecule of the chloramine just sufficing to augment an alcohol group to an aldehyde group. The two hypochlorous chlorine atoms contained in the molecule of the dichloramines may be expected to augment the alkyl groups to carbylic acid groups, $RCH_2^{+} \rightarrow RC^{\ddagger}$.

Methyldichloramine, $CH_3N^{=\ddagger}Cl_2$. When heated, methyldichloramine decomposes into hydrocyanic acid (formic anammonide) and hydrochloric acid (5).

Ethyldichloramine, $CH_3CH_2N^{=\ddagger}Cl_2$. The formation of acetic acid by the action of potassium hydroxide on this ester of an ammonohypochlorous acid as observed by Berg (7) may be represented as taking the course



$$\begin{array}{l}CH_3CH_2\\ \quad\vert\\ \quad N^{=\ddagger}Cl_2\end{array} \rightarrow \begin{array}{l}CH_3CCl_2\\ \quad\vert\\ \quad NH_2\end{array} \xrightarrow[-NH_3-2HCl]{+2H_2O} CH_3C\begin{array}{l}\nearrow O\\ \searrow OH\end{array}$$

in accordance with which an acetic acid amide-chloride is primarily formed to decompose in the presence of potassium hydroxide to form aquo-acetic acid.

Isoamyldichloramine, $C_5H_{11}N{=}{\ddagger}Cl_2$. Berg found also that isoamyldichloramine, when heated with potassium hydroxide, yields isovaleronitrile or isovaleric acid, depending upon the conditions under which the decomposition is effected. It is to be taken as a matter of course that the reactions involved are similar to those discussed above.

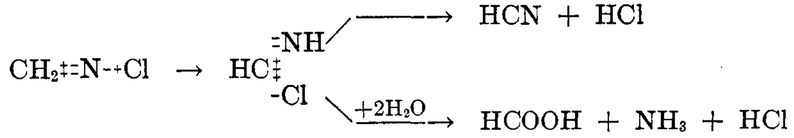
INTRAMOLECULAR AUGMENTATION OF ALDEHYDES AND KETONES TO CARBYLIC ACIDS

The same sort of intramolecular reactions as those which have been discussed above as consisting in the augmentation of alcohols to aldehydes and ketones and of alcohols to carbylic acids or nitriles are also involved in the rearrangement of certain aldehyde and ketone derivatives of monochloramine, hydrazoic acid, and hydroxylamine to carbylic acids.

Alkylidenechlorimines

Methylenechlorimine, $CH_2{\ddagger}{=}N{-}{+}Cl$. By the action of chloramine on formaldehyde in water solution, Cross, Bevan, and Bacon (15) obtained a compound which they believed to be a dimer of methylenechlorimine, $(CH_2{=}N{-}{+}Cl)_2$. This unstable compound when warmed yields hydrocyanic acid and hydrochloric acid as the main products of decomposition.

Delépine (19) has shown that by the action of hypochlorous acid on hexamethylenetetramine a trimer of methylenechlorimine, $(CH_2{=}N{-}{+}Cl)_3$, is formed which on treatment with sodium ethylate gives abundant yields of formic acid and ammonia. The decomposition of the dimer of methylenechlorimine into hydrocyanic acid and hydrochloric acid and the action of sodium ethylate on the trimer to form formic acid and ammonia may be explained as follows. Writing the monomolecular formula for methylenechlorimine, the scheme



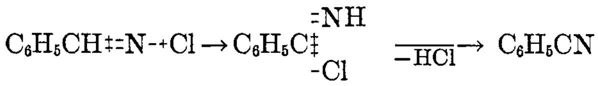
$$CH_2{\ddagger}{=}N{-}{+}Cl \rightarrow HC{\ddagger}\begin{array}{l}{=}NH \\ \\ {-}Cl\end{array}\begin{array}{l}\nearrow\xrightarrow{\hspace{3em}} HCN + HCl \\ \\ \searrow\xrightarrow{+2H_2O} HCOOH + NH_3 + HCl\end{array}$$

represents: first, the rearrangement of the chlorimine to formic acid imide-chloride after the manner of a Beckmann rearrangement; second, the decomposition of this unknown acid imide-chloride to form hydrocyanic acid and hydrochloric acid; and third, its hydrolysis to formic acid, ammonia, and hydrochloric acid.

Benzylidenechlorimine, $C_6H_5CH{\ddagger}{=}N{-}{+}Cl$. Raschig (54) obtained this benzaldehyde hypochlorous acid acetal in the form of an unstable yellow oil mixed with more or less benzaldehyde, by shaking a water solution of chloramine with benzaldehyde.

$$C_6H_5CH{=}O + H_2N\text{-+}Cl = C_6H_5CH{\ddagger}{=}N\text{-+}Cl + H_2O$$

When this oil was warmed with sodium hydroxide solution, or even with water, phenyl cyanide was formed. Clearly the decomposition of benzylidenechlorimine into benzonitrile and hydrochloric acid may be said to consist, in principle, in the augmentation of an aldehyde to a carbylic acid and the reduction of hypochlorous acid to hydrochloric acid,



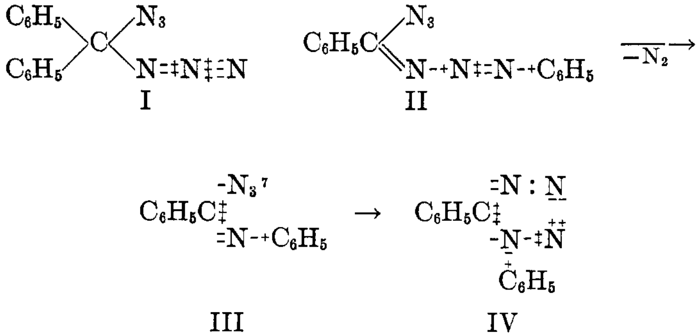
$$C_6H_5CH{\ddagger}{=}N\text{-+}Cl \rightarrow C_6H_5C{\ddagger}\begin{matrix}{=}NH\\ \text{-}Cl\end{matrix} \xrightarrow{-HCl} C_6H_5CN$$

It is important to note in this connection that attempts to effect the rearrangement of benzophenonechlorimine have failed (66).

