PREPARATION AND PROPERTIES OF IMIDO INTERMEDIATES (IMIDOGENS)

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CONTENTS

I. INTRODUCTION, NOMENCLATURE, AND SCOPE

This review is concerned with the chemistry of species containing a monovalent nitrogen atom, *i.e.*, an electron-deficient nitrogen atom having a sextet of electrons in its outer shell, which are formed, or have been postulated, as intermediates in a large number of reactions. Such intermediates have the general formula R–N, where R may be hydrogen, a halogen, an alkyl, an aryl, an acyl, a sulfonyl, a phosphazyl, or an amino group, and are isoelectronic with the carbenes to which they bear a great resemblance. Also included in this review is a brief discussion of the isoelectronic protonated or divalent positively charged species $R-\overset{+}{N}-R'$, somewhat related to carbonium ions. In this sense the species R–N differ from the carbenes in that they can form a conjugate acid $R\overset{+}{N}H$ while still retaining an unshared pair of electrons. These species may theoretically either exist in the triplet diradical state $R-\underset{\cdot\cdot}{\dot{N}}\cdot$ or in the singlet state $R-\underset{\cdot\cdot}{\ddot{N}}$ in which the electron-deficient nitrogen would be highly electrophilic.

The problem of nomenclature for these intermediates has been a vexing one, and a variety of names are found and recommended by various authors in the literature: nitrenes (5, 35, 191, 289), azenes (72, 281, 290), azylenes (283), imine radicals (136, 254), azacarbenes (178), and others. The term "imene" is used in the German literature (141, 189). Nitrene has previously been used to designate azomethine-ylides (301), and compounds having this structure have recently been synthesized unambiguously (149). In any event, the ending "ene" is now reserved for olefins and aromatic hydrocarbons. The term used for NH by *Chemical Abstracts Index* is "Imidogen" and the species R–N will be referred to here as an imido intermediate or an imidogen, *e.g.*, Cl–N, chloroimido intermediate or chloroimidogen; CH_3–N, methylimido intermediate; C_6H_5–N, phenylimido intermediate; $C_6H_5SO_2N$, phenylsulfonylimido intermediate or benzenesulfonylimido intermediate. According to this system, the species R_2N-N will be called aminoimido intermediates instead of diazines (36) or diazenes (196), and $R-\overset{+}{N}-R'$ becomes the imidonium ion.

The parent compound, imidogen, is of great interest to the astrophysicist since NH has been observed to be a component of comet heads (156, 259, 306, 326), tails (155), and of the sun (116), and its spectral bands have been observed in the night sky spectrum (169, 180). It has been suggested (249) that some of the colors on Jupiter may be due to condensed reactive species such as $(NH)_n$, since the conditions in Jupiter's atmosphere may be similar to those which have been used in the laboratory to trap NH radicals at low temperatures. The work on the oxidation of hydrazines in liquid rocket fuel research has also stimulated a lot of interest in the chemistry of NH and its halogenated derivatives.

The formation of imido intermediates had been postulated by Stieglitz many years ago to account for the mechanisms of the Hofmann, Curtius, Lossen, and Beckmann rearrangements (242) as well as for a number of rearrangements involving compounds of the type $(C_6H_5)_3CNHX$ (215, 299, 324). The disproof of the intermediacy of a monovalent nitrogen derivative in the Beckmann rearrangement cast a simultaneous shadow on its postulated participation in other reactions. There is no doubt now that imido intermediates can be formed and detected both by physical and by chemical means. The recent great increase in interest in the preparation and properties of imido intermediates is undoubtedly tied in with the renaissance in carbene chemistry.

It is not proposed to discuss in detail the chemistry of the Hofmann, Curtius, Beckmann, and related rearrangements which has been reviewed adequately elsewhere (102, 275); only those points of mechanism concerning the formation, or otherwise, of imido intermediates in these reactions will be taken up. A brief review of some of the aspects of the chemistry of imido intermediates has appeared recently (141).

II. Preparation, Properties, and Evidence for the Formation of Imido Intermediates

A. IMIDOGEN AND DEUTERIOIMIDOGEN

The literature on the preparation and properties of NH is rather extensive. The intermediacy of NH in the Raschig hydrazine synthesis from chloramine and ammonia was suggested in 1924 (246). This rather controversial topic will be discussed a little further on.

The most commonly used method for the generation of imidogen is the decomposition of hydrazoic acid, a method analogous to the production of carbene from diazomethane. Nitrogen is liberated giving the very reactive NH intermediate. A variety of sources of energy have been used to effect the dissociation of HN_3. When gaseous hydrazoic acid was decomposed by the ultraviolet radiation from an aluminum spark, hydrogen, nitrogen, and ammonia were formed (40). Illumination of an aqueous sulfuric acid solution of hydrazoic acid with a mercury lamp gave rise to hydroxylamine and some ammonia (NH_2OH–NH_3 ratio = 100) (122). This reaction was formulated as

$$HN_3 + h\nu \rightarrow N_2 + [NH] \xrightarrow{H_2O} NH_2OH$$
$$2HN_3 \rightarrow NH_3 + N_2$$

Meyers and Beckman (205) proposed the following mechanism for the mercury-sensitized decomposition of hydrazoic acid.

$$\left.\begin{array}{r} h\nu + Hg \rightarrow Hg^* \\ Hg^* + HN_3 \rightarrow Hg + N_2 + NH \\ NH + HN_3 \rightarrow H_2 + 2N_2 \end{array}\right\}\text{ i}$$
$$\left.\begin{array}{r} NH + HN_3 \rightarrow N_2H_2 + N_2 \\ N_2H_2 + HN_3 \rightarrow 2N_2 + NH_3 \\ NH_3 + HN_3 \rightarrow NH_4N_3 \end{array}\right\}\text{ ii}$$

They estimated that of 100 molecules, 18 follow path i and the rest path ii above. A rather similar scheme was proposed for the decomposition of the metal azides (53). The bands of free NH were first detected spectroscopically by Eder (who did not assign them to this species) (105) and measured by Fowler and Gregory (116), and later again by Franck and Reichardt (118) and others. The detection of NH in the high intensity photolysis of hydrazoic acid in the gas phase was reviewed briefly by Thrush (310). The photolysis of hydrazoic acid in a solid frozen inert matrix (nitrogen, argon, or xenon) at low temperatures has been the subject of some important recent work (39, 318). In the most rigid of the three matrices, xenon, at 20°K., the infrared bands attributable to HN_3 gradually decrease in intensity upon ultraviolet irradiation, up to 40% of the azide undergoing decomposition. On warming the sample to 74°K., the infrared bands of the usual product, ammonium azide, appear. This is explained by assuming that NH is produced and stored in the rigid matrix at the low temperature. In solid nitrogen, in which diffusion of the reactive intermediates can occur more readily, different results were obtained (318). In the presence of water, a band at 1136 cm.$^{-1}$ was observed which was attributed to hydroxylamine.

$$\cdot\underset{\cdot\cdot}{\dot{N}}H + H_2O \rightarrow \cdot NH_2 + \cdot OH \rightarrow NH_2OH$$

(An alternative formulation might be $:\ddot{N}H + H_2O \rightarrow \overset{-}{N}H\text{–}\overset{+}{O}H_2 \rightarrow NH_2OH$.) In the absence of water, bands were observed in the infrared at 1290 and 1325 cm.$^{-1}$, and photolysis of DN_3 indicated that these bands were due to relatively pure hydrogen bending motions. Two possible reaction schemes were considered (among others which were rejected) which are shown in Scheme I. The authors favor the scheme

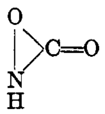
Scheme I

$$HN_3 + h\nu \rightarrow NH + N_2\ (DN_3 + h\nu \rightarrow ND + N_2)$$
$$\text{A}\qquad NH + HN_3 \rightarrow NH_2 + N_3$$
$$NH_2 + HN_3 \rightarrow NH_3 + N_3$$
$$\text{B}\qquad NH + HN_3 \rightarrow N_2H_2 + N_2$$
$$(\text{or } NH + NH \rightarrow N_2H_2)$$
$$N_2H_2 + HN_3 \rightarrow NH_3 + 2N_2$$
$$(\text{or } NH + N_2H_2 \rightarrow NH_3 + N_2)$$

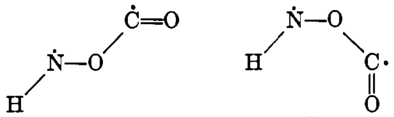
which involves the formation of diimide over that in which the NH_2 radical is produced (241), attributing the band at 1290 cm.$^{-1}$ to *trans*-NH=NH and that at 1325 cm.$^{-1}$ to *cis*-NH=NH. The disappearance of these two bands at 35°K. may be accounted for by the reaction of diimide with NH to give ammonia and nitrogen. A similar study of the photodecomposition products of HN_3 trapped in krypton and xenon at 4.2°K. and an examination of the electronic absorption spectrum apparently clearly demonstrate the presence of NH in considerable amounts and of NH_2 as a secondary reaction product (173). In this case, the photolysis was carried out using the full arc of a Xe high pressure lamp either (i) during the deposition of Kr or Xe onto HN_3, or (ii) after the hydrazoic acid had been deposited for 6 hr. in the dark. The amount of NH formed (the solid contained roughly 0.3% of NH) in case ii was not dependent on the rare gas used. If the solid matrix is not inert, or if it contains a reactive substance, then the imidogen initially formed may be trapped by reaction with this substance. For example, the photolysis of hydrazoic acid in solid nitrogen at 20°K. with oxygen present yields both *cis*- and *trans*-nitrous acid (30).

$$NH + O_2 \rightarrow HO{-}N{=}O \text{ (\textit{cis}- and \textit{trans}-)}$$

Photolysis of HN_3 and DN_3 in solid carbon dioxide at 20 and 53°K. gives rise to HNO and DNO, respectively (211). A 1:1 compound between NH and CO_2 was detected spectroscopically as being formed initially. Of the possible structures suggested for this transient compound, I and II seem the more likely,



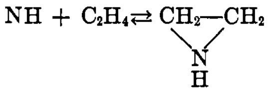
I



trans *cis*

II

since a straightforward route is available for their decomposition into HNO and CO. In the presence of ethylene and acetylene, imidogen, generated photochemically in a solid argon matrix at 4°K., gives ethyleneimine and what is probably keteneimine, respectively (164).



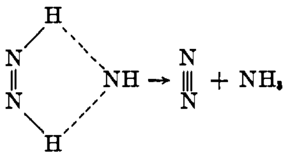
$$NH + C_2H_2 \rightarrow CH_2{=}C{=}NH$$

Possible mechanisms for these reactions are discussed.

A number of other methods have been employed to generate imidogen and deuterioimidogen from HN_3 and DN_3. Thermal decomposition (250, 254), decomposition of the vapor by means of an electrical discharge (84, 115, 193, 237, 328), electron impact (119, 120), attack by nonluminous active nitrogen (304), and explosive decomposition (312) have all been used. Much of this work involved the decomposition of hydrazoic acid at low pressure, followed by rapid freezing of the reaction products onto a liquid nitrogen-cooled surface, and the spectroscopic examination of the resulting solid. In this way, it was found (250, 251, 253) that if gaseous hydrazoic acid was decomposed thermally at 1000° and at a pressure of 0.05–0.2 mm., or photochemically, or by means of a silent electrical discharge, a paramagnetic deep blue solid condensed on the liquid nitrogen-cooled finger. This much discussed condensate, commonly referred to as Rice's Blue Material, turns colorless on warming, the transition temperature varying from −150° to −125° depending on the amount of deposit on the cold finger and being independent of the matrix material if one is used (84). The solid consists mainly of the colorless ammonium azide. It was initially suggested that the blue color could be due to a forbidden transition of NH, the restrictions being relaxed for the solid state. An over-all weight balance of the decomposition indicates the following stoichiometry (251): $6HN_3 \rightarrow 7N_2 + H_2 + (NH)_4$. The ultraviolet absorption spectrum of the material shows the characteristic absorption due to ammonium azide as well as bands at 3500 and 6500 Å. which disappear at the transition temperature. The former is attributed to NH. The latter, which gives rise to the blue color, has been attributed to various species (it has been generally accepted that the substance giving rise to the blue color is present only in very small amounts): diimide (251), the NH_2 radical (193, 198) [see, however, Rice and Ingalls (253) who failed to find any hydrazine in the warmed-up products, whereas Wannagat (328) was able to isolate 0.1% N_2H_4 as it hydrazoic acid salt], the species $HN{=}N\cdot$ (239), a species $\overset{-}{HN}{-}\overset{+}{NH}{=}NH$ whose structure is analogous to that of ozone (328), or a mechanism similar to an F center (121). On the basis of X-ray studies, it has also been described as a low-temperature glass to which it is not necessarily possible to ascribe a simple chemical formula (52). A mass spectroscopic study of the decomposition products which had been condensed at 77°K. showed the main products of decomposition to be H_2, N_2, NH_3, and unchanged HN_3 (120). Attempts to identify NH failed, indicating that it must be present in quantities too small (<1%) for it to be detected. At the blue → colorless transition point a small amount of N_2 was evolved, while the amount of ammonium azide remained almost unchanged. On the other hand, when the gaseous products from the silent discharge decomposition of HN_3 were analyzed mass spectroscopically, about 2% turned out to be diimide NH=NH (confirmed by using DN_3) (115). The failure to observe NH was attributed to the rapidity of the reaction forming diimide: $NH + HN_3 \rightarrow N_2H_2 + N_2 + 98$ kcal./mole (in the condensed phase one could visualize the process: $2NH \rightarrow N_2H_2$). The production of ammonia in this process may now be readily understood as

$$NH + N_2H_2 \rightarrow NH_3 + N_2$$

which, by analogy with the well-established stereochemistry of the reduction of olefins by diimide (92, 159), may be formulated as a three-center process (16). This might account for the small amount of



nitrogen liberated at the transition temperature. If ammonia was passed through the decomposition products of HN_3, the yield of hydrazine was raised 3–10-fold, whereas a 30-fold increase was observed when HN_3 and NH_3 were subjected to the electrical discharge together (328).

$$NH + NH_3 \rightarrow N_2H_4$$

In support of his suggested structure for the blue material, Papazian (239) reported that some strong bands of ammonium azide were not present in the product of photolysis of solid HN_3 at $-183°$ and did not appear until the transition temperature, when a "considerable" amount of nitrogen was evolved. A band at 2050 cm.$^{-1}$ was attributed to a salt of H_2N_4 and HN_3 (the former arising according to $H\underset{..}{N}{=}N{=}\ddot{N}: + \underset{..}{\dot{N}}H \rightarrow H\ddot{N}{=}\ddot{N}{-}\ddot{N}{=}\ddot{N}H$, and the diiminohydrazine dissociating to the proposed radical $H_2N_4 \rightleftarrows HN{=}N\cdot$). The absence of certain infrared bands due to NH_4N_3 at the low temperature might also be due to differences in crystal structures at these temperatures. The blue material gives a single asymmetric electron spin resonance line at $g = 2.003 \pm 0.002$, which disappears at the transition temperature (121). The resonance line from the thermal decomposition condensation products is broader (36 gauss) than those from the photochemical and electrical discharge condensation products (11.5 gauss). Though an F-center mechanism is a possibility, the species $HN{=}N\cdot$ and $NH{=}\overset{+}{N}H{-}\overset{-}{N}H \leftrightarrow \dot{N}H{-}NH{-}\dot{N}H$ would also be paramagnetic. That the color of Rice's Blue Material is probably due to a polymeric form of NH is supported by the observation that it is also formed when solid chloramine is subjected to ultraviolet irradiation at $-190°$ (166): $NH_2Cl + h\nu \rightarrow NH + HCl$. The formation of diiminohydrazine is ruled out as a possibility here. The exact cause of the blue color still remains to be established. NH and ND have been formed in moderately large concentrations and trapped in argon, krypton, and xenon matrices at 4.2°K. and identified spectroscopically (198).

The formation of NH from starting materials other than hydrazoic acid has often been suggested or assumed, but has only been definitely established in a few cases. The existence of free NH formed by the high temperature (2000°) pyrolysis of ammonia was shown spectroscopically (118). The flash photolysis of ammonia also leads to imidogen, which was detected both spectroscopically and by its reaction with ammonia to form hydrazine (127).

$$NH_3 \xrightarrow[\text{or } h\nu]{2000°} NH + H_2 \text{ (or } NH + 2H)$$

A study of the kinetics and isotope effects in the ammonia synthesis on a moderately well-reduced surface indicates that the rate-determining step is the chemisorption of nitrogen on a surface mainly covered with NH radicals (233).

$$N_2(\text{gas}) \rightarrow N{=}N(\text{adsorbed}) \rightarrow NH{-}NH \rightarrow (NH)_a + (NH)_a$$

$$\left.\begin{array}{r} N_2 \rightarrow 2N_a \\ (NH)_a + H_2 \rightleftarrows NH_3 \end{array}\right\} \text{rate-determining}$$

NH is also formed by passing an electric discharge through ammonia (198). The thermal (100), flash photolytic (243), and electrical discharge (198) decompositions of hydrazine are also reported to give rise to some imidogen. The thermal decomposition is said to produce NH in the following way (100).

$$N_2H_4 + M \xrightarrow{k_1} N_2H_4^*$$

$$N_2H_4^* \xrightarrow{k_2} 2NH_2$$

$$NH_2 + NH_2 \xrightarrow{k_3} NH_3 + NH$$

Though NH is considered the likeliest intermediate at the high temperature, it has not been unequivocably identified.

The formation of NH has been postulated in the reaction of active nitrogen with a number of inorganic substances. It was initially suggested that it was an intermediate in the synthesis of ammonia from active nitrogen and atomic hydrogen (188, 302); kinetic data support the postulated formation of NH, the rate constant for the reaction of nitrogen atoms with hydrogen atoms being $k = 4.87 \pm 0.8 \times 10^{14}$ ml.^{2} mole^{-2} sec.$^{-1}$ over the range of pressures from 2.5 to 4.5 mm. in an unheated reaction tube poisoned with phosphoric acid (195). A spectroscopic study of the reaction confirms the formation of NH (129, 194, 238). The reaction of active nitrogen with HBr and HI gives imidogen as an intermediate (104, 109, 212) which then reacts further with HBr to give ammonium bromide, bromine, and a trace of NH_2Br and $NHBr_2$.

$$N + HBr \rightarrow [H\text{-}Br\text{-}N]$$

$$[H\text{-}Br\text{-}N] \rightarrow NH + Br$$

$$NH + HBr \rightarrow NH_2 + Br$$
$$NH_2 + HBr \rightarrow NH_3 + Br$$

The reaction of active nitrogen with phosphine gives hydrogen and the α-form of polymeric PN *via* NH (206).

$$PH_3 + N \rightarrow NH + PH_2$$
$$PH_2 + N \rightarrow PN + H_2$$

Wolfhard and Parker (338) have studied the ammonia–oxygen diffusion flame and have shown that NH is an important reactant. NH has been studied spectroscopically in the diffusion flames of NH_3–HNO_3 and NH_3–NO_2 (111), and has been observed when cyanogen is burned with wet oxygen (235). In the latter case, the following reaction is assumed: $CN^* + OH \rightarrow NH^* + CO$. The reaction of difluoramine with hydriodic acid is said to involve the formation of NH as an intermediate (234).

$$NF_2H + 2HI \rightarrow I_2 + 2HF + NH$$
$$NH + 2HI \rightarrow I_2 + NH_3$$

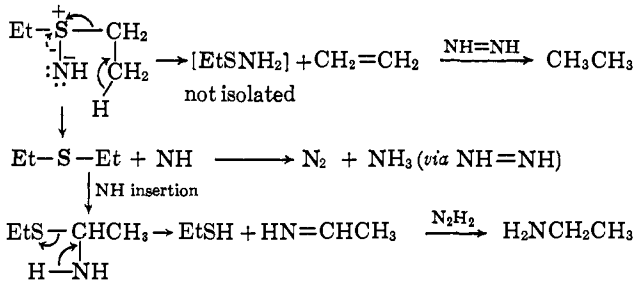
The formation of NH_2 in moderate concentration from low-pressure discharges containing hydrogen and nitrogen in many forms indicates that it is easily built up from smaller fragments, a fact which may be important in the explanation of the origin of these radicals in comets. Since the pressure in a comet tail is 10^{-12} mm., the three-body process $N + H + M \rightarrow NH + M$ followed by $NH + H + M \rightarrow NH_2 + M$ is considered (257) much less likely than

$$N + MH \rightarrow NH + M$$
$$NH + MH \rightarrow NH_2 + M$$

The formation of NH has been postulated to explain the nature of the products from the thermal decomposition of aliphatic sulfimines (18).

$$(C_2H_5)_2S{=}NH \rightarrow (C_2H_5)_2S + NH_3 + N_2 + C_2H_5SH + C_2H_5NH_2 + C_2H_6 + CH_2{=}CH_2$$

It is suggested that these are formed in the following way.



Imidogen may possibly be formed in the decomposition of compounds $R_3\overset{+}{N}\text{–}\overset{-}{N}H$ (14).

Differences of opinion exist as to whether NH is an intermediate in the various and interesting reactions of chloramine and hydroxylamine-O-sulfonic acid. Raschig (246) suggested that, in the synthesis of hydrazine from hypochlorite and ammonia, NH was produced from chloramine and attacked ammonia to give N_2H_4. It was proposed (26, 27) that $NHCl^-$ was formed initially and that this could either give NH (this would be the equivalent of the well-known base-initiated α-eliminations undergone by alkyl halides to give carbenes) or, alternatively, attack ammonia directly in an SN2-type process

$$OH^- + NH_2Cl \rightarrow NHCl^-$$
$$NHCl^- \rightarrow NH + Cl^-$$
$$NH + NH_3 \rightarrow N_2H_4$$

or

$$NHCl^- + NH_3 \rightarrow N_2H_4 + Cl^-$$

In support of this, Jander (165) found that the yield of hydrazine in the reaction of chloramine with liquid ammonia increased when potassium amide was added. On the other hand, since the formation of hydrazine from chloramine in aqueous ammonia solution is first order in either reagent at pH 11, Bodenstein (51) suggested a direct SN2 mechanism

$$NH_3 + NH_2Cl \xrightarrow{\text{slow}} N_2H_5^+ + Cl^- \xrightarrow{OH^-} N_2H_4 + Cl^- + H_2O$$

and this was in accord with the effect of concentration changes upon the yield of hydrazine (77). The kinetics of the formation of hydrazine from chloramine in liquid ammonia agree with the SN2 mechanism (89). Whereas chloramine will undergo nucleophilic substitution by primary and secondary amines in anhydrous ether solution (220), it will not react with ammonia in the same solvent (273, 335). The electrical conductances of solutions of chloramine in liquid ammonia are very low, making the process $NH_2Cl + NH_3 \rightarrow NH_4^+ + NHCl^-$ seem rather doubtful (88); but the conductivity of NH_2Br in liquid NH_3 (168) and of bromamine in ether saturated with ammonia (113, 167) shows that dissociation can take place. That NH can be formed from NH_2Cl is demonstrated by the fact that photolysis of solid chloramine at −190° gives Rice's Blue Material and that hydrogen cyanate is formed during the thermal decomposition (500°) of gaseous chloramine in the presence of carbon monoxide (166). Taken in

$$NH_2Cl + h\nu \rightarrow NH + HCl$$
$$NH + CO \rightarrow HCNO$$

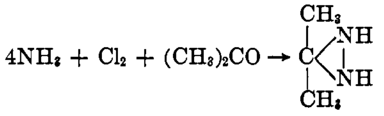
conjunction with the observation (329) that imidogen and ammonia react to form hydrazine, this shows that, should imidogen actually be formed under the conditions of the Raschig synthesis, it could indeed react to form hydrazine. According to a more recent kinetic investigation (340), the reaction between chloramine and ammonia in strong base is first order in both reactants, and as it is base independent up to about pH 14, the Bodenstein SN2 mechanism seems the most plausible one. At higher alkalinities a base-catalyzed path becomes apparent and the following mechanism is suggested.

$$OH^- + NH_2Cl \rightleftharpoons NHCl^- + H_2O \quad \text{(pre-equilibrium)}$$

$$NH_3 + NHCl^- \xrightarrow{\text{slow}} N_2H_4 + Cl^-$$

A fast pre-equilibrium $NHCl^- \rightleftharpoons NH + Cl^-$ with a slow $NH + NH_3$ reaction was excluded, since Cl^- had no retarding effect on the reaction rate. A slow decomposition step $NHCl^- \rightarrow NH + Cl^-$ is eliminated by the first-order dependence of the rate upon the ammonia concentration.

The balance of the evidence favors the SN2 mechanism for the chloramine reactions rather than the formation of free NH. This applies as well to the recent interesting applications of the use of chloramine in the synthesis of a variety of heterocyclic compounds, *e.g.*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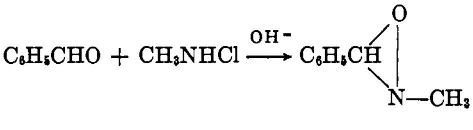
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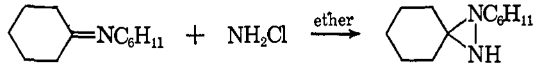
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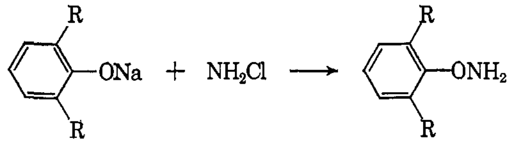
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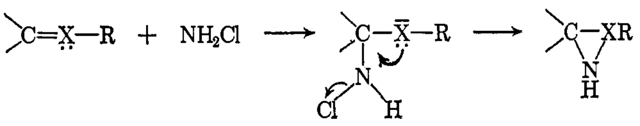
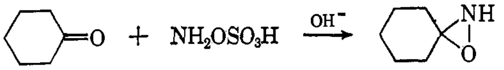
These are best regarded as nucleophilic addition or substitution reactions



and the rate of product formation depends markedly upon the nature of the substrate, which would not be expected if NH were being formed in the rate-determining step (264). A few reactions of chloramine, such as its alkaline decomposition which gives rise to some nitrogen and hydrogen (246), are perhaps best understood if a mechanism involving the formation of an NH intermediate followed by the formation of diimide is postulated.

A somewhat similar situation exists with the reactions of hydroxylamine-O-sulfonic acid, a reagent which has found much use in recent years in effecting a variety of "iminations." A few examples are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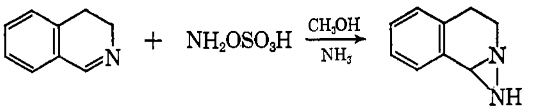
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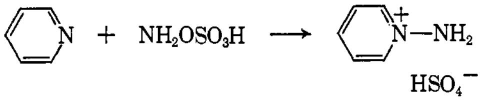
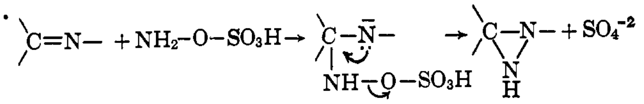
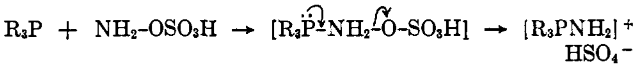

(126)

$$C_6H_5\text{—}OK + NH_2OSO_3H \rightarrow C_6H_5\text{—}ONH_2 \quad (68)$$

These reactions most probably involve attack by the undissociated NH_2OSO_3H, *e.g.*

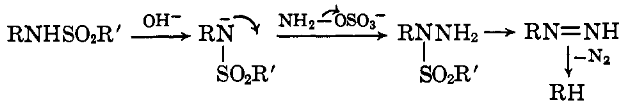


Thus, in the imination of the phosphines R_3P, the absence of N_2 evolution, even on addition of sodium ethoxide, is best explained on the basis of an SN2 mechanism (19).



$$R_3P + NH_2\text{-}OSO_3H \rightarrow [R_3P\text{-}NH_2\text{-}O\text{-}SO_3H] \rightarrow \underset{HSO_4^-}{[R_3PNH_2]^+}$$

Similarly, the rate of reaction of hydroxylamine-O-sulfonic acid in 0.5 *N* sodium hydroxide at 25° with various nucleophiles depends appreciably upon the nature of the nucleophile, which would not be the case if NH were formed in the rate-determining step (264). The deamination of aliphatic amines by the reaction of a sulfonamide derivative of the amine with hydroxylamine-O-sulfonic acid in alkaline medium is said to involve the formation of an N-N bond with NH (219). This sequence may also be formulated as a concerted attack upon NH_2OSO_3H and elimination of sulfonate ion.



$$RNHSO_2R' \xrightarrow{OH^-} \underset{SO_2R'}{R\bar{N}} \xrightarrow{NH_2\text{-}OSO_3^-} \underset{SO_2R'}{RNNH_2} \rightarrow \underset{RH}{\underset{\downarrow -N_2}{RN{=}NH}}$$

On the other hand, a number of reactions involving hydroxylamine-O-sulfonic acid are best accounted for by postulating the formation of NH as an intermediate. Thus, benzene and other aromatic compounds including pyridine have been aminated with hydroxylamine-O-sulfonic acid in the presence of aluminum chloride (170, 171). It was suggested that NH, or

$$C_6H_5CH_3 + NH_2OSO_3H \xrightarrow{AlCl_3} CH_3C_6H_4NH_2$$

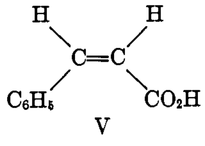
perhaps NH_2^+, was the active aminating species. When hydroxylamine-O-sulfonic acid was treated with sodium methoxide in methanol saturated with butadiene, some pyrroline (III) was obtained (15).

$$NH_2OSO_3^- \xrightarrow{OCH_3^-} NH + SO_4^{-2} + CH_3OH$$

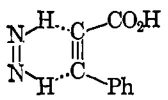
III

The very interesting use of hydroxylamine-O-sulfonic acid in alkaline solution as a hydrogenating agent (16) must also be mentioned in this context. Thus, fumaric acid gives succinic acid, ethylene gives ethane, and cyclohexene yields cyclohexane, each in 30–40% yields. The formation of *cis*- (V), but no *trans*-cinnamic acid from propiolic acid is strong evidence in favor of the formation of diimide as the active reducing agent (92, 159).

$$\underset{\text{IV}}{C_6H_5C{\equiv}CCO_2H} \xrightarrow[\text{NaOH}]{2NH_2OSO_3H} C_6H_5CH_2CH_2CO_2H +$$



V



The alkaline decomposition of hydroxylamine-O-sulfonic acid gives much more N_2 than H_2 (unlike the oxidation of hydrazine to give diimide which, in the absence of an olefin, gives equimolar quantities of N_2 and H_2). The decreased amount of H_2 is attributed to the reaction $N_2H_2 + NH \rightarrow N_2 + NH_3$ in the hydroxylamine-O-sulfonic acid decomposition, a pathway not available in the oxidation of hydrazine (16). The ease of dimerization of NH, as compared with methylene which shows little inclination to dimerize, is explained by the increase in bonding energy on going from an N–N single bond to N=N. The reaction of hydroxylamine-O-sulfonic acid with thioethers in the presence of sodium methoxide to form sulfimines (18) may also involve the intermediacy of free NH since much N_2 and NH_3 is evolved.

$$R_2S + NH_2OSO_3H + 2NaOCH_3 \rightarrow R_2S{=}NH + Na_2SO_4 + 2CH_3OH$$

B. HALOGENATED IMIDO INTERMEDIATES XN

The fluoro, chloro, and bromo derivatives have been prepared by the photolysis of the corresponding azide in solid argon or nitrogen (molar ratio 1:100–400) at 4.2 and 20°K. and their appearance observed spectroscopically (207, 210).

$$X{-}N_3 + h\nu \xrightarrow[\text{Ar}]{4.2°\text{K.}} X{-}N + N_2 \ (X = \text{F, Cl, or Br})$$

The azides were prepared by passing an Ar:X_2 mixture (X = Cl, Br) through dry NaN_3 (210, 298); for the preparation of FN_3 a dilute gaseous mixture of F_2 in Ar (1:200) was treated with gaseous HN_3 (210). A green phosphorescence, observed after the ultraviolet light was extinguished, in the irradiation of ClN_3 at 4.2°K., and which reappeared on warming near 20°K., was initially attributed to the formation or decomposition of N_2Cl_2 (207). It is now thought that the green phosphorescence is due to N atoms trapped in the matrix at 4.2°K., and that a blue-green chemiluminescence, observed on warm-up, is independent of the nature of the halogen in XN_3 and is, therefore, not contributed by a halogen-containing species (210).

It has been reported that NF is also formed on evaporation of FN_3 and dimerizes to a mixture of *cis*- and *trans*-difluorodiazine (132)

$$FN_3 \rightarrow N_2 + FN \rightarrow F{-}N{=}N{-}F$$

The intermediacy of NF in the reactions of difluoramine with primary and secondary amines has been postulated to explain the observed deaminations and the nature of other products obtained (70)

$$R_2NH + HNF_2 \rightarrow [R_2\overset{+}{N}H_2NF_2^-] \rightarrow R_2\overset{+}{N}H_2F^- + NF$$

Its formation from the electronically excited difluoramino free radical has also been suggested (69).

$$N_2F_4 \rightleftharpoons 2F_2N\cdot \xrightarrow{h\nu} F_2N\cdot^* \rightarrow F\cdot + NF \rightarrow N_2F_2$$

The orange flame observed when active nitrogen reacts with bromine or with HBr (bromine is formed in this case) has been attributed to NBr, and this has been confirmed spectroscopically (107, 210, 212, 213).

$$N + Br_2 \rightarrow NBr + Br$$
$$N + NBr \rightarrow N_2 + Br$$

C. ALKYL AND ARYL IMIDO INTERMEDIATES RN

1. *From Alkyl and Aryl Azides*

The thermal decomposition of methyl azide was first studied by Ramsperger (244) who found it to be a homogeneous first-order reaction but did not determine the nature of the products formed. An analysis of the products resulting from the high-conversion decomposition at 200–240° and 0.8–46.6 cm. pressure showed the presence of hexamethylenetetramine, hydrazoic acid, ethylene, ethane, and nitrogen (184).

$$CH_3N_3 \rightarrow N_2 + CH_3N$$
$$CH_3N \rightarrow CH_2{=}NH$$
$$6CH_2{=}NH \rightarrow (CH_2)_6N_4 + 2NH_3$$
$$CH_2{=}NH \rightarrow C_2H_6 + N_2$$
$$CH_3N_3 \rightarrow CH_2 + HN_3$$
$$2CH_2 \rightarrow C_2H_4$$

The methylimido intermediate formed underwent a rapid 1,2-hydrogen shift to give methyleneimine. An attempt to stabilize the CH_3N or other active species by freezing the products of the thermal decomposition of CH_3N_3 (1.00 mole) in a high-speed flow system resulted in the detection of nitrogen (0.98 mole), hydrogen (0.25 mole), methane (trace), ammonia (0.30 mole), HCN (0.25 mole), and polymeric material (0.15 mole) (252). The following mechanism was proposed.

$$CH_3N_3 \rightarrow CH_3N + N_2$$
$$0.25CH_3N \rightarrow 0.25HCN + 0.25H_2$$
$$0.75CH_3N \rightarrow 0.3NH_3 + 0.15C_5N_3H_9$$

The polymeric material was thought to arise either from CH_3N or from $CH_2{=}NH$ which polymerized in the presence of CH_3N. The dissociation of methyl azide by electron impact has been examined (119). A spectroscopic study of the products of photolysis of methyl azide and methyl azide-d_3 at high dilution in solid argon (4.2°K.) and carbon dioxide (50°K.) matrices indicated the formation of methyleneimine and methyleneimine-d_3, respectively, presumably from the intermediates CH_3N and CD_3N (208). Prolonged photolysis in an Ar matrix at 4°K. produces HNC by the photolytic decomposition of the initially formed $CH_2{=}NH$ (209).

$$CH_3N_3 + h\nu \xrightarrow{4°K.} N_2 + CH_3N \rightarrow CH_2{=}NH \xrightarrow{h\nu} \overset{-}{C}{\equiv}\overset{+}{N}{-}H$$

The photolysis of methyl azide has been investigated in the vapor phase *at low conversions* and various ranges of pressure, temperature, intensity, and wave length (94). The principal gaseous product was N_2 with small amounts of H_2 (5–11%) and traces of CH_4, C_2H_4, and C_2H_6. A condensate, identified as $(CH_3N)_x$, was also found. Experiments with added CO_2, $CH_3N{=}NCH_3$, and C_2H_4 indicated the presence of a short chain carried mainly by the CH_3N radical. The heavy product contained 3% of $(CH_2)_6N_4$ and much larger amounts of other N-containing compounds. The only important *primary* act is thought to be $CH_3N_3 + h\nu \rightarrow CH_3N + N_2$. Possible secondary reactions suggested include

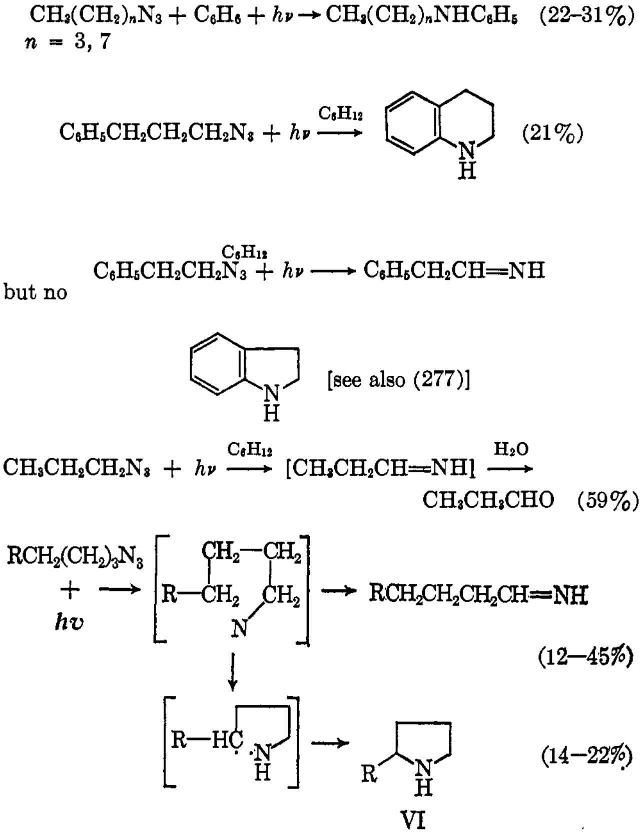
$$CH_3N + CH_3N_3 \rightarrow (CH_3N)_2 + N_2$$
$$CH_3N + (CH_3N)_2 \rightarrow (CH_3N)_3$$

and

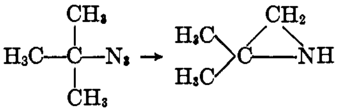
$$CH_3N^* \rightarrow H_2 + HCN$$

Early work on the acid, base, and thermal decomposition of alkyl and aryl azides has been surveyed (55). More recently, a study of the photolysis (the type of lamp used in the photolyses may be of importance) of more complex azides, usually in cyclohexane or other solvents, led to the conclusion that "activated" imido intermediates are formed which can stabilize themselves in three ways: (i) isomerization to the imine, (ii) hydrogen abstraction from the solvent to give amine, and (iii) 1,5-hydrogen abstraction followed by cyclization to pyrrolidines (35). To these must be added the ability to undergo insertion into C–H bonds and addition to olefinic double bonds. These reactions parallel those undergone by carbenes. Dimerization to the azo compound has been suggested in a few instances (258, 341), and aromatic substitution has been shown to take place (35, 175, 285) (see Scheme II). The thermal decomposition of *n*-octyl azide in *n*-hexadecane at 230° gave *n*-octanal imine (32%) but no detectable amount of the pyrrolidine (VI), whereas photolysis resulted in a 35% yield of VI (R = $CH_3(CH_2)_3$) (35). Conceivably, the imido intermediates produced under these different conditions are in different electronic states, *e.g.*, singlet state from the thermal, and triplet from the photochemical decompositions. Photolysis of cyclohexyl azide gave a mixture of cyclohexanone imine and cyclohexylamine (hydrogen abstraction from solvent), while *t*-butyl azide (VII) gave 1,1-dimethylethyleneimine (VIII) (35).