Ketone azides

No aldehyde azides appear to be known. However, at least two ketone azides have been observed to undergo intramolecular reactions which resemble the Beckmann rearrangement of the ketoximes.

Benzophenone diazide, $(C_6H_5)_2C(N{=}{\ddagger}N{\ddagger}{=}N)_2$. Schroeter (56) has shown that this ketone nitric acid acetal is converted into 1,5-diphenyltetrazole when heated in an indifferent solvent. It is reasonable to suppose that the reactions involved follow the course,



The ketone diazide (I) undergoes intramolecular nitridation of the diphenylketone group to a benzoic acid group and reduction of nitric acid nitrogen to nitrous acid nitrogen to form the hypothetical compound II,[8]

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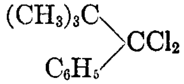
[7] The azide group is here assumed to act as a nitrous acid hydrazide (cf. p. 222.)

[8] Compare the rearrangement of benzyl azide (p. 227) and of triphenylmethyl hydroperoxide (p. 234).

which, splitting off nitrogen (nitrous anammonide), yields III. Finally, after the manner of the intramolecular ammonation of guanyl azide to 5-aminotetrazole the azide (III) is transformed into 1,5-diphenyltetrazole (IV).[9]

Independently of whether the primary reaction consists in the formation of an univalent nitrogen compound, as was assumed by Schroeter, or of rearrangement to the benzoic acid nitrous acid derivative (II), what happens first and last is that by the nitridizing action of nitric acid nitrogen a diphenyl ketone is converted into a derivative of benzoic acid.

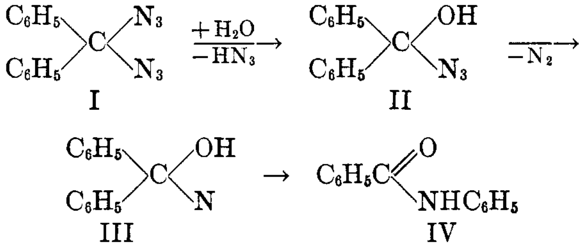
Just as benzophenone diazide is converted into 1,5-diphenyltetrazole, as explained above, so in a similar manner 1-*tertiary*-butyl-5-phenyltetrazole is formed when pivalophenone dichloride,



$$\begin{matrix}(CH_3)_3C\\ C_6H_5\end{matrix}\!>\!CCl_2$$

is heated with silver azide in amyl ether solution (58).

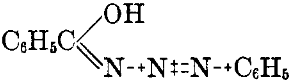
Götzky (30), who has recently isolated benzophenone diazide, has shown that quantitative yields of benzanilide are obtained when benzophenone diazide is treated with cold 70 per cent sulfuric acid. According to Götzky the reactions follow the course,



$$\underset{\text{I}}{\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!>\!C\!<\!\begin{matrix}N_3\\ N_3\end{matrix}} \xrightarrow[-HN_3]{+H_2O} \underset{\text{II}}{\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ N_3\end{matrix}} \xrightarrow[-N_2]{}$$

$$\underset{\text{III}}{\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ N\end{matrix}} \rightarrow \underset{\text{IV}}{C_6H_5C\!\begin{matrix}{\nearrow}O\\ \searrow NHC_6H_5\end{matrix}}$$

Quite as reasonably it may be assumed that compound II, instead of losing nitrogen directly to form III, rearranges into



$$C_6H_5C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown N{-}{+}N{\ddagger}{=}N{-}{+}C_6H_5\end{matrix}$$

which by the elimination of a molecule of nitrogen (nitrous anammonide) passes over into benzanilide (IV). Whatever course the reactions involved may follow, it is clear that first and last a ketone is augmented to a carboxazylic acid.

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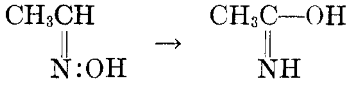
[9] 1,5-Diphenyltetrazole is a cyclic benzoic acid nitrous acid hydrazide, and at the same time a phenyl ester of a mixed benzoic nitrous acid.

Aldoximes and ketoximes

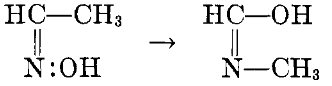
The aldoximes and ketoximes in general under the influence of certain reagents undergo the familiar Beckmann rearrangement to acid amides. Acetaldoxime, for example, on treatment with phosphorus pentachloride is converted into a mixture of acetamide and methylformamide (23).

Representing the formation of acetamide by the equation,



$$\begin{array}{c}\mathrm{CH_3CH}\\ \|\\ \mathrm{N{:}OH}\end{array} \rightarrow \begin{array}{c}\mathrm{CH_3C{-}OH}\\ \|\\ \mathrm{NH}\end{array}$$

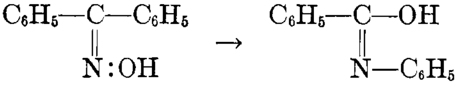
and of methylformamide by



$$\begin{array}{c}\mathrm{HC{-}CH_3}\\ \|\\ \mathrm{N{:}OH}\end{array} \rightarrow \begin{array}{c}\mathrm{HC{-}OH}\\ \|\\ \mathrm{N{-}CH_3}\end{array}$$

it may be said that by processes of intramolecular augmentation and reduction, acetaldehyde is converted partly into an aquo-ammonoacetic acid and partly into an *N*-methyl ester of an aquo-ammonoformic acid. Whatever the detailed mechanism of the Beckmann rearrangement may be, it is here represented as consisting simply in an exchange of positions on the part of aldehyde hydrogen and the OH of the oxime group in the one case and of the methyl group and the OH group on the other. In both cases aldehyde carbon is augmented to carbylic acid carbon, while the hydroxylamine residue is at the same time, in effect, reduced to ammonia and water.

In a similar manner the ketoximes undergo rearrangement to carboxazylic acid esters; benzophenoneoxime, for example, to benzanilide,



$$\begin{array}{c}\mathrm{C_6H_5{-}C{-}C_6H_5}\\ \|\\ \mathrm{N{:}OH}\end{array} \rightarrow \begin{array}{c}\mathrm{C_6H_5{-}C{-}OH}\\ \|\\ \mathrm{N{-}C_6H_5}\end{array}$$

O-Methylbenzophenoneoxime does not undergo the Beckmann rearrangement. When heated with acids it is hydrolyzed to benzophenone and *O*-methylhydroxylamine (1).