SCHEME II

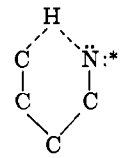


$$CH_3(CH_2)_nN_3 + C_6H_6 + h\nu \rightarrow CH_3(CH_2)_nNHC_6H_5 \quad (22\text{–}31\%)$$
$$n = 3, 7$$

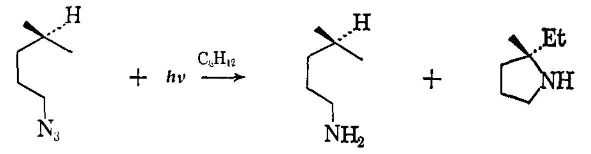


VII VIII

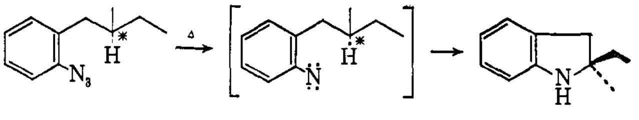
Numerous other examples are reported (35). It has been suggested that an important conformational requirement has to be met if cyclization of the activated imido intermediate is to proceed smoothly, namely, that a "six-membered" transition state (IX) be attainable, either by the preferred conformation of the starting material or by a conformation which is readily populated as a result of thermal equilibrium. This may explain the aromatic substitution leading to the formation of 1,2,3,4-tetrahydroquinoline and not of indoline, in the examples previously given. The question as to whether cyclization to give pyrrolidines involved a bond-insertion mechanism or a hydrogen-abstraction pathway, followed by radical dimerization, was considered in a study of the stereochemical course of the photolysis of (+)-4-methylhexyl azide (X) in cyclohexane (35); (+)-4-methylcyclohexylamine (XI) (35%) and racemic 2-ethyl-2-methylpyrrolidine (XII) (16%) were said to have been obtained, presumably excluding a bond-insertion mechanism in which retention of stereochemistry is implied. A number of attempts to repeat this work, however, have been unsuccessful (288). In fact, that insertion by an imido intermediate into an aliphatic C–H bond can actually take place has been shown by the fact that pyrolysis of (+)-1-azido-2-(2-methylbutyl)benzene (XIII) in the vapor phase and in diphenyl ether solution resulted in the formation of optically active 2-ethyl-2-methylindoline (XV) in yields of 50 and 43%, respectively (288). An imido intermediate (XIV) in the singlet state is probably involved here. Photolysis or pyrolysis of 6β-azidocholestane gave 6-iminocholestane and other unidentified nitrogenous products, the properties of one of which suggested that it was an aza-*B*-homocholestene. No product of insertion into the angular C-10–CH_3 was reported (183).



IX

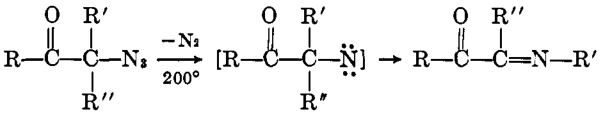


X XI XII



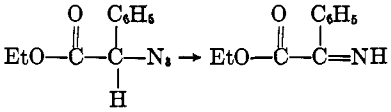
XIII, $[\alpha]_D$ +11.3° XIV XV, $[\alpha]_D$ −9.6°

The pyrolysis of α-azidocarbonyl compounds has been studied by Boyer and Straw (59–61). The general reaction observed is

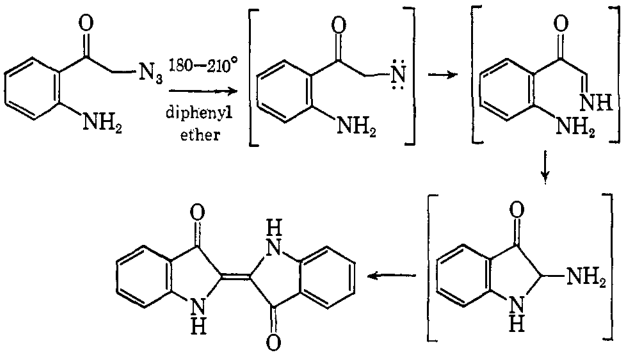


$$R-\overset{O}{\overset{\|}{C}}-\underset{R''}{\overset{R'}{C}}-N_3 \xrightarrow[200°]{-N_2} [R-\overset{O}{\overset{\|}{C}}-\underset{R''}{\overset{R'}{C}}-\ddot{N}] \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{R''}{C}=N-R'$$

When R′ = H and R″ = CH_3 or C_6H_5, H migrates exclusively, whereas if R′ = C_6H_5 and R″ = CH_3, then C_6H_5 migrates preferentially. In no case does R migrate, not even when it is OC_2H_5. Both the temperatures required to effect decomposition and the observed migratory aptitudes seem to rule out a concerted process in the elimination and 1,2-shift and speak for the intervention of an imido intermediate. Pyrolysis of *o*-aminophenacyl azide gave indigo in excellent yield.



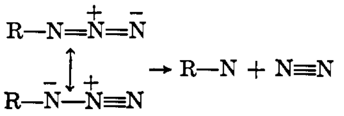
$$EtO-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{C_6H_5}{C}}-N_3 \rightarrow EtO-\overset{O}{\overset{\|}{C}}-\overset{C_6H_5}{C}=NH$$



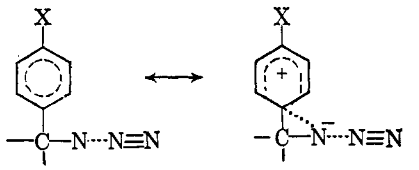
When triarylmethyl azides are heated at 170–190°, aryl-group migration takes place and benzophenone anils are obtained (272). It was suggested that a

$$Ar_3CN_3 \xrightarrow{\Delta} Ar_3C-N \rightarrow Ar_2C=N-Ar$$

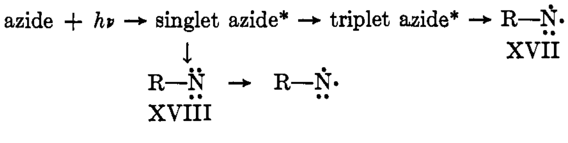
monovalent nitrogen intermediate was first formed. The effect of substituents in the aryl radicals upon the migrating aptitudes and the rates of decomposition of *p*-$XC_6H_4(C_6H_5)_2CN_3$ (XVI) was examined systematically by Saunders and Ware (263). The migratory aptitudes were found to be relatively insensitive to the nature of the aryl group—*p*-anisyl, for example, migrates only 2.5 times faster than phenyl, while *p*-nitrophenyl only 0.20 times as fast as phenyl—as were the first-order rate constants in Dibutyl Carbitol solution. An isokinetic relationship between energies and entropies of activation was found to hold, the isokinetic temperature being 188°. If the substituents exerted a simple inductive effect on the rate of nitrogen loss, one might expect the rates to follow the Hammett equation, whereas all substituted azides reacted faster than did trityl azide itself. Similarly, the variation of rate with solvent, though small, is in the direction of greater speed in the more polar solvents, which is contrary to what would have been expected if a dispersal of charge was accompanying the formation of the transition state



On this basis, Saunders and Ware suggest participation by the migrating group in the elimination of nitrogen, *i.e.*, a discrete imido intermediate is not formed. The effect of substituents upon relative rates and migratory aptitudes indicates that aryl participation, if it occurs at all, must only do so to a very small extent, particularly in the case of, say, the *p*-nitrophenyl derivative, so that one might expect a range of mechanisms with the formation of the imido intermediate as a limiting one. If one applies the treatment used by Smith and Hall (281) in a study of the decomposition of aryl azides in which a similar situation arises, and considers only the effect of substituents on ΔH^*, it is clear that in the present case the inductive order is followed and the postulation of a discrete imido intermediate is possible. The observed solvent effect is not readily explained on this basis, however. A study of the effects of *meta* substituents would be valuable since these would not be expected to facilitate or retard aryl participation.

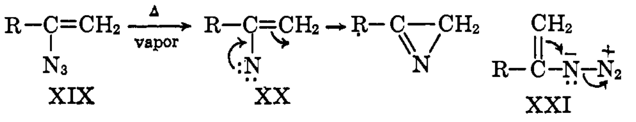


Irradiation of triarylmethyl azides in hexane solution at room temperature by a low-pressure mercury-vapor lamp gives the same results, qualitatively, as the thermal decomposition (261, 262). The substituent X in XVI has little, if any, effect upon migratory aptitudes in the photochemical reaction. Thermal and photochemical reactions of 1,1-diphenylethyl and 2-phenyl-2-propyl azides show similar, but not entirely regular, behavior (Ph/Me migration aptitudes 2.4–4.0 for thermal and 2.2–1.0 for photochemical processes). It is suggested that the photochemical reaction involves a discrete imido intermediate.

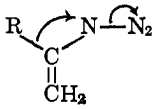


The formation of the triplet imido intermediate (XVII) is thought to be more likely in photochemical rearrangements (262). The lack of marked selectivity in the migrations would then be rationalized since a free radical would not show much preference for one substituted phenyl group over another. If it is supposed that an imido intermediate could also be involved in the thermal decompositions, then one would assume it to be in the singlet state (XVIII) when, as a highly reactive electrophilic species, it might be expected to show the slight but definite discrimination which is observed.

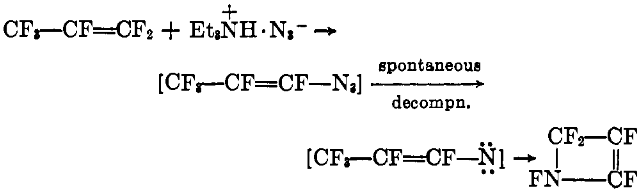
If the azido group is attached to an olefinic double bond, as in α-azidostyrene (XIX, R = C_6H_5) and 2-azido-1-hexene, vapor phase pyrolysis leads to the formation of azacyclopropenes (291, 293).

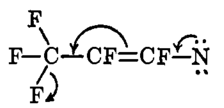


Products such as $RN{=}C{=}CH_2$, by analogy with the Curtius rearrangement

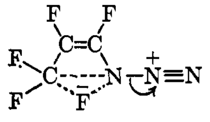


account for no more than 5–6% of the pyrolysate. Though the imido intermediate (XX) mechanism has not been completely established, the similarity with cyclopropene formation from alkenylcarbenes (86) makes it likelier than the alternative concerted process (XXI). A similar addition of an imido intermediate to an olefinic double bond, but leading to indole formation, was also reported independently (5); more recently, the addition of an imido intermediate to an olefinic double bond to give a pyrazoline ring system has been achieved (67). A reaction sequence which, on the surface, looks similar to those described above has been stated to involve an imido intermediate (178).



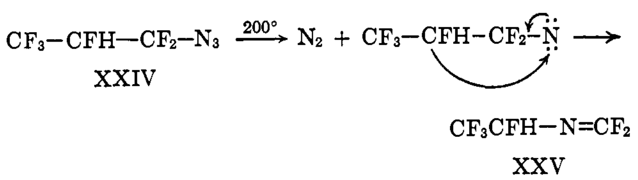


XXII



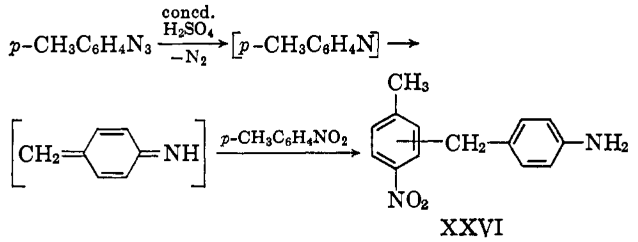
XXIII

This process is said to be the result of conjugation of the bonds (XXII) in the imido intermediate like that in the allylic rearrangement. It seems most unlikely that a discrete imido intermediate is actually formed in view of the extremely mild conditions under which the azide decomposes, conditions which would indicate a high degree of participation in the elimination of nitrogen. A transition state such as XXIII might account for the observations. On the other hand, an imido intermediate is indicated and has been postulated (179) in the thermal rearrangement of XXIV to XXV, a process bearing a resemblance to the Curtius rearrangement (see section IID).


$$CF_3{-}CFH{-}CF_2{-}N_3 \xrightarrow{200^\circ} N_2 + CF_3{-}CFH{-}CF_2{-}\ddot{N}: \longrightarrow CF_3CFH{-}N{=}CF_2$$

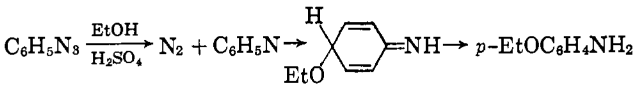
XXIV XXV

Turning to the aromatic azides, the thermal decomposition of phenyl azide in benzene and *p*-xylene was first studied by Bertho (42). When benzene and phenyl azide were heated at 150–160°, the main product formed was azobenzene, together with a small amount of aniline. With *p*-xylene, a much larger amount of aniline was obtained (hydrogen abstractions from the side chain), as well as 1,2-di-*p*-tolylethane and a small amount of azobenzene. No *p*-xylylphenylamines were formed. The decomposition of *p*-tolyl azide in concentrated sulfuric acid in the presence of *p*-nitrotoluene gave diphenylmethane derivatives (XXVI) whose formation was formulated (32) as


$$p\text{-}CH_3C_6H_4N_3 \xrightarrow[-N_2]{\text{concd. } H_2SO_4} [p\text{-}CH_3C_6H_4N] \longrightarrow$$

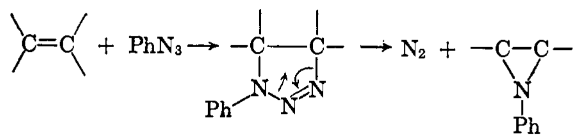
XXVI

The decomposition of phenyl azide in ethanolic sulfuric acid at 100° for 25 hr. was found to give 4-aminodiphenylamine and *o*- and *p*-phenetidine (32). The latter, for example, was thought to arise as

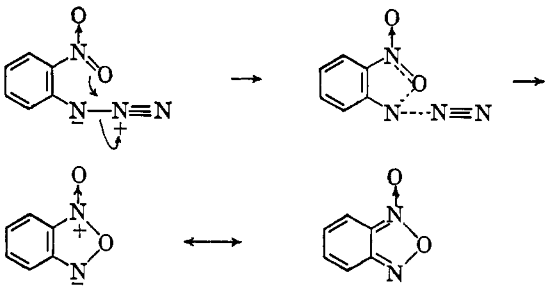

$$C_6H_5N_3 \xrightarrow[H_2SO_4]{EtOH} N_2 + C_6H_5N \rightarrow \cdots{=}NH \rightarrow p\text{-}EtOC_6H_4NH_2$$

These mechanisms are unlikely and more probably either involve the formation of a protonated imido derivative $C_6H_5\overset{+}{N}H$ or a concerted attack by the nucleophile and elimination of nitrogen. This will be discussed later in the section on imidonium intermediates.

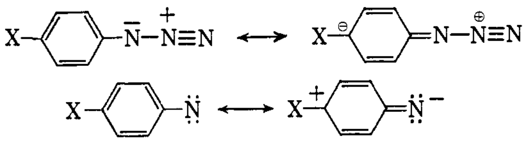
The rates of unimolecular decomposition of phenyl azide in both nitrobenzene and tetralin solutions were found to be the same, indicating that the solvent was not participating in the rate-determining step (260) and that phenylimidogen was formed as an intermediate: $PhN_3 \rightarrow PhN + N_2$. When methyl methacrylate was used as solvent, nitrogen evolution was much more rapid; the formation of a triazoline, which breaks down in the usual manner, was indicated and no imido intermediate was formed.



This was also the case when a suitable substituent, *e.g.*, a nitro group, which could participate in the elimination of nitrogen, was present *ortho* to the azide function. A lower decomposition temperature was generally observed and ΔH^* for the process was appreciably lower than in the unassisted decompositions (45, 110).