Hydrazones

In view of the many similarities in the behavior of hydroxylamine and hydrazine, it might be expected that hydrazones would be found to undergo rearrangements in accordance with the equation, $\mathrm{RCH}\ddagger{=}\mathrm{N{:}NH_2} \rightarrow \mathrm{RC(NH)NH_2}$, which represents an hypothetical transformation whereby an aldehyde hydrazone, undergoing intramolecular augmentation and reduction, is converted into a carbazylic acid.

Apparently none of the aldehyde and ketone derivatives of hydrazine or of phenylhydrazine have been observed to undergo the rearrangements. Instead, with loss of ammonia, certain phenylhydrazones are converted into derivatives of indole (11, 25).

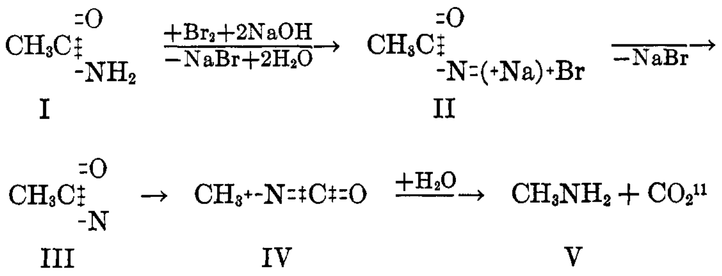
INTRAMOLECULAR AUGMENTATION OF CARBYLIC ACIDS TO CARBONIC ACIDS

The reactions involved in the conversion of acetbromamide into methyl isocyanate and hydrobromic acid, of benzoyl azide into phenyl isocyanate and nitrogen, of benzohydroxamic acid into phenyl isocyanate and water, and of benzamidoxime into phenylurea may be looked upon as consisting in the intramolecular augmentation of carbylic acids to carbonic acids, and the reduction, respectively, of hypobromous acid bromine to hydrobromic acid bromine, of nitric acid nitrogen to nitrous acid nitrogen, and of hydroxylamine nitrogen and oxygen to ammonia nitrogen and water oxygen.

Acyl halogen amides

These compounds are formed by the action of alkali hypohalites on acid amides and in turn are converted into primary amines and alkali carbonates by the action of hot alkali solution.

Acetbromamide, $CH_3CO^{+-}NH^{-+}Br$. The reactions concerned in the well-known process of Hofmann (35, 72) for the preparation of methylamine from acetamide have been explained as following the steps represented by the scheme,[10]



$$\underset{\text{I}}{CH_3C\ddagger^{=O}_{-NH_2}} \xrightarrow[-NaBr+2H_2O]{+Br_2+2NaOH} \underset{\text{II}}{CH_3C\ddagger^{=O}_{-N^{=}(^{+}Na)^{+}Br}} \xrightarrow[-NaBr]{}$$

$$\underset{\text{III}}{CH_3C\ddagger^{=O}_{-N}} \rightarrow \underset{\text{IV}}{CH_3{}^{+-}N^{=}\ddagger C\ddagger^{=}O} \xrightarrow{+H_2O} \underset{\text{V}}{CH_3NH_2 + CO_2}{}^{11}$$

Under the action of bromine and sodium hydroxide an aquo-ammonoacetic acid (I) is converted into the sodium salt of a mixed aquo-ammonoacetic ammonohypobromous acid (II). This salt, losing sodium bromide,

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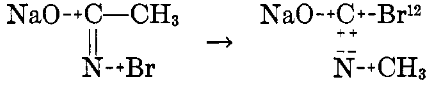
[10] Excepting that the small plus and minus signs are used in the sense already explained (p. 221).

[11] No one of the formulas, $CH_3CONHBr$, $CH_3C(OH)Br$ or $CH_3C(NH)OBr$, has been established as representing the constitution of acetbromamide. According to Hantzsch (34) the sodium salt of acetbromamide has the constitution represented by the formula, $CH_3C(NH)ONa$. Whether the metal is attached to oxygen or nitrogen, or neither, is a question which need not concern us here.

forms the univalent nitrogen compound III. The *N*-methyl aquo-ammonocarbonate (IV) formed by the rearrangement of III is hydrolyzed by the action of sodium hydroxide to sodium carbonate and the ammono alcohol V.

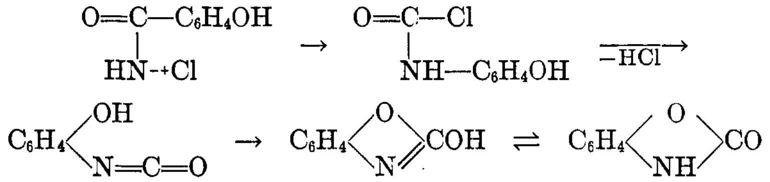
Quite as reasonably it may be assumed that the hypobromite bromine contained in the sodium salt of acetbromamide augments the carbon to carbon bond by simply changing places with the methyl group



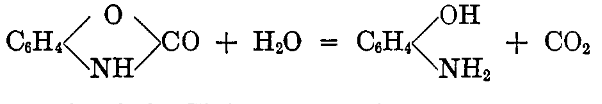
$$\begin{array}{c} \text{NaO}^{-+}\text{C—CH}_3 \\ \| \\ \text{N}^{-+}\text{Br} \end{array} \rightarrow \begin{array}{c} \text{NaO}^{-+}\text{C}^{+-}\text{Br}[12] \\ \overset{++}{--} \\ \text{N}^{-+}\text{CH}_3 \end{array}$$

thereby bringing about a Beckmann-like rearrangement; and that the compound thus formed, which is at the same time a bromide, a sodium salt, and an *N*-methyl ester of a carbonic acid, loses sodium bromide to yield methyl isocyanate.[13]

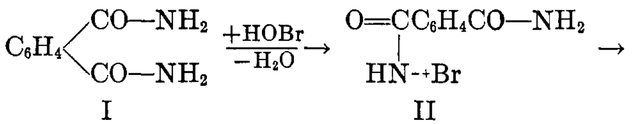
An example of the conversion of a carboxazylic acid into a cyclic aquo-ammonocarbonic acid is the formation of oxycarbanil by the action of sodium hypochlorite in alkali solution on salicylamide (31) as represented by the scheme



A silver salt, $C_7H_4O_2NAg$, and several *N*-esters and *O*-esters of this cyclic phenylene aquo-ammonocarbonate have been prepared. Oxycarbanil has been hydrolyzed to *o*-aminophenol and carbon dioxide.