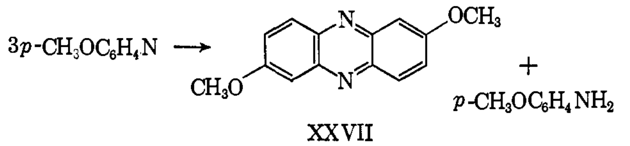
The kinetics of the thermal decomposition of a group of substituted phenyl and 2-biphenylyl azides at several temperatures and in different media have been the object of two recent independent studies (281, 327). In their somewhat more extensive study, Smith and Hall (281) found that in solvents such as decalin, nitrobenzene, and bis(2-ethoxyethyl) ether the variation in first-order rate constants with substitution is small, confirming Appl and Huisgen's earlier results (20). The reactions with substituted 2-azidobiphenyls gave much more consistent results than those with the phenyl azides. All *para* substituents studied accelerated the reaction slightly, and there was no simple correlation with Hammett's substituent constants. Changes in the ring onto which cyclization occurs have little effect on the rate, and an isokinetic relationship holds between ΔH^* and ΔS^*. The results strongly suggest that the rate-determining step is the same in the azidophenyl system as with simple phenyl azides, and is not concerned with the formation of the various types of products isolated, but with a common initial step, namely, the formation of a phenylimido intermediate without anchimeric assistance, as concluded also by Appl and Huisgen (20). Attempts to interpret the effects of substituents were more fruitful in terms of activation enthalpies than of rate constants. There was a considerable variation of ΔH^* with *para* substituents but not with *meta* ones. Qualitatively, the order was the same as that of $\Delta\sigma = (\sigma_p - \sigma_m)$, a measure of the extent to which the group takes part in conjugation with the azido residue [see also (282)]. The similarity of the above results



with those obtained in the triphenylmethyl azide series (263) is obvious if one considers that in the latter case, the *para* substituent cannot conjugate with the azido group so that the order of ΔH^* should then follow the inductive order, which it does. The triarylmethyl azides generally decompose thermally more slowly than do the aryl azides. Walker and Waters also concluded that in inert media the thermal decomposition of aryl azides—which have a higher activation energy than in unsaturated solvents, have small entropy requirements, and are unimolecular—involves the rate-determining formation of Ar-N (327). In an unsaturated medium such as indene and styrene, participation by the olefinic double bond in the nitrogen elimination led to faster rates and energies of activation lower by 15–20 kcal./mole. Since in indene the rate of disappearance of azide was the same as the rate of elimination of nitrogen, a concerted mechanism leading to the aziridine was put forward. The thermal decomposition of phenyl azide in decalin gave mainly aniline, some azobenzene, and a very small amount of hydrazobenzene. When *p*-methoxyphenyl azide was decomposed in boiling cumene, *p*-methoxyaniline and 4,4′-dimethoxyazobenzene were the main products, together with dicumyl and a small amount of 2,7-dimethoxyphenazine (XXVII). The conclusion that the azo compound is formed by the dimerization of $Ph\ddot{N}H$ followed by hydrogen abstraction from the hydrazobenzene rather than directly from PhN is

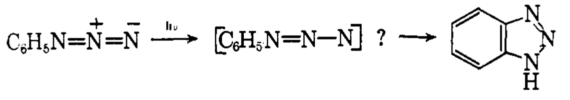
$$PhN + HR \rightarrow Ph\dot{N}H \rightarrow Ph{-}NH{-}NH{-}Ph$$
$$PhNH{-}NH{-}Ph + 2PhN \rightarrow PhN{=}N{-}Ph + 2PhNH\cdot$$

not mandatory since azo compounds have been obtained in good yields from phenylimido intermediates under conditions where hydrogen abstraction and the subsequent steps are rather unlikely (5, 6, 292). The phenazine (XXVII) was thought to arise in the following way.



XXVII

In contrast to *p*-methoxyphenyl azide (143, 144), photolysis of phenyl azide gave no azobenzene; instead, it was slowly converted into benzotriazole (XXVIII).



XXVIII

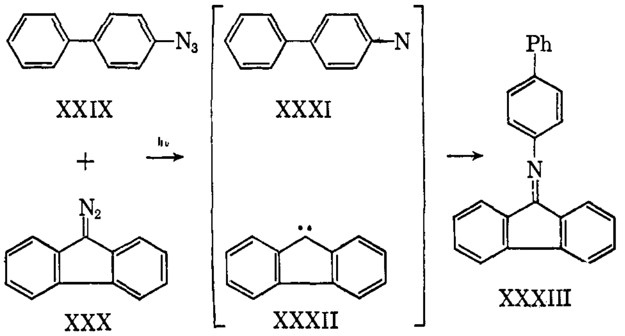
The photolysis or thermolysis of suitably substituted aryl azides gives azo compounds in good yield (143).

$$2p\text{-}RC_6H_4N_3 \xrightarrow{h\nu} N_2 + p\text{-}RC_6H_4N{=}NC_6H_4R\text{-}p \quad (R = OCH_3, C_6H_5)$$

Electron-donating substituents in the aryl azide as well as certain solvents raise the yield of azo compound. Photolysis of phenyl azide, *p*-nitrophenyl azide, *o*-azidobenzoic acid, and *p*-chlorophenyl azide did not give well-defined products [contrast the preparation of azo compounds from nitro compounds and ferrous oxalate (6)]. In cross-over experiments using different azides, mixtures of the symmetrical and unsymmetrical azo compounds were obtained, supporting the formation of a discrete imido intermediate.

$$p\text{-}CH_3OC_6H_4N_3 + p\text{-}C_6H_5C_6H_4N_3 \rightarrow p\text{-}CH_3OC_6H_4N{=}NC_6H_4\text{-}OCH_3\text{-}p + p\text{-}C_6H_5C_6H_4N{=}NC_6H_4C_6H_5\text{-}p + p\text{-}CH_3OC_6H_4N{=}NC_6H_4C_6H_5\text{-}p$$

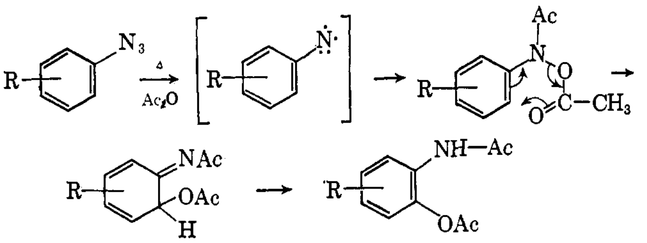
Similarly, irradiation of a mixture of 4-azidobiphenyl (XXIX) and 9-diazofluorene (XXX) gave 4-fluorenylidene aminobiphenyl (XXXIII) which, formally, might be thought to arise by the combination of the intermediate imidogen (XXXI) and carbene (XXXII) or by attack of XXXI upon XXX. Photolysis of phenyl azide in glacial acetic acid resulted in a measurable yield of *p*-aminophenol diacetate (XXXIV) and of *o*-acetamidophenol (XXXV). Addition of



XXIX XXXI XXX XXXII XXXIII

$$C_6H_5N_3 \xrightarrow[CH_3CO_2H]{h\nu} \underset{XXXIV}{p\text{-}CH_3CO_2C_6H_4NHCOCH_3} + \underset{XXXV}{o\text{-}CH_3CONHC_6H_4OH} + \text{resinous product}$$

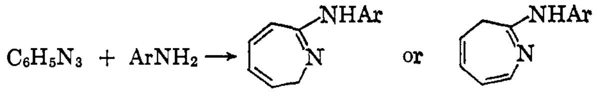
acetic acid to the imido intermediate, rearrangement, and acyl migration are suggested (143). Alternatively, a mechanism of the type postulated by Bamberger (32) and later modified by Ingold (163b) for the rearrangements of hydroxylamines would account nicely for the products obtained. The thermal decomposition of substituted aryl azides in acetic anhydride yields diacylated *o*-aminophenols (XXXVI), together with varying amounts of azo compounds and primary amines (274). A mechanism similar to that of the Claisen rearrangement has been suggested, which involves the formation of an imido intermediate.



XXXVI

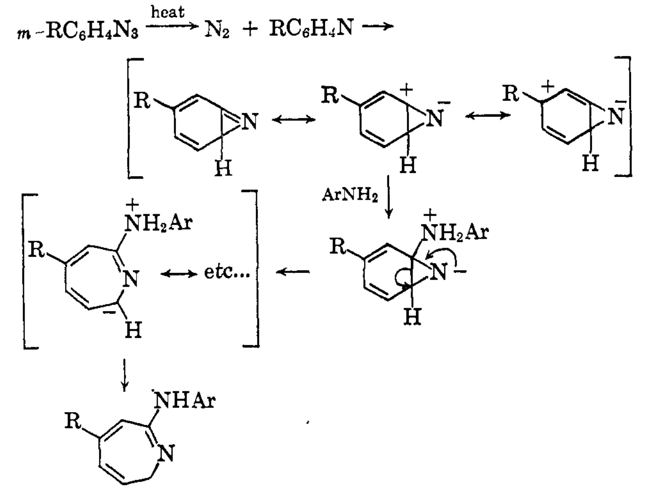
The possibility of a concerted attack by acetate and nitrogen elimination cannot be ruled out, however.

The very interesting thermal decomposition of phenyl azide in aniline to give "dibenzamil," first studied by Wolff (337) was reinvestigated, explained, and extended by Huisgen and his group (20, 152, 154). Dibenzamil was shown to be a seven-membered ring amidine, XXXVII or XXXVIII (Ar = C_6H_5), and



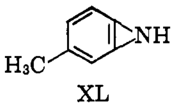
XXXVII XXXVIII

analogous products were obtained from phenyl azide and *p*-toluidine, *p*-phenetidine, *N*-methylaniline, benzylamine, and cyclohexylamine (154). The following mechanism was suggested (152).

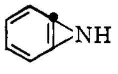


XXXIX

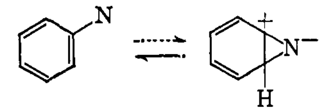
Support for this mechanism comes from the fact that using *p*-tolyl azide gives only one methylated product, whereas two products would have been expected had an intermediate such as XL been involved and



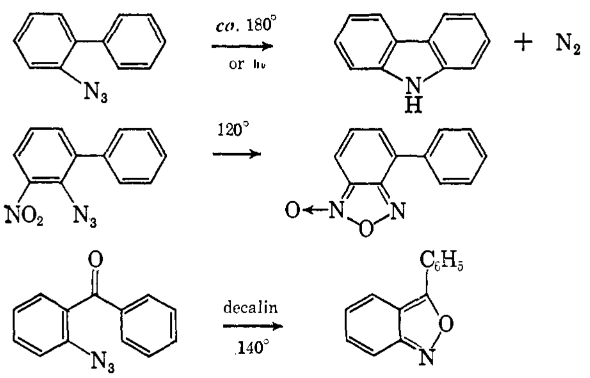
XL



also because when phenyl azide 1-C^{14} is used, all the label resides in the carbon attached to the anilino group in XXXIX. That closure of the azirine ring is not concerted with nitrogen elimination, is shown by the almost complete absence of a substituent effect upon the rate when R = H, *m*-CH_3, *m*-OCH_3, and *m*-NO_2 (20). That the rate of evolution of nitrogen is about the same in nitrobenzene as in aniline speaks against the argument (292) that the aniline must be participating before any rearrangement occurs. It is still of interest, however, that the decomposition in amines is the only one that seems to occur *via* the postulated azirine ring formation. An attempt to trap such an azirine with an excess of thiophenol failed, the products being diphenyl disulfide and aniline (292). One could conceive of an equilibrium between the imido and azirine intermediate, lying well to the side of the very reactive imido species so that the azirine would be detectable only if intercepted by a strong enough nucleophile.



If an alternative to the pathway leading to the formation of the azo compound is readily available, then the imido intermediate formed by the thermolysis or photolysis of aromatic azides will prefer to take it and thus lead to a variety of interesting products. For examples, the thermal or photochemical decomposition of 2-azidobiphenyls gives carbazole derivatives unless a nitro (or other similar) group is *ortho* to the azide function, in which case participation leading to benzofurazan is more facile (3, 4, 276, 277, 279–281, 290).

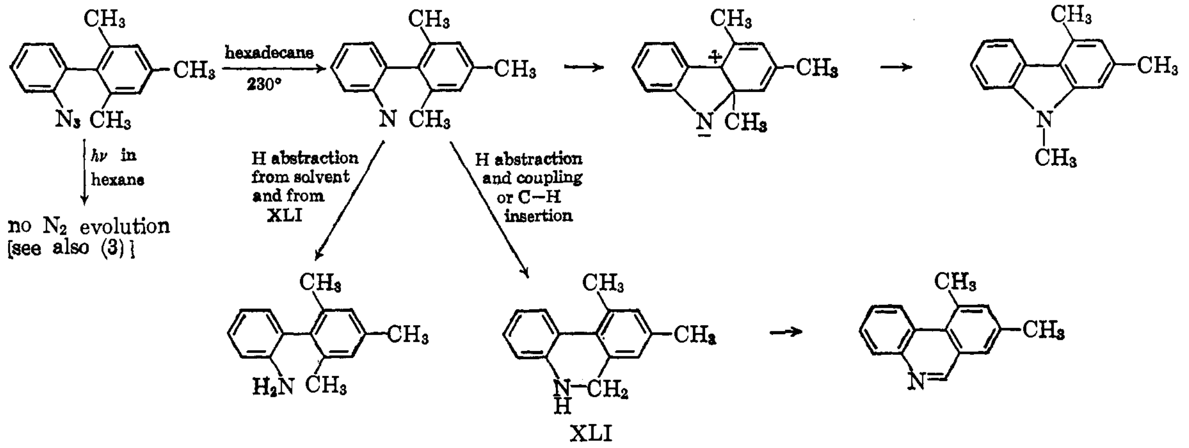


Other modes of intramolecular reaction undergone by arylimido intermediates are illustrated by the original work of Smolinsky (289, 290, 292) and are outlined briefly in Scheme III.

Amine formation was explained by postulating that the imido intermediate in the triplet state abstracted hydrogen atoms from the surroundings (see Scheme IV). Evidence that the imido intermediate in the singlet state can undergo C–H insertion has already been presented (288) (XIII → XV).

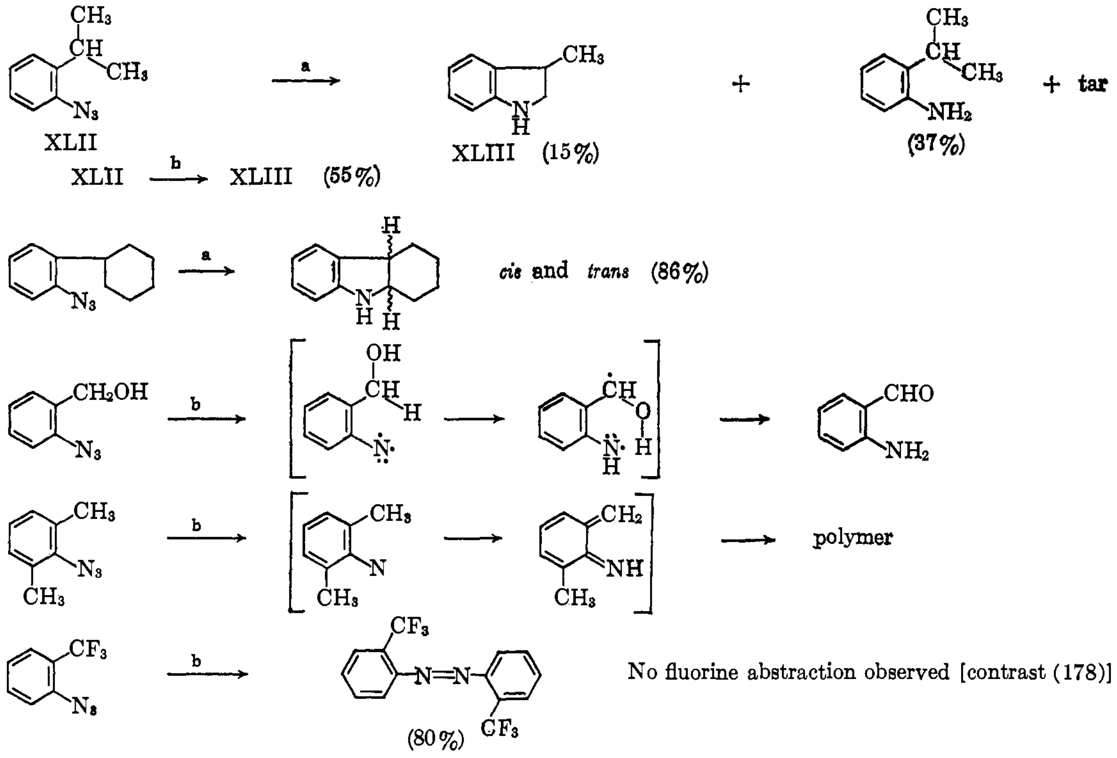
Insertions, or hydrogen abstraction followed by radical coupling, of RN, from the thermal decomposition of azides in nitrobenzene (which also acts as a dehydrogenating agent of the dihydrobenzimidazole

SCHEME III



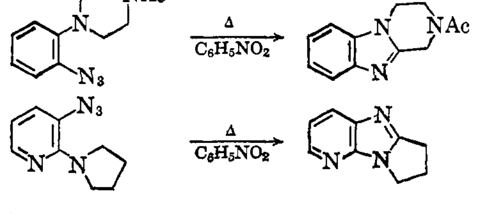
XLI

SCHEME IV

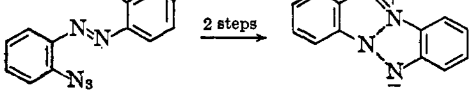


(a) Heating in diphenyl ether at 220°.
(b) Vapor phase pyrolysis.

first formed), into aliphatic C–H groups can lead to benzimidazoles (202, 271).



The formation of dibenzo-1,3a,4,6a-tetraazapentalene (XLV) from XLIV (78) undoubtedly involves a concerted nitrogen elimination in the first step, followed by an unassisted decomposition and cyclization *via* an imido intermediate.

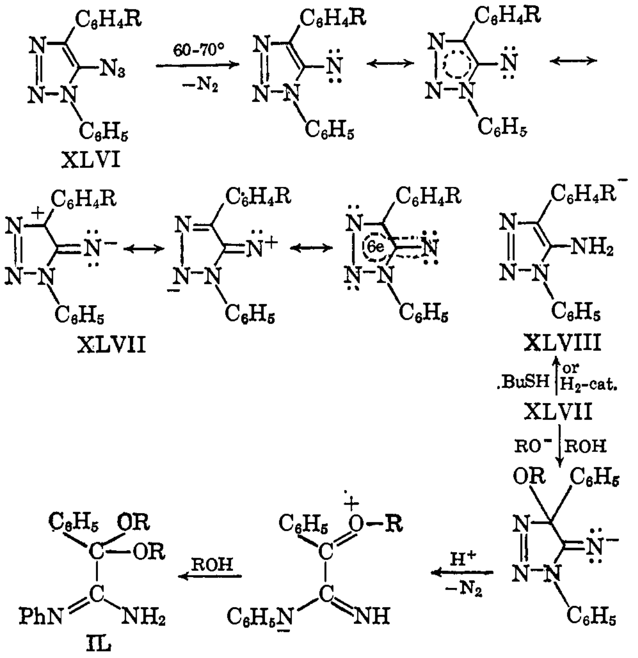


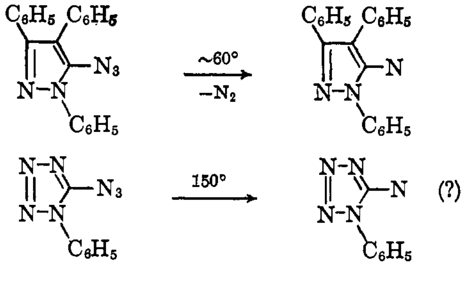
XLIV XLV

Mention should finally be made of the solid electron-deficient intermediates isolated by Smith, Krbechek, and Resemann (283, 284). When 1,4-diphenyl-5-azido-1,2,3-triazole (XLVI, R = H) is heated to 60°, it forms the red monomeric solid imido derivative

XLVII whose structure has been supported by reduction to the corresponding 5-aminotriazole (XLVIII), by its n.m.r. spectrum, by the use of isotopically labeled compounds showing that nitrogen is lost only from the azido group, and by the nature of the degradation products obtained (see Scheme V). For example, XLVI (R = H) reacts at room temperature with methanol, more difficulty with higher alcohols, to give the ketal-amidine (IL, R = CH_3) (for e.s.r. spectral study, see section IIIC). Kinetics of the decomposition indicate that the rate is almost insensitive to substituents on either phenyl nucleus. Other monomeric imido derivatives have also been prepared. It is interesting to note that XLVII is not stable at temperatures above 150°, which are those usually required for the decomposition of most aryl azides. The fact that compounds XLVII do not dimerize, however, seems to indicate that they possess additional stability over other imido intermediates.