A third example of the Hofmann transformation is the formation of benzoyleneurea by the action of potassium hypobromite on phthalamid (37). The reactions involved may be represented by the scheme,



I II

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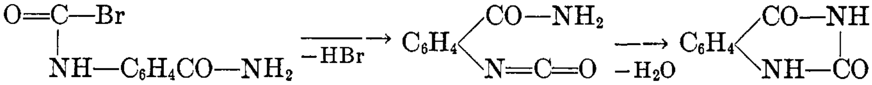
[12] Mohr (47) has shown that almost certainly an *N*-phenylcarbamate, $C_6H_5NH—CO—OK$, is formed as an intermediate product when benzchloramide undergoes rearrangement under the action of aqueous potassium hydroxide.

[13] Hoogewerff and van Dorp (36) first suggested that this unknown carbonic acid derivative is the primary product of the rearrangement of bromoacetamide.



III IV V

and explained as consisting: first, in the conversion of a carboxazylic acid group into a carboxazylic acid ammonohypobromous acid group under the action of potassium aquohypobromite (I to II); second, in the intramolecular augmentation (nitridation) of a carbylic acid carbon to a phenylene carbon union and the simultaneous reduction of hypobromous bromine to hydrobromic acid bromine (II to III); third, in the loss of hydrobromic acid from this carbonic acid ester bromide to give the aquo-ammonocarbonic derivative (IV); and finally, in the intramolecular ammonation of this compound to form the cyclic benzoic acid carbonic acid ester (V).

In support of his hypothesis that the primary step involved in the Hofmann rearrangement is the formation of a univalent nitrogen compound, Stieglitz (63) calls attention to the fact that neither the *N*-alkyl (aryl) derivatives of the acyl halogen amides, RCON(Hl)R′, nor their isomers, the *N*-halogen acyl imino esters, RC(NHl)OR′, undergo this rearrangement (38, 61).

Acyl azides

In some cases when heated alone and in general when heated in an indifferent solvent, the acid azides decompose into nitrogen and isocyanates.

Benzoyl azide, C_6H_5CO+-N=‡N‡≡N. Schroeter (18, 57) has shown that benzoyl azide decomposes quantitatively to form phenyl isocyanate and nitrogen when heated in the presence of dry benzene. While the decomposition is generally assumed to follow the course

$$C_6H_5CO{-}N{=}N{\equiv}N \xrightarrow[-N_2]{} C_6H_5CO{-}N \rightarrow C_6H_5NCO$$

by way of an univalent nitrogen compound, it may be that the acid azide, by intramolecular nitridation and reduction, first rearranges to a nitrous acid carbonic acid derivative of the formula, C_6H_5+-N=‡N+-N=‡C‡=O,[14] which unknown compound should break down to form phenyl isocyanate and nitrogen. Clearly a benzoic acid derivative is augmented to an *N*-phenyl ester of an aquo-ammonocarbonic acid, while at the same time ammononitric acid undergoes reduction to a nitrous acid which appears in the form of its anammonide, namely as free nitrogen.

[14] Two nearly related compounds of the formulas, C_6H_5+-NH-+CO+-NH-+N‡=N-+C_6H_4COOH and C_6H_5+-NH-+CO+-NH-+N‡=N-+$C_6H_4COOC_2H_5$, which are derivatives of an hypothetical nitrous carbonic acid, H_2N-+CO+-NH-+N‡=NH, have been prepared (21).

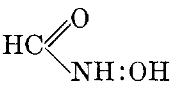
Hydroxamic acids

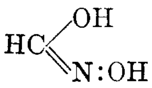
Just as one may look upon acetbromamide as an aquo-ammonoacetic acid the amide group of which is "bromidized" to an ammonohypobromous acid group, and upon benzoyl azide as an aquo-ammonobenzoic acid whose amido group is nitridized to an ammononitric acid group, so similarly acethydroxamic acid may be said to be an aquo-ammonoacetic acid in which the amido group is oxidized to the oxime group.

$$CH_3CONH_2 \rightarrow CH_3CONH{:}OH$$

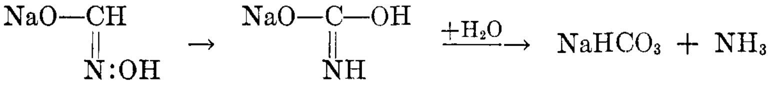
Many hydroxamic acids undergo intramolecular reactions which resemble closely those involved in the Hofmann-Beckmann-Curtius transformations discussed above. Following are examples of the many known Lossen rearrangements.

Formohydroxamic acid,





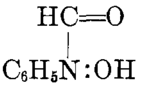
Excepting that the formation of sodium carbonate and ammonia by the slow decomposition of the sodium salt of formohydroxamic acid (10) may be interpreted as taking place in accordance with the scheme,



$$\begin{array}{c}NaO{-}CH\\ \| \\ N{:}OH\end{array} \rightarrow \begin{array}{c}NaO{-}C{-}OH\\ \| \\ NH\end{array} \xrightarrow{+H_2O} NaHCO_3 + NH_3$$

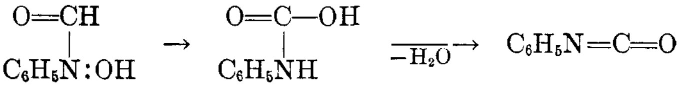
none of the aliphatic hydroxamic acids has been observed to undergo the Lossen rearrangement.