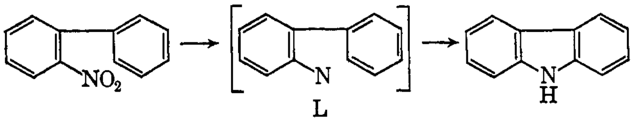
SCHEME V



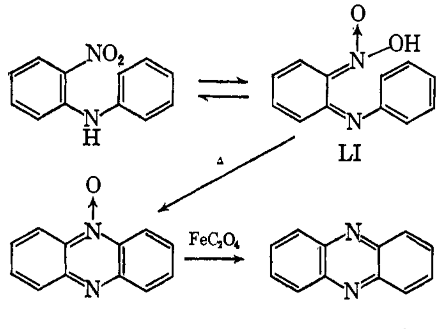


2. From Nitro Compounds

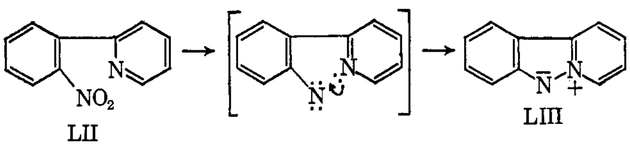
The Waterman and Vivian phenazine synthesis consists of heating a 2-nitrodiphenylamine derivative with ferrous oxalate at 250–300° (319, 320, 330). Carbazoles may be obtained from 2-nitrobiphenyls. It was suggested that pyrophoric ferrous oxide, produced by the thermal decomposition of the oxalate, was the active cyclizing agent (330), and it was later postulated that it abstracted two oxygen atoms from the nitro group, giving an aryl imido intermediate (L) which underwent cyclization (3). An alternative mechanism proposed for the phenazine synthesis suggests an uncatalyzed cyclization through the *aci*-nitro form LI (287). An immediate difficulty arising out of this mechanism is that no *aci*-nitro structure can be written for the 2-nitrobiphenyls; the suggestion here is that the carbazole is formed by the cyclization of the 2-aminobiphenyl, actually found as a by-product. No mention is made of where the reducing agent comes from that will give the primary amino group. Thus, when 2-nitrobiphenyl is heated with ferrous oxalate, carbazole (35%) and 2-aminobiphenyl (18%) are formed, whereas on heating alone or with sand only, tars and starting material are obtained (287). Convincing evidence has been accumulated which supports the imido intermediate mechanism. Cyclization of 2-*o*-nitrophenylpyridine (LII) gives pyrido[1,2-*b*]indazole (LIII), presumably by attack of the electron-deficient nitrogen upon the pyridine nitrogen lone-pair of electrons (3). LIII was also obtained by thermolysis, but not photolysis, of 2-*o*-azidophenylpyridine. In this case a concerted process may be involved. On the other hand, the cyclization of 3-*o*-nitrophenylpyridine occurs readily to give a mixture of α- and γ-carboline, in which the former predominates (9), and a similar cyclization of 4-*o*-nitrophenylpyridine to give β-carboline also takes place without difficulty (10). Hence, the pyridine carbon nucleus, known to be



L

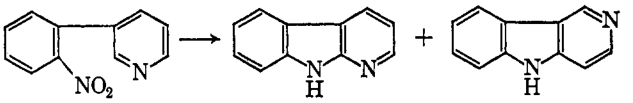


LI

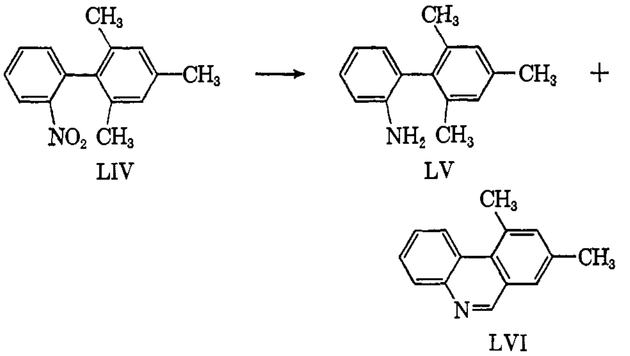


LII

LIII



highly resistant to electrophilic attack and therefore not a ready source of electron-rich sites, is substituted readily in this case, a result easily accommodated by an attack by an imido intermediate at the surface of a paramagnetic solid which can catalyze singlet–triplet transitions. A number of other reactions, which find a parallel both in carbene chemistry as well as in the chemistry of imido intermediates generated in an unambiguous fashion, have been reported. *o*-Nitrocinnamic acid with ferrous oxalate at 270–280° gave a mixture of indole-2-carboxylic acid and of indole, a reaction which can be looked upon as the addition of an imido intermediate to an olefinic double bond (5). 2′-Nitro-2,4,6-trimethylbiphenyl (LIV) gave a mixture of 2′-amino-2,4,6-trimethylbiphenyl (LV) and of 8,10-dimethylphenanthridine (LVI). It was shown that LV must be formed by hydrogen abstraction mainly from methyl groups in another molecule. Dehydrogenation of the intermediate dihydrophenanthridine, resulting either from C–H insertion of the imido intermediate or by hydrogen abstraction followed by radical coupling, takes place readily with ferrous oxalate at high temperature. Evidence was adduced that the reaction takes place at the surface of the oxalate, the decomposition of the latter being catalyzed by the adsorbed nitro compound, and this in turn causes the imido intermediate to be formed (5). *o*-Nitrophenylcyclohexane gave a mixture of *o*-aminophenylcyclohexane (51.7%), by hydrogen abstraction, and carbazole (40%), by hydrogen abstraction and coupling or by insertion, followed by dehydrogenation. When nitrobenzene in a mixture of 1-hexadecene in hexadecane was boiled under reflux with ferrous oxalate, some aniline was formed together with a small amount of a compound $C_{22}H_{37}N$ to which structure LVII was assigned (5). The reaction of simple aromatic nitro compounds with ferrous, nickel, and cobaltous oxalate gives results consistent with the proposed formation of arylimido intermediates (5, 6). When,



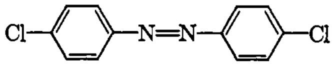
LIV LV LVI

$$C_6H_5NO_2 \rightarrow C_6H_5\ddot{\dot{N}}\cdot \xrightarrow{CH_3(CH_2)_{12}CH_2CH{=}CH_2} C_6H_5\ddot{\dot{N}}H +$$

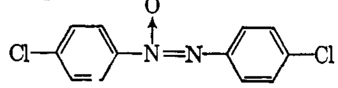
$$\begin{matrix} CH_3(CH_2)_{12}\underset{\cdot}{C}HCH{=}CH_2 \\ \updownarrow \\ CH_3(CH_2)_{12}CH{=}CH\dot{C}H_2 \end{matrix} \rightarrow$$

$$\underset{\text{LVII}}{CH_3(CH_2)_{12}CH{=}CHCH_2NHC_6H_5}$$

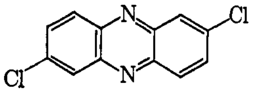
for example, *p*-chloronitrobenzene in excess is heated with ferrous oxalate, a mixture of 4,4′-dichloroazobenzene (LVIII) and 4,4′-dichloroazoxybenzene (LIX) is obtained. With smaller nitro compound to oxalate ratios, no azoxy compound was formed; LVIII was formed in good yield together with some 2,7-dichlorophenazine (LX). Other nitro compounds, including nitrobenzene itself, gave similar results [*cf.* the decomposition of azyl azides (143)]. The synthesis of benzimidazoles (2, 12, 287) also parallels the reaction using aryl azides



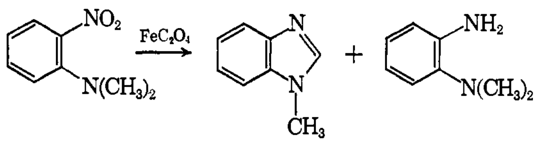
LVIII



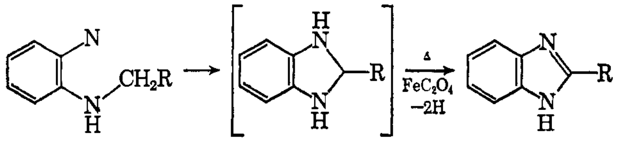
LIX



LX

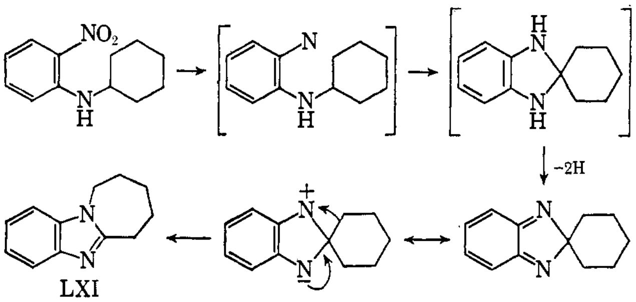


and a likely mechanism would be



which would explain the interesting ring expansion to LXI observed in one such reaction (287) rather more neatly than does the previously proposed mechanism shown in Scheme VI.

SCHEME VI



LXI

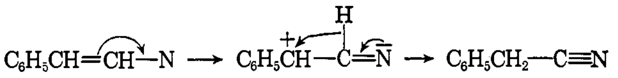
Following the deoxygenation of C-nitroso compounds by triethyl phosphite (see section IIC3) it has been shown that nitro compounds will also react with the same reagent, albeit under much more vigorous conditions, to give products analogous to those obtained from the nitroso derivatives (75, 76). Though the starting materials are more readily available than the C-nitroso compounds, the yields in this case are much lower. It is likely, but has not been proved, that imido intermediates are produced by the deoxygenation of nitro groups.

$$\underset{\text{excess}}{(EtO)_3P} + \text{2-nitrobiphenyl} \xrightarrow[\substack{\text{9 hr.}\\ N_2}]{160^\circ} \text{carbazole}$$

$$(EtO)_3P + \text{2-nitrodiphenylamine} \rightarrow \text{phenazine}$$

$$(EtO)_3P + \underset{(cis\text{ or }trans)}{o\text{-nitrostilbene}} \rightarrow \text{2-phenylindazole}$$

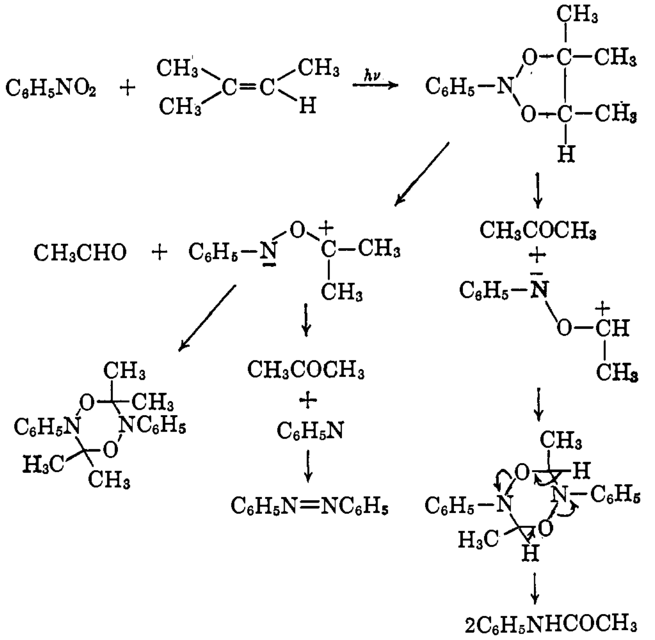
ω-Nitrostyrene is reported to give phenylacetonitrile (6%), an amine which is probably aniline (2%) (identified only by gas chromatography), and a compound giving a positive indolic test (332). The formation of phenylacetonitrile from the imido intermediate is relatively easy to visualize, but the formation of aniline, which is more difficult to rationalize, will have to be confirmed.



$$C_6H_5CH=CH-N \longrightarrow C_6H_5\overset{+}{C}H-\overset{H}{C}=\bar{N} \longrightarrow C_6H_5CH_2-C\equiv N$$

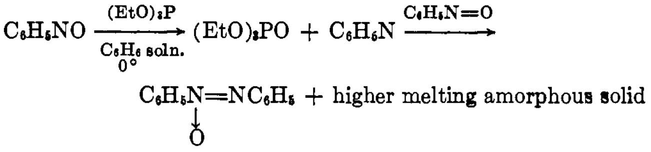
The light-catalyzed oxidation of olefins with nitrobenzene gives azobenzene together with the products of cleavage of the double bond and has been speculatively formulated (66) as shown in Scheme VII.

SCHEME VII



3. From Aromatic C-Nitroso Compounds

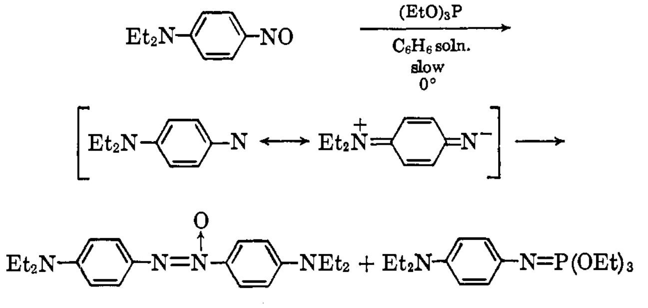
The deoxygenation of aromatic C-nitroso compounds with triethyl phosphite has been postulated to lead to arylimido intermediates which can then undergo further reaction either with unchanged nitroso compound or with adjacent nuclei, in rather the same manner as do the intermediates from the corresponding azides and nitro compounds (71, 72).



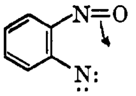
$$C_6H_5NO \xrightarrow[\substack{C_6H_6\text{ soln.}\\ 0^\circ}]{(EtO)_3P} (EtO)_3PO + C_6H_5N \xrightarrow{C_6H_5N=O} \underset{\substack{\downarrow\\ O}}{C_6H_5N}=NC_6H_5 + \text{higher melting amorphous solid}$$

The introduction of a *p*-dimethylamino substituent stabilizes the postulated imido intermediate and allows the excess triethyl phosphite to compete with the nitroso compound for the electron-deficient nitrogen atom (see Scheme VIII).

SCHEME VIII



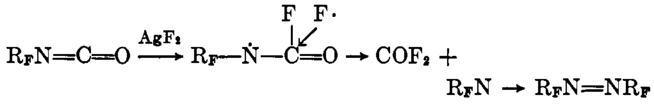
Cyclization to carbazoles and carbolines occurs readily, the latter suggesting that the reactive intermediate may be the triplet diradical in this case. The preparation of benzofurazan from *o*-dinitrosobenzene (57) may involve LXII (72). No example of C-H bond insertion has yet been reported in this reaction, the example chosen for this purpose (72) being unsuitable (5) and, to that extent, the mechanism of the reaction is still in doubt. Further work is needed to prove or disprove the formation of imido intermediates.



LXII

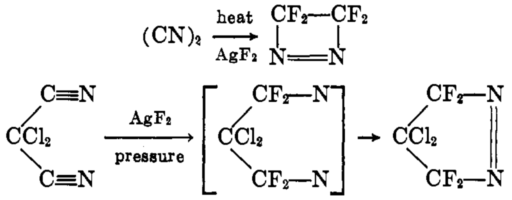
4. Miscellaneous Methods

The indirect fluorination of some fluorocarbon nitrogen derivatives with AgF₂ is said to give rise to products *via* an imido intermediate. For example, reaction of a fluorocarbon isocyanate with AgF_2 gives carbonyl fluoride and the fluorocarbon azoalkane (341).

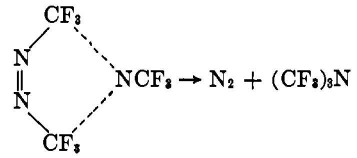


$$R_FN=C=O \xrightarrow{AgF_2} R_F-\dot{N}-\overset{F\ \ F\cdot}{C}=O \rightarrow COF_2 + R_FN \rightarrow R_FN=NR_F$$

Similarly, the reaction of argentic fluoride with dichloroand difluoromalononitrile and other dicarboxylic acid nitriles gives products which may arise by the internal dimerization of a diimido intermediate (108, 161).



The formation and subsequent reaction of imido intermediates has also been suggested to account for the products of the direct fluorination of nitriles (48, 49, 258). For example, the origin of the products (underlined) of the fluorination of HCN and cyanogen is explained in Scheme IX (258). Some of the results of the fluorination of HCN might also be accounted for by the alternate scheme indicated by the broken arrows. For example, tri(trifluoromethyl)amine could arise from a three-center process, similar to that suggested previously for the reduction of imidogen by diimide, and insertion of CF_3N into $CF_3N{=}NCF_3$ followed by fluorinolysis would explain the formation of CF_4 and $(CF_3)_2NF$.



Cofluorination of HCN and CF_3CN in a jet reactor at 100° gave, among other products, $CF_3N{=}NCF_2CF_3$ by the dimerization of CF_3CF_2N and CF_3N (258). The direct jet fluorination of perfluorinated malono-, succino-, and glutaronitriles gives complicated mixtures of products, and once again it is suggested that imido intermediates are involved in their formation (47–49). For example, with perfluorosuccinonitrile, perfluoropyrrolidine (LXIII), $CF_3CF_2CF_2CF_2NF_2$, $CF_3CF_2CF{=}NCF_3$, and $CF_3NFC_3F_7$ are obtained. A possible scheme which would explain the formation of the first two compounds is shown in Scheme X.

Fluorazoalkanes ($R_FN{=}NR_F$) have also been synthesized by the reaction of lower valent metal fluorides and chlorine or bromine with cyanogen chloride and with carbonitriles of fluorocarbons and chlorocarbons (83), a reaction which might also involve imido intermediates.

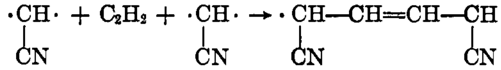
$$2ClCN + 2Cl_2 + 6NaF \xrightarrow[\text{pressure}]{225°} CF_3N{=}NCF_3 + 6NaCl$$

The latter may also participate in the synthesis of fluoroalkyl isocyanates by the reaction of CO with $R_FN{=}NR_F$ at 325° under 650 atm. for 5 hr. (83).

$$CF_3N{=}NCF_3 \rightarrow [2CF_3N] \xrightarrow{2C{=}O} 2CF_3N{=}C{=}O$$

Imido intermediates have been postulated in the reactions of active nitrogen with a number of organic molecules. The initial reaction of active nitrogen with acetylene is probably $N + CH{\equiv}CH \rightarrow N—CH{=}CH\cdot$ which may initiate a chain reaction, *e.g.*, $NCH{=}CH\cdot + C_2H_2 \rightarrow NCH{=}CHCH{=}CH\cdot$, or lose hydrogen to form a cyanomethylene radical which can then polymerize with acetylene molecules (200).

$$N—CH{=}CH\cdot \rightarrow N{\equiv}C—\dot{C}H + H$$



$$\underset{CN}{\cdot CH\cdot} + C_2H_2 + \underset{CN}{\cdot CH\cdot} \rightarrow \cdot\underset{CN}{CH}—CH{=}CH—\underset{CN}{CH}\cdot$$

The HCN formed in the reaction of active nitrogen with methanol is thought to arise from CH_3N (297).