Formylphenylhydroxylamine,



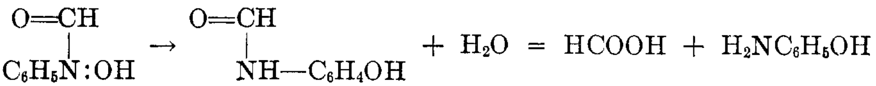
$$\begin{array}{c}HC{=}O\\ | \\ C_6H_5N{:}OH\end{array}$$

When heated with phosphorus pentoxide formylphenylhydroxylamine undergoes the Lossen rearrangement to form phenyl isocyanate (4). The yield is small.



$$\begin{array}{c}O{=}CH\\ | \\ C_6H_5N{:}OH\end{array} \rightarrow \begin{array}{c}O{=}C{-}OH\\ | \\ C_6H_5NH\end{array} \xrightarrow[-H_2O]{} C_6H_5N{=}C{=}O$$

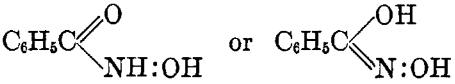
Under the action of boiling normal sulfuric acid the oxime yields formic acid and *p*-aminophenol (2).



$$\begin{array}{c}O{=}CH\\ | \\ C_6H_5N{:}OH\end{array} \rightarrow \begin{array}{c}O{=}CH\\ | \\ NH{-}C_6H_4OH\end{array} + H_2O = HCOOH + H_2NC_6H_5OH$$

In the one case formic acid carbon is augmented to carbonic acid carbon; in the other a phenyl group is augmented to a phenylene group.

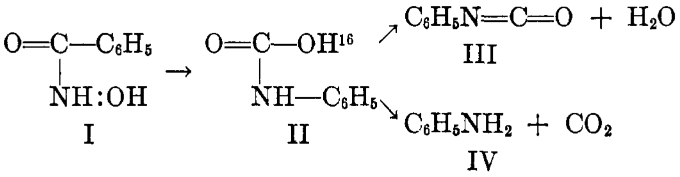
Benzohydroxamic acid,



Aniline, carbon dioxide, phenyl isocyanate, and benzoic acid have been identified among the products of the destructive distillation of benzohydroxamic acid (33, 42).

By the action of thionyl chloride on benzohydroxamic acid in the presence of boiling benzene, phenyl isocyanate is formed (45).

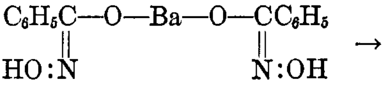
The formation of these compounds, excepting benzoic acid,[15] may be explained as taking place either by way of the univalent nitrogen compound, C_6H_5CO-N, or in accordance with the equation,



which represents the benzoic acid oxime (I) as undergoing rearrangement to form an *N*-phenyl aquo-ammonocarbonate (II), which may on the one hand lose water to form the phenyl aquo-ammonocarbonate (III)[17] and on the other break down to form carbon dioxide and aniline (IV).

When the barium salt of benzohydroxamic acid is strongly heated, two molecules of aniline and one each of barium carbonate and carbon dioxide are obtained from each molecule of the salt, $(C_6H_5CO-NH:O)_2Ba \cdot H_2O$, used (43).[18]

As represented by the scheme



$$\underset{\text{HO:N}}{\overset{\displaystyle C_6H_5C}{\|}}\text{—O—Ba—O—}\underset{\text{N:OH}}{\overset{\displaystyle CC_6H_5}{\|}} \rightarrow$$

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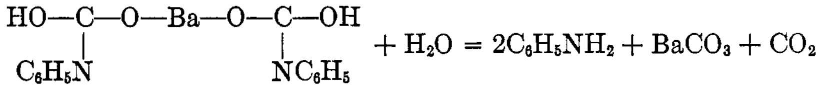
[15] The presence of benzoic acid is to be accounted for on the supposition that water set free in the dehydration of II to III hydrolyzes benzohydroxamic acid to aquobenzoic acid and hydroxylamine. Benzohydroxamic acid is known to undergo this hydrolytic decomposition.

[16] Mohr (48) has shown that phenylcarbamates are formed as intermediate products in the Hofmann rearrangement of benzochloramide.

[17] Phenylcarbamic acid is apparently not known to decompose in this manner.

[18] Lossen (41) prepared this salt and reported it as containing no water of crystallization. As a matter of fact the barium content found by Lossen agrees almost exactly with the formula given above for the monohydrated salt.

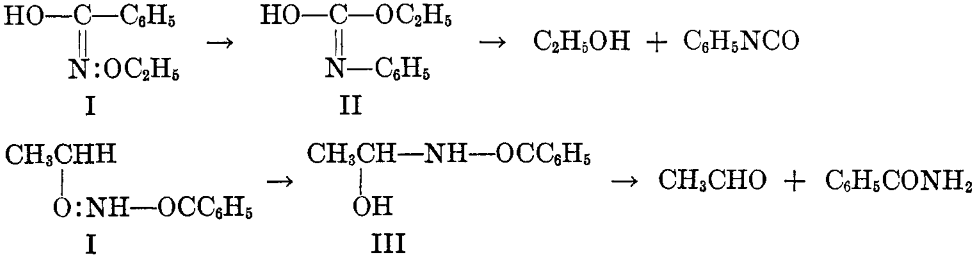


$$\underset{C_6H_5N}{HO-\overset{}{C}}-O-Ba-O-\underset{NC_6H_5}{C-OH} + H_2O = 2C_6H_5NH_2 + BaCO_3 + CO_2$$

barium benzohydroxamate rearranges to the barium salt of a phenylcarbamic acid; this latter compound is then hydrolyzed, by the water of crystallization present in the original salt, to aniline, barium aquocarbonate, and carbon dioxide.

N-Benzoyl-O-ethylhydroxylamine, $C_6H_5CO—NH:O—C_2H_5$. When heated at 190°C. this compound yields phenyl isocyanate, ethyl alcohol, acetaldehyde, and benzamide (32).

The formation of these products may be explained on the assumption that benzoylethylhydroxylamine rearranges in two ways as follows:



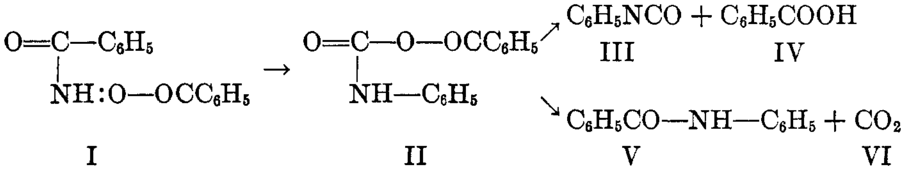
$$\underset{\text{I}}{\underset{N:OC_2H_5}{HO-C-C_6H_5}} \rightarrow \underset{\text{II}}{\underset{N-C_6H_5}{HO-C-OC_2H_5}} \rightarrow C_2H_5OH + C_6H_5NCO$$

$$\underset{\text{I}}{\underset{O:NH-OCC_6H_5}{CH_3CHH}} \rightarrow \underset{\text{III}}{\underset{OH}{CH_3CH-NH-OCC_6H_5}} \rightarrow CH_3CHO + C_6H_5CONH_2$$

the one rearrangement resulting in the formation of an *O*-ethyl-*N*-phenyl aquo-ammonocarbonate (II) (phenylurethan) which is known to lose alcohol to form phenyl isocyanate, the other in the formation of an unknown *N*-benzoyl acetaldehyde ammonia (III) which should easily decompose to form acetaldehyde and benzamide. Recalling our manner of speaking in earlier connections, it may be said that on the one hand benzoic acid is augmented to an aquo-ammonocarbonic acid (I to II), and that on the other hand ethyl alcohol is augmented to acetaldehyde (I to III), the augmenting agent, hydroxylamine, at the same time undergoing reduction to ammonia and water.

N,O-dibenzoylhydroxylamine, $C_6H_5CO—NH:O—OCC_6H_5$. When this compound is heated it decomposes almost quantitatively to form phenyl isocyanate, benzoic acid, benzanilide, and carbon dioxide (20, 52).

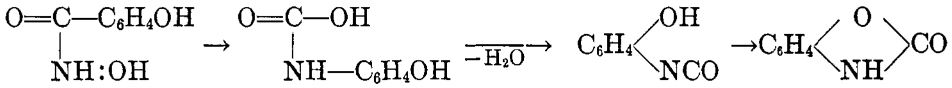
It may be assumed that the reactions involved take place as represented by the scheme,



$$\underset{\text{I}}{\underset{NH:O-OCC_6H_5}{O{=}C-C_6H_5}} \rightarrow \underset{\text{II}}{\underset{NH-C_6H_5}{O{=}C-O-OCC_6H_5}} \begin{array}{l} \nearrow \underset{\text{III}}{C_6H_5NCO} + \underset{\text{IV}}{C_6H_5COOH} \\ \searrow \underset{\text{V}}{C_6H_5CO-NH-C_6H_5} + \underset{\text{VI}}{CO_2} \end{array}$$

in accordance with which an *N*-phenyl ester of a benzoylcarbonic acid, resulting from the Lossen rearrangement of I to II, breaks down partly to form the aquo-ammonocarbonic acid ester (III) and aquobenzoic acid (IV), and partly to the phenyl aquo-ammonobenzoate (V) and carbonic anhydride.

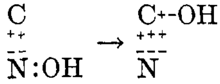
Salicylhydroxamic acid, $\mathrm{HO{-}C_5H_4CO{-}NH{:}OH}$. Under the influence of thionyl chloride in the presence of boiling benzene, salicylhydroxamic acid is converted into oxycarbanil (46, 59). As represented by the scheme,



salicylhydroxamic acid undergoes the Lossen rearrangement to form a cyclic *o*-phenylene aquo-ammonocarbonate (cf. p. 241).

Fulminic acid, carbonous acid oxime, $\mathrm{C}^{+}_{+}{}^{-}_{-}\mathrm{N{:}OH}$. A clean-cut rearrangement of fulminic acid to cyanic acid or of a metallic fulminate to a metallic cyanate has apparently never been accomplished. None the less, observations are on record which show that this carbonous acid oxime undergoes rearrangement in a manner identical in principle with the Lossen transformation of the hydroxamic acids.

Schischkow (55) found many years ago that "isocyanic acid" appears among the products formed by the action of boiling aqueous solutions of alkali halides on mercuric fulminate and that potassium cyanate—or rather its hydrolytic products, potassium carbonate and ammonia—are formed in considerable yields when mercuric fulminate is exposed to the action of boiling potassium hydroxide solution. The reactions involved may be interpreted as constituting a Lossen rearrangement



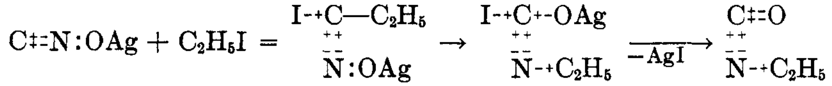
$$\begin{array}{l} \mathrm{C} \\ {}^{+\,+} \\ {}_{-\,-} \\ \mathrm{N{:}OH} \end{array} \longrightarrow \begin{array}{l} \mathrm{C}^{+}\text{-}\mathrm{OH} \\ {}^{+\,+\,+} \\ {}_{-\,-\,-} \\ \mathrm{N} \end{array}$$

in accordance with which carbonous acid carbon is augmented to carbonic acid carbon, while at the same time hydroxylamine is reduced, in principle, to ammonia and water.

When mercuric fulminate is heated with dilute sulfuric acid carbon dioxide, ammonia, hydroxylamine, and mercurous sulfate are formed (13). Carbon dioxide and ammonia, it may be assumed, result from a Lossen rearrangement of fulminic acid.

$$\mathrm{C}^{+}_{+}{}^{-}_{-}\mathrm{N{:}OH} \rightarrow \mathrm{OCNH} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{NH_3}$$

Nef (49) has shown that ethyl isocyanate, in the monomolecular and trimolecular states, is formed when ethyl iodide in ether solution is allowed to stand in contact with silver fulminate. Whatever the course of the reactions involved may be, say, as a reasonable surmise in accordance with the scheme,



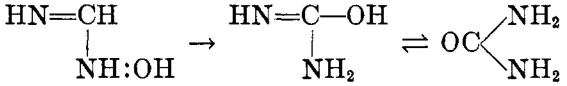
$$\mathrm{C}\ddagger{=}\mathrm{N{:}OAg} + \mathrm{C_2H_5I} = \begin{array}{l} \mathrm{I{-+}C{-}C_2H_5} \\ \;{}^{++}_{--} \\ \mathrm{N{:}OAg} \end{array} \rightarrow \begin{array}{l} \mathrm{I{-+}C{+-}OAg} \\ \;{}^{++}_{--} \\ \mathrm{N{-+}C_2H_5} \end{array} \xrightarrow[-\mathrm{AgI}]{} \begin{array}{l} \mathrm{C}\ddagger{=}\mathrm{O} \\ \;{}^{++}_{--} \\ \mathrm{N{-+}C_2H_5} \end{array}$$

it is clear that a carbonous acid oxime undergoes a Lossen rearrangement to form an aquo-ammonocarbonic acid ester.