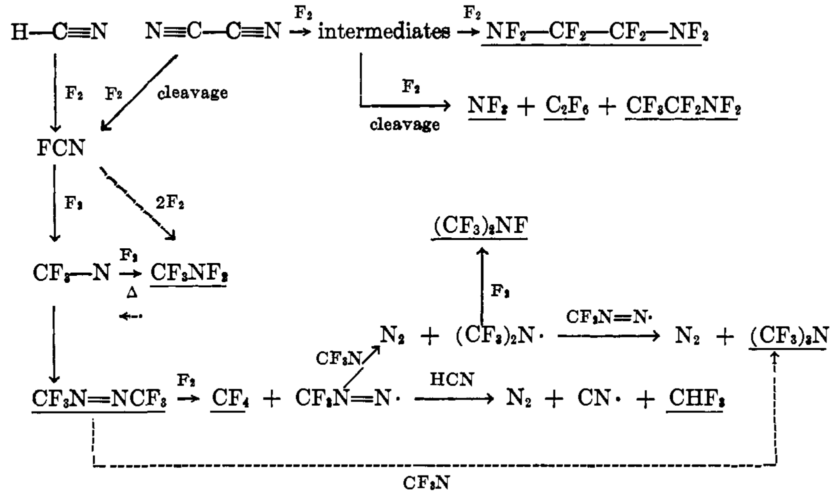
$$N + CH_3OH \rightarrow [NCH_3OH] \rightarrow NCH_3 + OH$$

$$NCH_3 \rightarrow HCN + 2H \text{ (or } H_2)$$

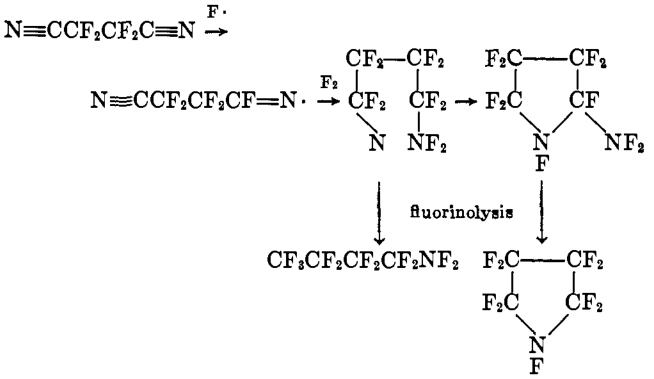
Imido intermediates may well also be involved in the reactions of active nitrogen with alkyl chlorides (103), butadiene (314), and other organic substrates.

The mechanism proposed for the Neber rearrangement (93, 133) envisages the intermediacy of a vinylic

SCHEME IX

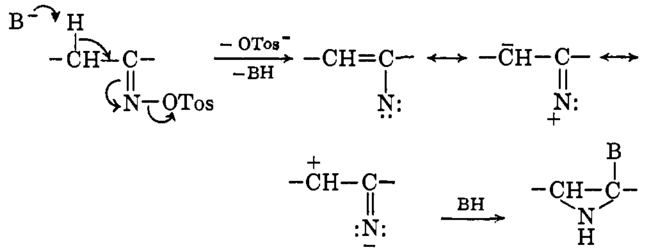


SCHEME X

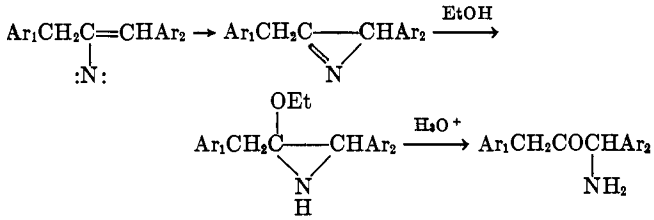


LXIII

electron-deficient nitrogen species which then undergoes cyclization to a three-membered ring.

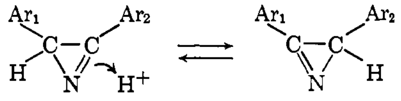


Support for this suggestion has been obtained more recently (147, 148) when it was confirmed that *cis* and *trans* oxime tosylates gave the same α-amino ketone and that cyclization occurs at the more acidic α-proton in $Ar_1CH_2C(=NOTos)CH_2Ar_2$.

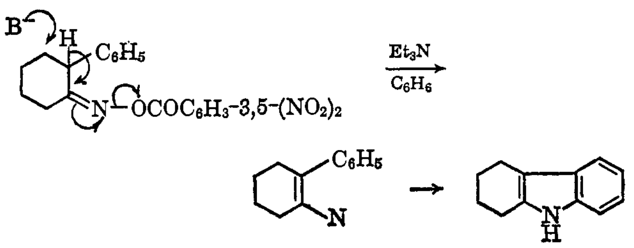


$Ar_1 = p\text{-}CH_3OC_6H_4$; $Ar_2 = p\text{-}NO_2C_6H_4$

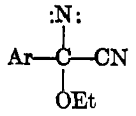
When Ar_1 and Ar_2 are essentially equivalent electronically, equilibrations of the type



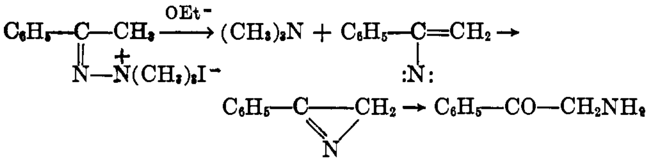
are not involved and neither is a symmetrical intermediate (147). Though a concerted loss of the tosyloxy function and closure of the three-membered ring is not ruled out by the evidence, it is considered less likely stereochemically than the mechanism involving a discrete imido intermediate (148). When the 3,5-dinitrobenzoate of α-phenylcyclohexanone oxime (LXIV) is heated with triethylamine in benzene, tetrahydrocarbazole is isolated as a minor product and is thought to result from the cyclization of a Neber rearrangement intermediate (333).



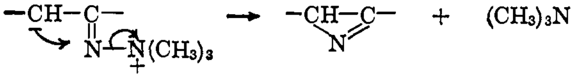
The base-catalyzed rearrangement of arylglyoxylonitrile oxime *p*-toluenesulfonate is either a concerted process or one involving the intermediacy (303) of



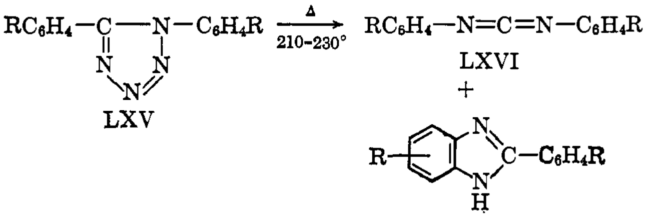
A rearrangement of quaternary hydrazones in the presence of sodium ethoxide in boiling ethanol under strictly anhydrous conditions is a variant on the Neber rearrangement theme (286), and an analogous mechanism may be suggested



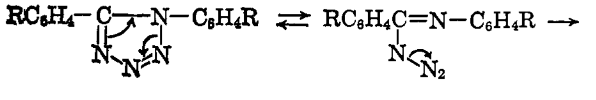
though a concerted nucleophilic displacement on nitrogen cannot be ruled out.



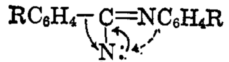
The thermal breakdown of diaryltetrazoles (LXV) gives diarylcarbodiimides (LXVI) and 2-arylbenzimidazoles (LXVII) (285, 317). It is suggested that at that temperature the tetrazole (LXV) is in equilibrium with the imidyl azide (LXVIII), and that it is the latter which decomposes to the imido intermediate (LXIX), which can either undergo a 1,2-shift to give LXVI or aromatic substitution to yield LXVII. By varying the nature of the substituent R, the expected competitive formation of LXVI and LXVII gave dif-



LXV LXVI LXVII



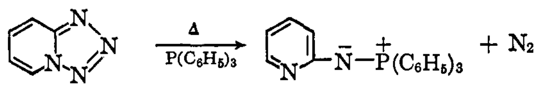
LXVIII

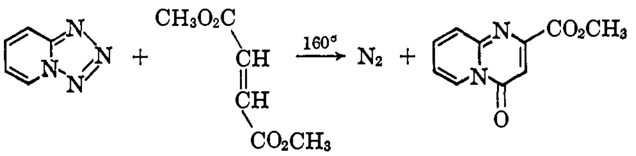


LXIX

ferent product ratios in a predictable manner. Thus, 1-phenyl-5-*p*-chlorophenyltetrazole gave a higher yield of the benzimidazole than did the unsubstituted compound, with concurrent reduction in the amount of product of 1,2-shift (317). The question of whether the imidogen is formed as a definite intermediate or whether a concerted decomposition of the imino azide (LXVIII) is involved is still an open one (150).

Whereas the thermal decomposition of LXV (R = H) gives a 65% yield of LXVI, the photochemical decomposition gives a 64% yield of LXVII (175). The intermediate from one such decomposition was trapped with triphenylphosphine (175). Addition of the intermediate to a variety of unsaturated compounds also takes place (150), *e.g.*





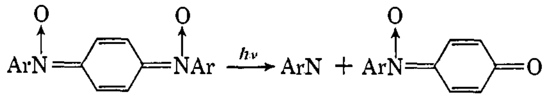
Other examples are reported (58, 150).

The generation of arylimido intermediates has been suggested in a variety of other reactions. N,N-Dichloro-*p*-nitroaniline (LXX), prepared from *p*-nitroaniline and hypochlorous acid at −20 to −30°, decomposes explosively at room temperature in the absence of a solvent, liberating chlorine gas and yielding 4,4′-dinitroazobenzene (125) [see also earlier work of Goldschmidt (124)].

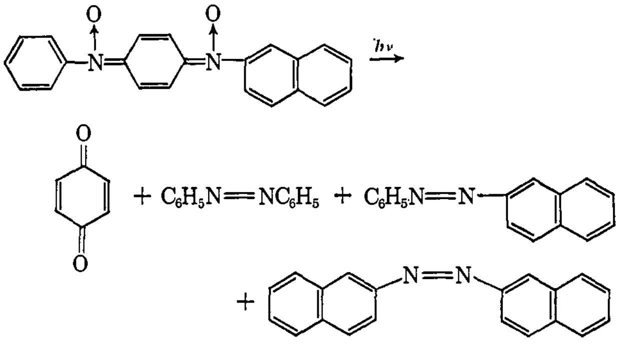
$$\underset{\text{LXX}}{p\text{-}NO_2C_6H_4NCl_2} \rightarrow Cl_2 + [p\text{-}NO_2C_6H_4N] \rightarrow p\text{-}NO_2C_6H_4N{=}NC_6H_4\text{-}p\text{-}NO_2$$

A similar reaction is observed with *m*-nitroaniline and with *o*-nitroaniline. In the latter case, no benzofurazan was reported indicating that this compound is only produced in the azide decomposition because of neighboring group assistance by the nitro function. Decachloroazobenzene is obtained by heating N,N-dichloropentachloroaniline in toluene.

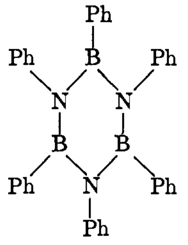
The oxidation of aniline with oxygen in aqueous solution by excitation with ultrasonic waves may result in the production of phenylimidogen (331). The photochemical decomposition of N,N′-disubstituted *p*-quinonediimine N,N′-dioxides gives *p*-benzoquinone and azo compounds by an intermolecular process (240) shown in Scheme XI. Kirmse has suggested (175) that an arylimido intermediate is formed.



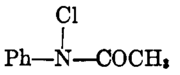
Scheme XI



An analogous reaction is the photochemical decomposition of azine monoxides (145). The formation of phenylimidogen has been proposed to account for the thermal decomposition of hexaphenylborazole (LXXI) (218) and for the decomposition of N-chloroacetanilide (LXXII) in alkaline solution (73).



LXXI

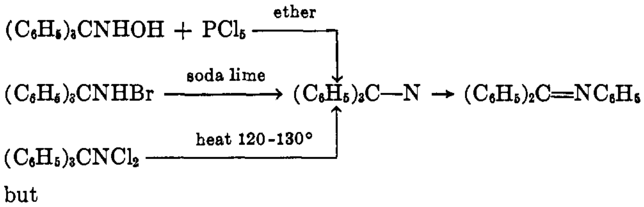


$$Ph{-}\overset{Cl}{\overset{|}{N}}{-}COCH_3$$

LXXII

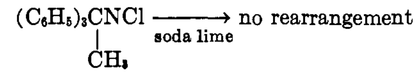
The various molecular rearrangements undergone by triarylmethyl amine derivatives studied in Stieglitz's laboratory may involve the formation of triarylmethylimido intermediates as suggested (185, 215, 272, 299, 305, 324) and as shown in Scheme XII, or could take place by concerted migration–elimination as has been proposed for the corresponding azides (263). Migratory aptitudes have been determined in the rearrangement of the hydroxylamines (217) and compare favorably with those in the triarylmethyl azide rearrangement.

Scheme XII



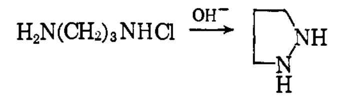
$$(C_6H_5)_3CNHOH + PCl_5 \xrightarrow{\text{ether}} (C_6H_5)_3C{-}N \rightarrow (C_6H_5)_2C{=}NC_6H_5$$
$$(C_6H_5)_3CNHBr \xrightarrow{\text{soda lime}} (C_6H_5)_3C{-}N$$
$$(C_6H_5)_3CNCl_2 \xrightarrow{\text{heat 120-130°}} (C_6H_5)_3C{-}N$$

but

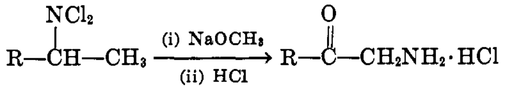


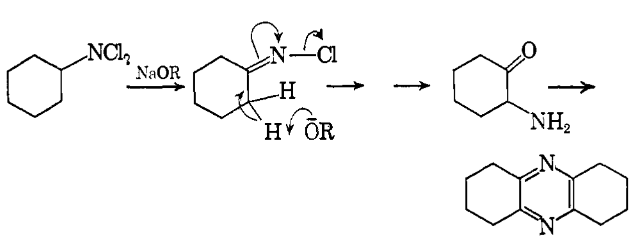
$$\underset{CH_3}{\underset{|}{(C_6H_5)_3CNCl}} \xrightarrow[\text{soda lime}]{} \text{no rearrangement}$$

Reactions analogous to those undergone by chloramine (see section IIA) are found with aliphatic chloramines (265, 266). Both α-elimination (189) and S$_N$2-type mechanisms (264) have been proposed. The formation of pyrazolidine (LXXIII) (189) from the reaction of 1,3-diaminopropane with sodium hypochlorite is best accounted for by an S_N2 process according to Horner and Christmann (141). On the other hand, and by analogy with the Neber rearrangement, it would seem as though the base-catalyzed rearrangement of N,N-dichloro-*sec*-alkylamines (37, 38, 267) might conceivably involve imido intermediates.



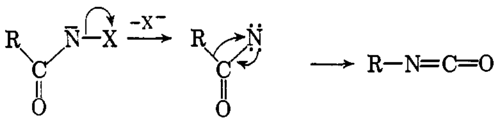
LXXIII

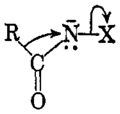

$\mathrm{R{-}\underset{}{\overset{NCl_2}{CH}}{-}CH_3 \xrightarrow[\text{(ii) HCl}]{\text{(i) NaOCH}_3} R{-}\overset{O}{\overset{\|}{C}}{-}CH_2NH_2\cdot HCl}$



D. ACYL AND SULFONYL IMIDO INTERMEDIATES ($RCON$ AND RSO_2N)

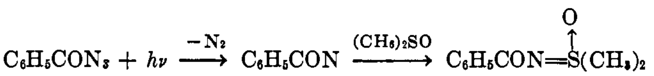
The Hofmann, Lossen, and Curtius rearrangements have usually been formulated as proceeding by the formation of a common acyl imido intermediate (163a). The main objections to this mechanism (139) are based on rather sketchy evidence. For example, no hydroxamic acid has been detected in the Hofmann rearrangement (134), whereas NH is known to react with water to form hydroxylamine (122). It should be noted, however, that in the latter case the NH was produced photochemically in aqueous acid solution, conditions somewhat different from those in the usual Hofmann rearrangement. Also, had any hydroxamic acid actually been formed, it is just conceivable that it might have undergone the Lossen rearrangement under the conditions of the reaction and thus not been detected. The kinetics of the Hofmann rearrangement indicate that electron-attracting groups in the acid retard, and electron-donating groups accelerate the rearrangement, and this has been taken as evidence for the concerted process (135).





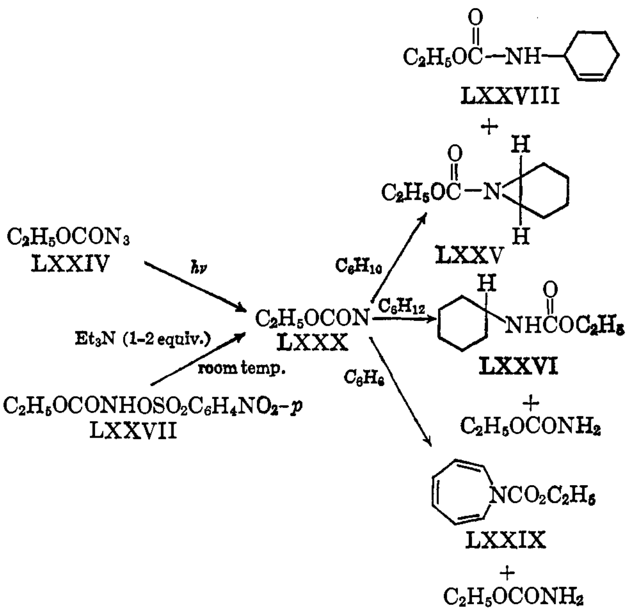
A closer look at the kinetic data points to certain peculiar features, *e.g.*, *m*-nitro-N-bromobenzamide and *p*-nitro-N-bromobenzamide rearrange at the same rate, and the heats of activation for the rearrangement of N-bromobenzamide and *m*-chloro-N-bromobenzamide are the same within the limits of experimental error. Kinetic studies of the Lossen (248) and Curtius (342, 343) rearrangements are equally inconclusive. Thus, in the Curtius rearrangement, rate differences attributable to substitution are small; electron-releasing groups in the *meta* position of benzazide increase the reaction rate, and electron-attracting groups decrease it. All substituents in the *para* position decreased the rate (342). According to more recent unpublished kinetic evidence (151) an acylimido intermediate is not formed in the Curtius rearrangement and attempts to intercept it have failed. On the other hand, from a study of the volume change of activation ($\Delta V^* = +2$ ml.) in a high-pressure study of the kinetics of the rearrangement of benzazide, Brower (62) has concluded that the predominance of bond breaking in the transition state is consistent with the formation of a discrete acylimido intermediate. It was argued that if bond formation were significantly involved in the transition state, ΔV^* would probably have been negative. The intermediacy of an acylimidogen in the Curtius reaction has also been argued on the basis of a study of the indirect fluorination of trifluoroacetic acid imide (341). The above discussion indicates that the question of the detailed mechanism of these rearrangements is far from settled and that much more work is necessary to clarify the situation. It is possible to visualize a whole continuum of mechanisms, ranging from those cases where substituents facilitate participation by the migrating group in the rate-determining elimination to those in which participation is so unlikely as to be excluded; in the latter case, trapping of the imido intermediate might become feasible.