Amidoximes

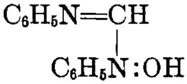
Like the hydroxamic acids, the amidoximes are carbylic acid oximes, and as such should be found to undergo intramolecular augmentation and reduction reactions similar to those discussed above.

Formamidoxime, $\mathrm{HC(NH)NH{:}OH}$, $\mathrm{HC(NH_2)N{:}OH}$, does not undergo clean-cut rearrangement. However, the presence of urea among the products formed by heating formamidoxime in water solution may be explained on the assumption that a Lossen rearrangement takes place (44).



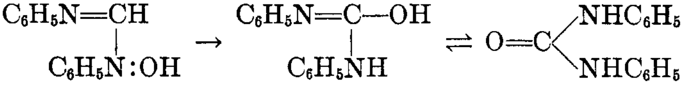
$$\begin{array}{l} \mathrm{HN{=}CH} \\ \mathrm{NH{:}OH} \end{array} \rightarrow \begin{array}{l} \mathrm{HN{=}C{-}OH} \\ \mathrm{NH_2} \end{array} \rightleftharpoons \mathrm{OC}\begin{array}{l} \mathrm{NH_2} \\ \mathrm{NH_2} \end{array}$$

N-Phenylimidoformyl-N-phenylhydroxylamine,



$$\begin{array}{l} \mathrm{C_6H_5N{=}CH} \\ \mathrm{C_6H_5N{:}OH} \end{array}$$

It has been found that this diphenyl derivative of formamidoxime gives a nearly quantitative yield of *N*,*N'*-diphenylurea when treated with acetic anhydride (3). The reactions involved as represented by the scheme,

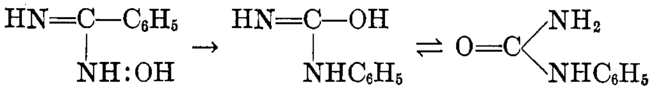


$$\begin{array}{l} \mathrm{C_6H_5N{=}CH} \\ \mathrm{C_6H_5N{:}OH} \end{array} \rightarrow \begin{array}{l} \mathrm{C_6H_5N{=}C{-}OH} \\ \mathrm{C_6H_5NH} \end{array} \rightleftharpoons \mathrm{O{=}C}\begin{array}{l} \mathrm{NHC_6H_5} \\ \mathrm{NHC_6H_5} \end{array}$$

may be said to consist in the intramolecular augmentation of a derivative of formic acid to a diphenyl aquo-ammonocarbonate with an hydroxylamine group functioning as augmenting agent.

Under the action of hot dilute sulfuric acid *N*-phenylimidoformyl-*N*-phenylhydroxylamine yields formic acid, aniline, and *p*-aminophenol instead of undergoing the Lossen rearrangement.

Benzamidoxime, $\mathrm{C_6H_5C(NH)NH{:}OH} \rightleftharpoons \mathrm{C_6H_5C(NH_2)N{:}OH}$. Neither when heated alone nor with acids or alkalies does this acid oxime undergo rearrangement. However Pinnow (53, 73) found that *N*-phenylurea is formed when a suspension, in chloroform, of an intimate mixture of benzamidoxime and sodium carbonate is treated with benzenesulfonyl chloride. The rearrangement, which may be represented as follows,

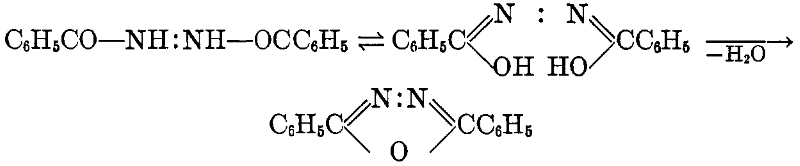


involves in effect the augmentation of a benzoic acid to a carbonic acid and the simultaneous reduction of hydroxylamine to ammonia and water.

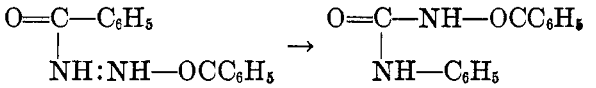
Acylhydrazides

As has already been noted, it is only occasionally that an alkyl or alkylidene derivative of hydrazine reacts in a manner interpretable as involving the nitridizing action of the hydrazine group. So with the decomposition of the acid derivatives of hydrazine, it is in a few cases only that hydrazine nitrogen undergoes reduction, thereby functioning as a nitridizing agent.

Symmetrical dibenzoylhydrazine, $C_6H_5CO-NH:NH-OCC_6H_5$. Gilbert (29) has shown that this compound, when heated for a time at 350°C., simply loses water



to form a cyclic dibenzoic hydrazide. When however the compound, in successive small portions, is suddenly subjected to a temperature of 450°C., good yields of aniline, phenyl cyanide, and carbon dioxide are obtained. The formation of these compounds may be explained by assuming that dibenzoylhydrazine undergoes rearrangement into *N*-phenyl-*N'*-benzoylurea



$$\begin{matrix} O{=}C{-}C_6H_5 \\ | \\ NH:NH{-}OCC_6H_5 \end{matrix} \rightarrow \begin{matrix} O{=}C{-}NH{-}OCC_6H_5 \\ | \\ NH{-}C_6H_5 \end{matrix}$$

and that this compound decomposes at high temperatures to yield the compounds named above.

Gilbert found also that *sym*-benzoyl-*p*-tolylhydrazine and benzoyl-*p*-chlorobenzoylhydrazine undergo decomposition in a manner resembling that of dibenzoylhydrazine.

REFERENCES

(1) ALLESSANDRI: R. A. L. [5] **23**, II, 348 (1914).
(1a) BAEYER AND VILLIGER: Ber. **34**, 443 (1901).
(2) BAMBERGER: Ber. **35**, 736 (1902).
(3) BAMBERGER AND DESTRAZ: Ber. **35**, 1876 (1902).

(4) Bamberger and Destraz: Ber. **35**, 1885 (1902).
(5) Bamberger and Renauld: Ber. **28**, 1683 (1895).
(6) Berg: Ann. chim. [7] **3**, 342 (1894).
(7) Berg: Ann. chim. [7] **3**, 343 (1894).
(8) Berg: Ann. chim. [7] **3**, 344 (1894).
(9) Berg: Bull. soc. chim. [3] **17**, 297 (1897).
(10) Biddle: Ann. **310**, 14 (1900).
(11) Brunner: Monatsh. **16**, 183, 849 (1895).
(12) Carlson: Ber. **40**, 4194 (1907).
(13) Carstangen and Ehrenberg: J. prakt. Chem. [2] **25**, 237 (1882).
(14) Chuck, Faw Yap: Thesis, Stanford University, 1925.
(15) Cross, Bevan, and Bacon: J. Chem. Soc. **97**, 2405 (1910).
(16) Curtius and Darapsky: J. prakt. Chem. [2] **63**, 428 (1901).
(17) Curtius and Ehrhart: Ber. **55**, 1559 (1922).
(18) Curtius and Hille: J. prakt. Chem. [2] **64**, 408 (1909).
(19) Delépine: Bull. soc. chim. [4] **9**, 1028 (1911).
(20) Dieckmann and Breest: Ber. **39**, 3052 (1906).
(21) Dimroth and Pfister: Ber. **43**, 2764 (1910).
(22) Dimroth and Pfister: Ber. **43**, 2765 (1910).
(23) Dunstan and Dymond: J. Chem. Soc. **65**, 206 (1894).
(24) Fernelius and Johnson: J. Chem. Education **7**, 1291, 1602, 1850 (1930).
(25) Fischer, E.: Ann. **236**, 116 (1886).
(26) Franklin: J. Am. Chem. Soc. **44**, 486 (1922).
(27) Franklin: J. Am. Chem. Soc. **46**, 2137 (1924).
(28) Franklin: The Nitrogen System of Compounds. The Chemical Catalog Co., New York (1934).
(29) Gilbert: J. Am. Chem. Soc. **49**, 286 (1927).
(30) Götzky: Ber. **64**, 1555 (1931).
(31) Graebe and Rostovzeff: Ber. **35**, 2751 (1902).
(32) Gürke: Ann. **205**, 290 (1880).
(33) Hantzsch: Ber. **27**, 1256 (1899).
(34) Hantzsch: Ber. **33**, 249 (1902).
(35) Hofmann: Ber. **15**, 407 (1882).
(36) Hoogewerff and van Dorp: Rec. trav. chim. **6**, 273 (1887); **8**, 173 (1889).
(37) Hoogewerff and van Dorp: Rec. trav. chim. **10**, 9 (1891).
(38) Houben and Schmidt: Ber. **46**, 3626 (1913).
(39) Kjellin: Ber. **30**, 1895 (1897).
(40) Lachman: J. Am. Chem. Soc. **43**, 2084 (1921).
(41) Lossen: Ann. **161**, 354 (1872).
(42) Lossen: Ann. **175**, 320 (1875).
(43) Lossen: Ann. **175**, 323 (1875).
(44) Lossen and Schifferdecker: Ann. **166**, 295 (1873).
(45) Marquis: Compt. rend. **143**, 464 (1906).
(46) Marquis: Compt. rend. **143**, 1163 (1906).
(47) Mohr: J. prakt. Chem. [2] **73**, 177, 228 (1906).
(48) Mohr: J. prakt. Chem. [2] **73**, 229 (1906).
(49) Nef: Ann. **280**, 303, 339 (1894).
(50) Nef: Ann. **309**, 175 (1899).
(51) Noyes, W. A.: Z. physik. Chem. **130**, 329 (1927).
(52) Pieschel: Ann. **175**, 305 (1875).

(53) PINNOW: Ber. **24**, 4171 (1891).
(54) RASCHIG: Schwefel- und Stickstoffstudien. Leipzig (1924).
(55) SCHISCHKOW: J. prakt. Chem. [1] **66**, 367 (1855); Ann. **101**, 213 (1857); Ann. Suppl. **1**, 112 (1861).
(56) SCHROETER: Ber. **42**, 2336, 2356 (1909).
(57) SCHROETER: Ber. **42**, 2339, 3356 (1909).
(58) SCHROETER: Ber. **44**, 1201 (1911).
(59) SCOTT AND MOTE: J. Am. Chem. Soc. **49**, 2545 (1927).
(60) SENIOR: J. Am. Chem. Soc. **38**, 2718 (1916).
(61) SLOSSON: Am. Chem. J. **29**, 303 (1903).
(62) STIEGLITZ: Am. Chem. J. **18**, 751 (1896).
(63) STIEGLITZ: Am. Chem. J. **29**, 67 (1903).
(64) STIEGLITZ: Proc. Nat. Acad. Sci. **1**, 202 (1915).
(65) STIEGLITZ: Proc. Nat. Acad. Sci. **1**, 2089 (1915).
(66) STIEGLITZ: Proc. Nat. Acad. Sci. **1**, 2094 (1915).
(67) STIEGLITZ AND BROWN: J. Am. Chem. Soc. **44**, 1274 (1922).
(68) STIEGLITZ AND LEECH: J. Am. Chem. Soc. **36**, 289 (1914).
(69) STIEGLITZ AND STAGNER: J. Am. Chem. Soc. **38**, 2065 (1916).
(70) STIEGLITZ AND VOSBURGH: Ber. **46**, 2151 (1913).
(71) STRAIN: J. Am. Chem. Soc. **49**, 1564 (1927).
(72) TIEMANN: Ber. **34**, 462 (1891).
(73) TIEMANN: Ber. **24**, 4164 (1891).
(74) VAN ERP: Ber. **29**, 474 (1896).
(75) VOSBURGH, ISABELLA: J. Am. Chem. Soc. **38**, 2081 (1916).
(76) WALDER: Ber. **19**, 1629, 3287 (1886).
(77) WIELAND: Ber. **44**, 2556 (1911).
(78) WIELAND AND MAIER: Ber. **64**, 1205 (1931).