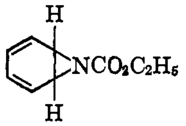
The photolytic decomposition of benzazide (146) proceeds *via* an acylimido intermediate since the latter has very recently been trapped with dimethyl sulfoxide (142).


$$C_6H_5CON_3 + h\nu \xrightarrow{-N_2} C_6H_5CON \xrightarrow{(CH_3)_2SO} C_6H_5CON{=}\overset{\overset{O}{\uparrow}}{S}(CH_3)_2$$

The first successful unambiguous evidence that discrete acylimido intermediates could be formed and trapped was obtained by ApSimon and Edwards (21) (whose results are discussed later) and then by Lwowski and Mattingly (191). The photochemical decomposition of ethyl azidoformate (LXXIV) (which does not undergo the Curtius rearrangement) in the presence of cyclohexene and cyclohexane gave 7-carbethoxy-7-azabicyclo[1.4.0]heptane (LXXV) and the cyclohexylurethane (LXXVI), respectively. The rate of evolution of nitrogen in the first case was equal to that of disappearance of azide, excluding the possible formation of a triazoline. α-Elimination of *p*-nitrobenzenesulfonic acid from its N-hydroxyurethane ester (LXXVII) in cyclohexane, cyclohexene, or benzene leads to the same products as does the photodecomposition of LXXIV in these substrates. Moreover, in the reactions in cyclohexene, 3-cyclohexenylurethane (LXXVIII) is formed as a by-product in about the same amount relative to LXXV (1:6) as with LXXIV (1:4.5) (190). See Scheme XIII. Hafner and König (131) showed that photolysis of ethyl azidoformate in benzene gave N-ethoxycarbonylazepine (LXXIX) in 70% yield, presumably *via* the aziridine (LXXXI), and the same product was obtained from LXXVII (190). Flash photolytic decomposition of gaseous methyl or ethyl azidoformate in CO_2 gives the unstable ROCON, which may be trapped by a suitable substrate, *e.g.*, $C_6H_{10} \rightarrow$ LXXV, or undergoes C–O bond cleavage to give NCO (41).

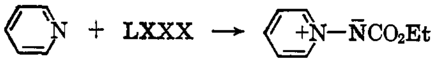
SCHEME XIII



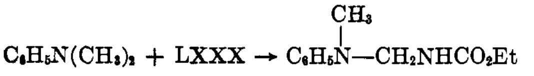


LXXXI

Ring expansion of aromatic compounds with LXXX, *generated both photochemically and thermally*, has been extended to toluene, xylene, and anisole (130). In many reactions, LXXX behaves as an electrophilic species, and it is not obvious in the first two examples whether LXXX is formed as a discrete intermediate or whether a concerted process is involved. Addition of LXXX across the double bond of dihydropyran could be a potentially interesting approach to the 2-aminodeoxy sugars (106) (see Scheme XIV).

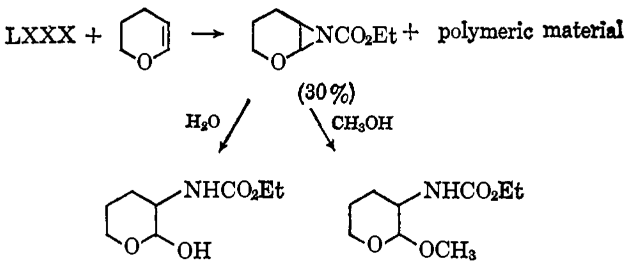


$$C_6H_5NHR + \text{LXXX} \rightarrow C_6H_5NRNHCO_2Et$$



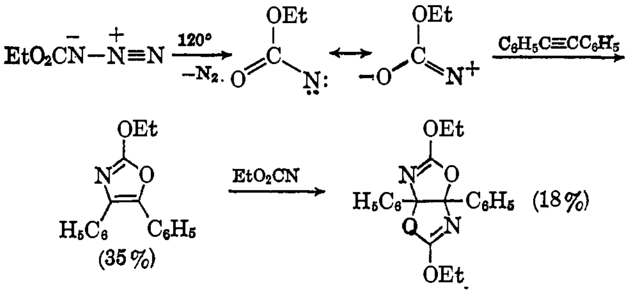
$$C_6H_5N(CH_3)_2 + \text{LXXX} \rightarrow C_6H_5\overset{CH_3}{\overset{|}{N}}—CH_2NHCO_2Et$$

SCHEME XIV



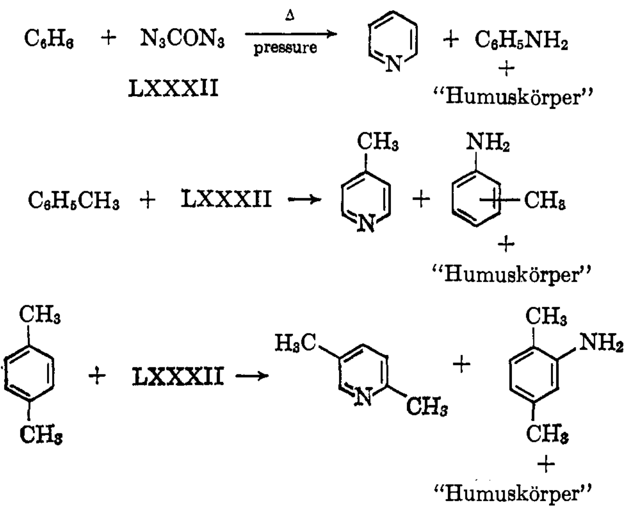
The thermal decomposition (120°) of alkyl azidoformates gives the carbalkoxyimido intermediate which may be written as a resonance hybrid of two canonical structures, one of which is a 1,3-dipole. As such, it might be expected to undergo addition to suitable 1,3-dipolarophiles, and this expectation has been fulfilled (153) (see Scheme XV).

SCHEME XV



Actually, the first reports of attack by acid azides upon aromatic systems antedate the above work by quite a few years. Thus, in 1926 Curtius and Bertho (96) reported their interesting work on the decomposition of carbonyl azide (LXXXII) in aromatic solvents in an autoclave, work which has been ignored by most of the recent authors. Benzene and carbonyl azide are said to yield pyridine and a small amount of aniline, together with what is described as a "Humuskörper," a brown amorphous substance of undetermined composition. Similarly, toluene gave 4-picoline, a mixture of *o*- (mainly) and *p*-anisidine and a "Humuskörper"; *p*-xylene gave 2,5-lutidine and *p*-xylidine in small amounts, the main product being the "Humuskörper"; and *p*-cymene gave either 2-isopropyl-5-methyl- or 5-isopropyl-2-methylpyridine and carvacrylamine (see Scheme XVI). Hydrolysis of the "Humuskörper" from the *p*-xylene reaction with concentrated hydrochloric acid gave CO, CO_2, a small amount of NH_3, traces of lutidine (recognized by its odor!), and small amounts of *p*-xylidine (10%). The mecha-

SCHEME XVI

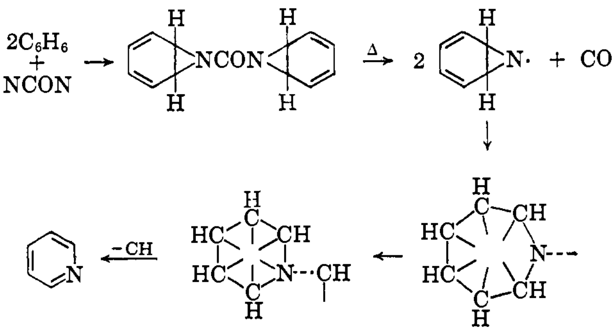


nism proposed for the formation of the anilines involved the generation and subsequent reaction of the carbonyl diimido intermediate.

$$2C_6H_6 + NCON \rightarrow C_6H_5NHCONHC_6H_5 \xrightarrow{2H_2O} 2C_6H_5NH_2 + CO_2$$

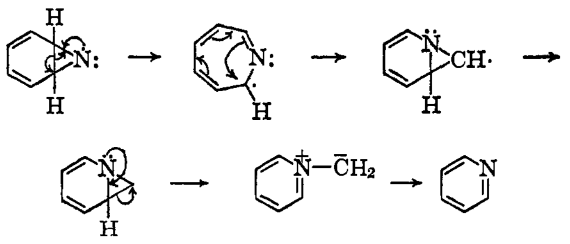
The remarkable formation of pyridine in this reaction was formulated as shown in Scheme XVII. If the

SCHEME XVII



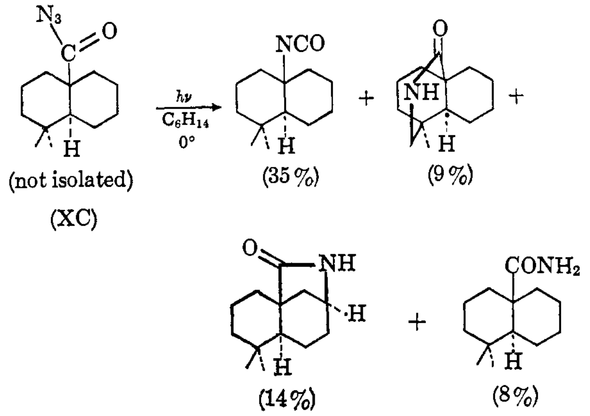
reaction does indeed yield pyridine as reported, then this interesting rearrangement and elimination of a methylene group might be rationalized in modern terms (see Scheme XVIII). This reaction clearly

SCHEME XVIII

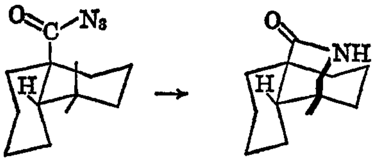


needs to be reinvestigated and the products unambiguously identified.

The acylimido intermediate from the photochemical decomposition of acid azides may be partially intercepted if a C–H bond is stereochemically suitably located to permit reaction of the activated imido intermediate with it before it can rearrange to the isocyanate (13, 21, 22, 203, 204). Irradiation of azides of diterpenoid acids with 1α- and 1β-carboxyl groups gave the corresponding isocyanates and *ca.* 25% yield of lactams. For example, the *trans-anti-cis*-azide (LXXXIII) gave the isocyanate (LXXXIV) (65%), the δ-lactam (LXXXV), and a trace of a γ-lactam (either LXXXVI or LXXXVII); the azide of the methyl ether of podocarpic acid (LXXXVIII) gave a 25% yield of the δ-lactam (LXXXIX) (22). Thermolysis of LXXXIII gave only LXXXIV. The apparent preferential formation of a piperidone over a pyrrolidone ring contrasts markedly with the suggested stereochemical requirement for such reactions as proposed by Barton and Morgan (35) if a hydrogen-abstraction mechanism is involved, but not if an insertion into a C–H bond takes place *via* a six-membered ring transition state (see Scheme XIX). Using a simpler system, Meyer and Levinson (204) found that slightly more γ-lactam was formed than δ-lactam, in contrast to the results of ApSimon and Edwards. From the *cis*-decalin derivative (63) the *cis*-δ-lactam (XCII) is



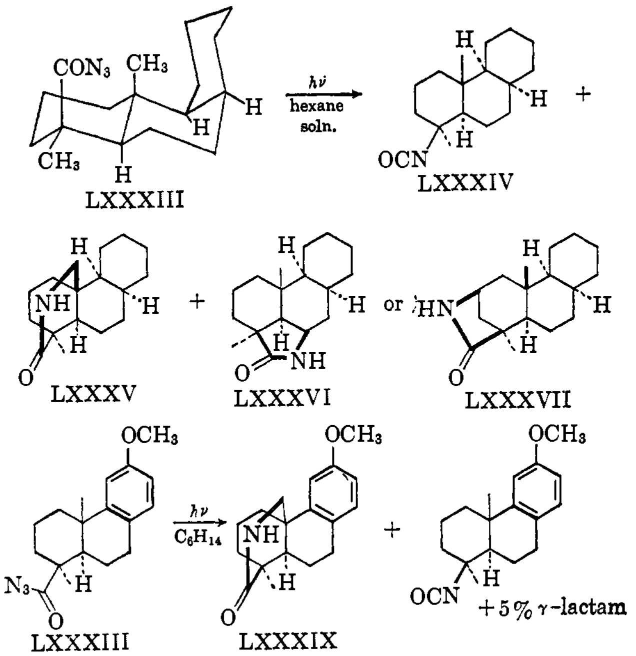
obtained predominantly. It has been suggested (204) that there is no strong preference for piperidone over pyrrolidone formation (22) or methyl over methylene



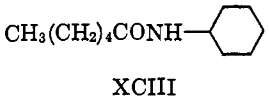
XCI XCII

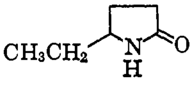
attack; instead, the accessibility of the δ-hydrogens and the inaccessibility of the γ-hydrogens played an important role in the high selectivity observed with the resin acid azides. This cannot be the case in the photolysis of hexanoyl azide, however, where mainly isocyanate and some amides (21%) were isolated (22). Of the latter, XCIII (3%), XCIV (3%),

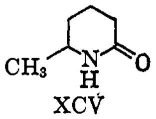
SCHEME XIX

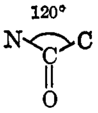


and XCV (12%) were identified (106). The predominance of δ-lactam might be a consequence of the geometry of the oxo imido intermediate

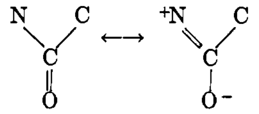

XCIII


XCIV

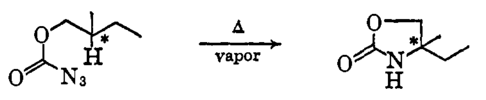

XCV



due to



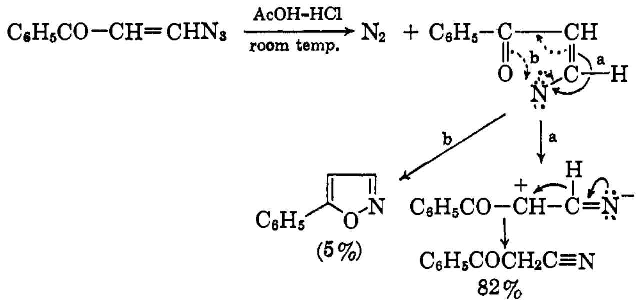
which would tend to make a seven-membered ring transition state required for hydrogen abstraction more favorable (106), or of a C–H insertion reaction, which would still be consistent with Barton's "rule of six." That carbonylimido intermediates can undergo insertion into C–H bonds is demonstrated by the fact that vapor-phase pyrolysis of optically active XCVI gives optically active XCVII ($[\alpha]^{25}_{589}$ +0.354°; $[\alpha]^{25}_{436}$ +1.53°) (288). In this case, five-membered ring formation is apparently preferred since XCVII is formed in 68% yield.



XCVI XCVII

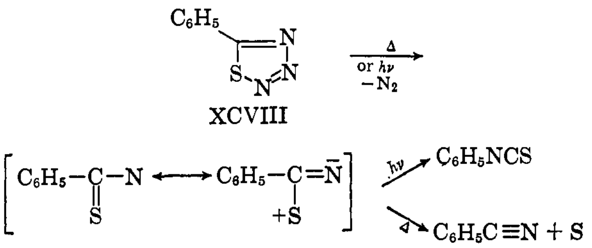
The decomposition of a vinylog of an acid azide in acetic acid and hydrogen chloride at room temperature has been formulated as going *via* an imido intermediate (216) (see Scheme XX).

SCHEME XX



The low temperature necessary to effect the reaction and the presence of acid make it seem doubtful that a discrete imido intermediate is involved here; but whereas one can readily postulate a concerted process after protonation of the azide group to account for the isoxazole, the formation of the nitrile is more difficult to explain in this way.

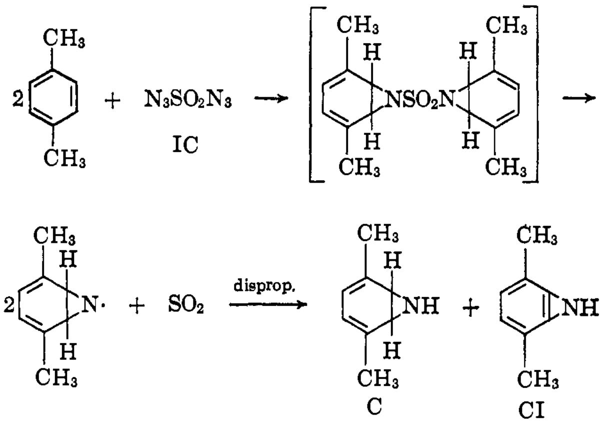
An attempt to trap the acylimido intermediate from the thermolysis or photolysis of succinamoyl azide was unsuccessful (85). An interesting variant on the Curtius rearrangement is the thermal or photochemical decomposition of 5-phenyl-1,2,3,4-thiotriazole (XCVIII) (175, 176).



XCVIII

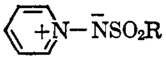
The thermal decomposition of sulfonyl azides was first investigated by Curtius and Schmidt (43, 44, 97). When *p*-xylene was heated with sulfonyl azide (IC), whether under pressure or not, four products were isolated (97): "pseudoxylidine," $C_8H_{11}N$, a liquid with a pyridine-like smell, which formed two (geometrically?) isomeric chloroplatinates, and a picrate; a liquid base, C_8H_9N, with a pyridine-like smell; an odorless, solid base, m.p. 112°, C_8H_9N, which again gave two chloroplatinates; and a neutral solid, C_8N_9N, m.p. 85°, insoluble in hydrochloric acid. Structure C was suggested for "pseudoxylidine" and CI for the pyridine-smelling liquid C_8H_9N. The mechanism proposed is shown in Scheme XXI. *p*-Xylidine, which would have arisen by direct substitution, rather than addition, by NSO_2N followed by hydrolysis, was never found among the products.

SCHEME XXI



The structures of all four products need careful reexamination making use of modern physical methods, particularly in view of Hafner's work with ethyl azidoformate.

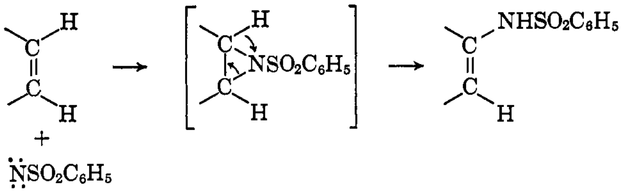
The thermal decomposition of sulfonyl azides in pyridine (95) was shown to yield N-sulfonimidopyridine derivatives (CII) and sulfonamides (CIII) (25, 65). It is reported that methyl acrylate and acrylonitrile polymerized at 110° in the presence of small amounts of decomposing benzenesulfonyl azide (98), and that this polymerization was inhibited by *p*-benzoquinone, but apparently no experimental data have been published in support of this statement. The orientation and partial and total rate factors in the substitution of benzene derivatives by the benzenesulfonimido radical have been studied (98, 136). The results were said to be consistent with an attack of the aromatic nucleus by the electrophilic free radical $C_6H_5SO_2\ddot{N}\cdot$ (136). The failure of compounds with *meta* directing substituents to produce the expected substitution products was attributed to complexing of the radical with the electron-rich substituent group. Benzoyl chloride gave a substitution product (6%) which turned out to be the *meta* isomer exclusively. A number of observations are not explained by the postulated mechanism: (i) The total rate ratios (from competitive reactions between C_6H_6 and C_6H_5X with $C_6H_5SO_2N_3$ at 105–120°) were not much different from unity, as expected for a homolytic substitution. However, the values of the total rate ratios ${}^{CH_3}_{H}K = 1.0$, ${}^{OCH_3}_{H}K = 0.96$, ${}^{OH}_{H}K = 0.80$ are unexpected, since these substituents should facilitate attack by an electrophilic free radical (336) and lead to total rate ratios greater than unity. (ii) The partial rate factor for attack at the *meta* position of toluene is unusually low ($f_m = 0.03$); there is no theoretical reason why f_m should be less than 1 in toluene, either for a free radical or for an electrophilic attack. (iii) Isomer ratios differed somewhat according to whether they were determined under competitive conditions or not. It is felt that this work needs careful quantitative re-examination before any conclusions concerning the mechanism of the reaction are reached. The thermal decomposition of methanesulfonyl azide in toluene indicates that the mesyl derivatives of *o*- and *p*-toluidine are formed (with the former predominating) but that very little *meta* isomer is present (8). The reaction of benzenesulfonyl azide with a refluxing saturated solution of anthracene in chlorobenzene yielded a mixture of anthracene monosulfonamides together with comparable amounts of *o*- and *p*-chlorobenzenesulfonamides. The main product of substitution of the anthracene was the 1-isomer (55%), while the 9-isomer was obtained in 15% yield. Some 2-isomer was also formed (311). Since normal free-radical substitution of anthracene, as well as electrophilic and nucleophilic substitution, take place exclusively at position 9, it was suggested that the sulfonylimido intermediate adds to the 1,2-bond, in agreement with calculated double bond localization energies (64). This suggestion merits futher consideration, particularly in view of the work of Curtius and Schmidt discussed above (97).



CII

RSO_2NH_2

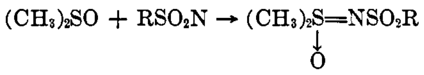
CIII



The thermal decomposition of mixtures of benzenesulfonyl azide and *t*-butyl hydroperoxide exhibits mutually induced decomposition of both reagents (186).

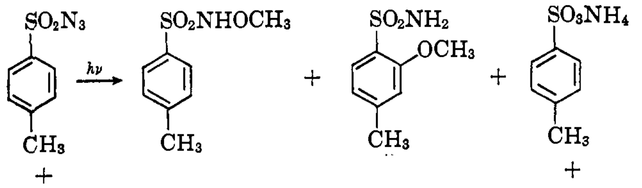
While sulfonyl azides and dimethyl sulfoxide do not react in the dark, photolysis or thermolysis of the azide gives nitrogen and the sulfonylimido intermediate which is trapped by reaction with dimethyl sulfoxide. For example, the thermal decomposition of *p*-methoxybenzenesulfonyl azide in dimethyl sulfoxide gives the sulfoximine in 31% yield, as compared with a 13% yield from the photolysis (142). Superior yields are

$$RSO_2N_3 \rightarrow RSO_2N + N_2$$



$$(CH_3)_2SO + RSO_2N \rightarrow (CH_3)_2\underset{\substack{\downarrow \\ O}}{S}{=}NSO_2R$$

obtained when thioethers are used, these being better able to trap the electrophilic imido intermediate. The photolysis of *p*-toluenesulfonyl azide in methanol gives mainly CIV, together with some CV, some ammonium *p*-toluenesulfonate (from NH → NH_3 + N_2 ?), and a compound of unknown structure (142). The reaction of Chloramine T with thioethers and



+ CH_3OH CIV CV + unidentified product

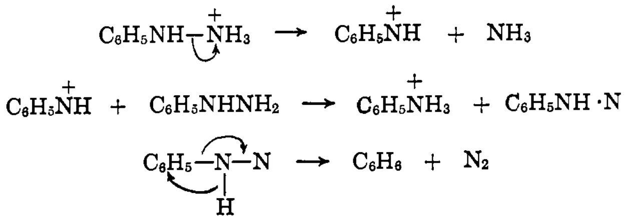
related reactions (308, 325) may involve imido intermediates or could well be concerted SN2-type substitutions.

E. AMINOIMIDO INTERMEDIATES $R_2N{-}N$

The suggestion that the oxidation of phenylhydrazine to anilinoimidogen, $C_6H_5NH{-}N$, might be involved in the formation of osazones [see, however, (112)] was put forward on the strength of the fact that when phenylhydrazine is heated with an equimolar amount of its hydrochloride at 165°, a vigorous reaction takes place in which benzene, aniline, ammonia, and nitrogen are formed (172).

$$C_6H_5NHNH_2 \xrightarrow{[O]} C_6H_5NH{-}N \rightarrow C_6H_6 + N_2$$

This might be explained as

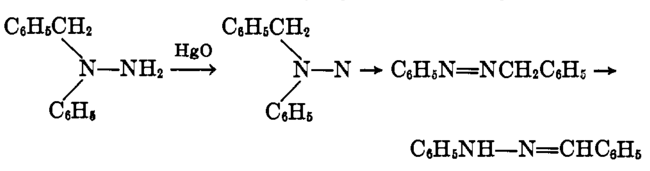


$$C_6H_5NH{-}\overset{+}{N}H_3 \longrightarrow C_6H_5\overset{+}{N}H + NH_3$$

$$C_6H_5\overset{+}{N}H + C_6H_5NHNH_2 \longrightarrow C_6H_5\overset{+}{N}H_3 + C_6H_5NH \cdot N$$

$$C_6H_5{-}\underset{H}{N}{-}N \longrightarrow C_6H_6 + N_2$$

The idea that an aminoimido intermediate could be formed in the mercuric oxide oxidation of unsymmetrically disubstituted benzylarylhydrazines was first put forward by Busch and Lang (74) and a considerable body of "circumstantial" evidence has been amassed since that time in support of that concept. Assuming benzyl migration, the oxidation of N-benzyl-N-phenylhydrazines to aldehyde arylhydrazones may be written



The oxidation of hydrazine itself in solution is more complex (77).

Spectrophotometric and chemical evidence has been obtained for the formation of a diazo-like intermediate (CVII) [stabilized as its conjugate acid (CVI)] in the two-electron oxidation of 1,1-dialkylhydrazines in acid solution (196, 197, 316). The spectral data indicates the absence of tetraalkyltetrazene in the initially oxidized solution of 1,1-dialkylhydrazine unless the acid solution is first neutralized, or the concentration of the ionic intermediate is high. The oxidized species may be reduced quantitatively by $SnCl_2$ in acid solution to the dialkylhydrazine, conditions that would not reduce the tetrazene. A compound $[(CH_3)_2\overset{+}{N}{=}NH]ClO_4^-$ could be isolated by the reaction of iodine, silver perchlorate, and 1,1-dimethylhydrazine in anhydrous ether. 1,1-Diethyl-4,4-dimethyltetrazene was formed as well as tetramethyltetrazene and tetraethyltetrazene when equimolar solutions of 1,1-dimethylhydrazine and 1,1-diethylhydrazine were oxidized separately, mixed, and coupled by careful neutralization of the resultant solution (196). Most of the other evidence for the mechanism of these oxidation reactions is based on the nature of the products obtained, and the fact that identical products result from starting materials other than the hydrazines, the only mechanistic common denominator being an aminoimido intermediate.

$$R_2N\overset{+}{N}H_3 \rightleftarrows 2H^+ + 2e^- + R_2\overset{+}{N}{=}NH \longleftrightarrow R_2N{-}\overset{+}{N}H$$

CVI

$$R_2\overset{+}{N}{=}NH + OH^- \rightleftarrows H_2O + R_2\overset{+}{N}{=}\overset{-}{N} \longleftrightarrow R_2N{-}\ddot{N}$$

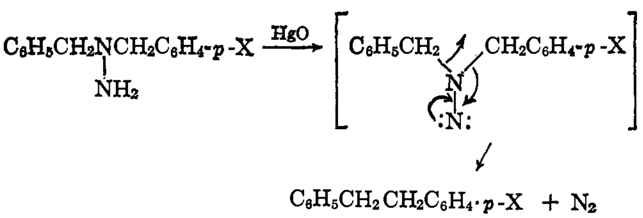
CVII

$$R_2N{-}N \rightleftarrows R_2NN{=}NNR_2$$

or

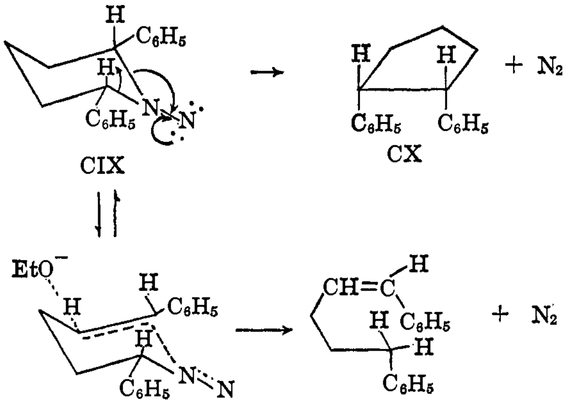
$$R_2NN + R_2\overset{+}{N}{=}NH \rightarrow R_2N\overset{+}{N}H{=}NNR_2$$

The products of oxidation of 1,1-disubstituted hydrazine derivatives has been studied extensively by Overberger and his school. If the oxidation is carried out so that the hydrazine is present in relatively high concentrations, *e.g.*, by the rapid addition of the hydrazine to the oxidizing agent, or by the rapid addition of the solid oxidizing agent to a solution of the amine, the aminoimido intermediate dimerizes to the tetrazene in the so-called "normal" manner (187, 221, 223, 228, 229, 232). If the nitrogen atoms in the aminoimido intermediate may be lost to yield a resonance-stabilized intermediate, then an alternate "abnormal" pathway becomes important, leading to fragmentation and recombination products (140, 223–226, 229). For example, the mercuric oxide oxidation of 1,1-dibenzylhydrazines is of preparative value in the synthesis of "mixed" bibenzyls (CVIII) (81, 140) and is mainly, but not wholly, an intramolecular reaction (231). Another example is the stereospecific oxidation of 1-amino-2,6-diphenylpiperidine in which the *trans* isomer gave mostly *trans*-1,2-di-

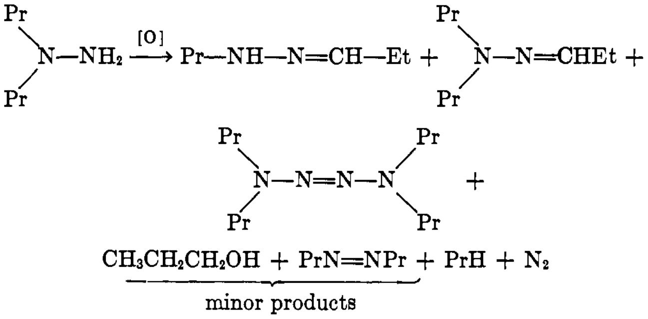


CVIII

phenylcyclopentane, while the *cis* isomer (CIX) gave only *cis*-1,2-diphenylcyclopentane (CX), a smaller amount of 1,5-diphenyl-1-pentene (CXI) being obtained from both hydrazines (224, 226) [see, however, (80)].


CIX CX CXI

The occurrence of tetrazene as the major product when the hydrazine concentration is high, compared to nitrogen elimination when it is low during the course of the oxidation, supports the role of the diazo-like intermediate in the formation of the tetrazene. The latter can arise either by dimerization of the aminoimido intermediate or by its reaction with a molecule of unreacted hydrazine to give a tetrazane which is subsequently oxidized to the tetrazene (187, 223). A recent study of the oxidation of 1,1-dipropylhydrazine (315) supports the formation of aminoimido intermediates which can (i) dimerize to give tetraalkyltetrazenes at low temperatures and high concentrations, (ii) undergo a 1,2-shift from N → N to give monoalkylhydrazones and the tautomeric azoalkanes, (iii) react to alkylate all bases present, presumably *via* the alkyldiimide.



$$Pr_2N{-}NH_2 \xrightarrow{[O]} Pr{-}NH{-}N{=}CH{-}Et + Pr_2N{-}N{=}CHEt + Pr_2N{-}N{=}N{-}NPr_2 + \underbrace{CH_3CH_2CH_2OH + PrN{=}NPr + PrH + N_2}_{\text{minor products}}$$

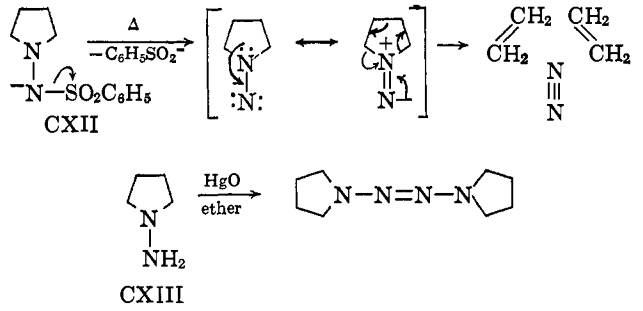
It has been suggested that alkaline degradation of 1,1-dibenzyl-2-benzenesulfonylhydrazides proceeds by an α-elimination of benzenesulfinate ion to give

$$(C_6H_5CH_2)_2\ddot{N}{-}NHSO_2C_6H_5 \xrightarrow{OH^-} (C_6H_5CH_2)_2\ddot{N}{-}\bar{N}{-}SO_2C_6H_5 \longrightarrow$$

$$(C_6H_5CH_2)_2\overset{+}{N}{=}\overset{-}{N} \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

the same aminoimido intermediate as is obtained by the oxidation of the corresponding hydrazine (29, 79, 80, 140) in view of the similarity in the nature of the products obtained in both reactions. More recently, a lack of parallelism between the two reactions has been found, and it has been suggested that different mechanisms are probably involved (187). For example, whereas the thermal decomposition of the sodium salt of N-benzenesulfonamidopyrrolidine (CXII) gives sodium benzenesulfinate, nitrogen, and two molecules of ethylene, the oxidation of N-aminopyrrolidine (CXIII) with mercuric oxide in ether, or of N-amino-2,5-dimethylpyrrolidine with potassium permanganate in acetone (232), leads to the corresponding tetrazene (see Scheme XXII).

SCHEME XXII



CXII CXIII

The sodium hydrosulfite reduction of N-nitroso secondary amines is said to involve the formation of the same aminoimido intermediate as is proposed for the oxidation of the corresponding hydrazines, the products obtained from both types of reaction being very similar (227, 230, 231). The reduction of optically active N-nitroso-α,α'-dimethyldibenzylamine, and the mercuric oxide oxidation of optically active N-amino-α,α'-dimethyldibenzylamine may be taken as an example (231). Similar yields of nitrogen, *meso*-2,3-diphenylbutane, partially optically active isomers, and a trace of styrene were obtained in each case.

$$>N{-}N{=}O \xrightarrow{Na_2S_2O_4} >N{-}NHOH \xrightarrow{B^-}$$

$$N{-}\bar{N}{-}OH \xrightarrow{-OH^-} >N{-}\ddot{N}$$

The intramolecular base-catalyzed rearrangement of sulfonhydrazides, $RCH_2NR'NHSO_2R''$, with alkali to give hydrazones, $RCH{=}NNHR'$, and sulfinic acid, which is first-order kinetically with respect to the anion of the hydrazide, probably involves the formation of an aminoimido intermediate (CXIV) (82).

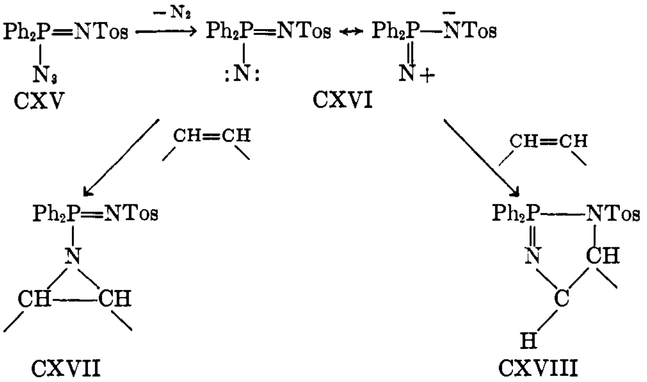
$$TosNHNPhCH_2Ph \xrightarrow{-H^+} Tos\bar{N}NPhCH_2Ph \xrightarrow[\text{slow}]{-Tos^-}$$

$$\underset{\text{CXIV}}{NNPhCH_2Ph} \rightarrow PhCH_2N{=}NPh \downarrow PhCH{=}NNHPh$$

F. MISCELLANEOUS IMIDO INTERMEDIATES

P-Diphenyl-N-tosylphosphazene azide (CXV) decomposes above 220° (a copper catalyst lowers the decomposition temperature to 120°) with the elimination of a molecule of nitrogen, and is postulated to give an unstable imido intermediate (CXVI) which can be formulated as a 1,3-dipole in a mesomeric structure. Reaction with the strained double bond of dicyclopentadiene traps the intermediate in the form of a 1:1 adduct which could either be the aziridine (CXVII) formed by addition of the imido intermediate, or the Δ^1-1,2,5-phosphadiazoline (CXVIII) resulting from a 1,3-dipolar addition (50) (see Scheme XXIII).

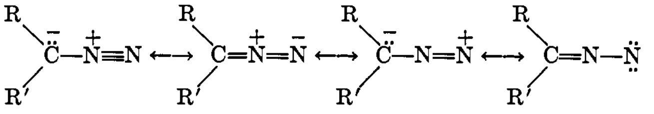
SCHEME XXIII



The photolytic decomposition of triphenylsilyl azide to give products of as yet undetermined structure is believed to involve the formation of the silylimido intermediate (334)

$$Ph_3SiN_3 \xrightarrow[30°]{h\nu} Ph_3Si—N$$

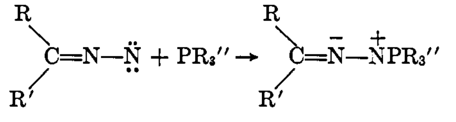
The azide is rather stable thermally, only 50% being destroyed after 10 hr. at 220° in *n*-hexadecane solution.



1,3-dipole

CXIX

The established dual behavior of carbethoxyimidogen, as an imido intermediate on the one hand and as a 1,3-dipole on the other (section IID), suggested the intriguing possibility that other suitable compounds which are known to behave as 1,3-dipoles might also have the properties of imido intermediates. The obvious example is that of diazomethane and its derivatives, one of the possible canonical structures for which would be CXIX. It is interesting to note that such reactions, some of which have already been and others might be attributed to the imido structure, are to be found in the literature (123), *e.g.*, addition to phosphines to give phosphazines



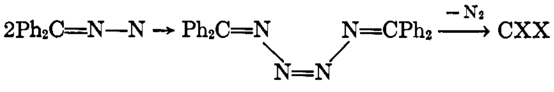
$$RR'C=N—\ddot{N} + PR_3'' \rightarrow RR'C=\overset{-}{N}—\overset{+}{N}PR_3''$$

and pyrolysis yielding ketazines (222, 300)

$$Ph_2\overset{-}{C}—\overset{+}{N}\equiv N \rightarrow Ph_2C: + N_2$$

$$Ph_2C=N—\ddot{N} + :CPh_2 \rightarrow \underset{\text{CXX}}{Ph_2C=N—N=CPh_2}$$

or

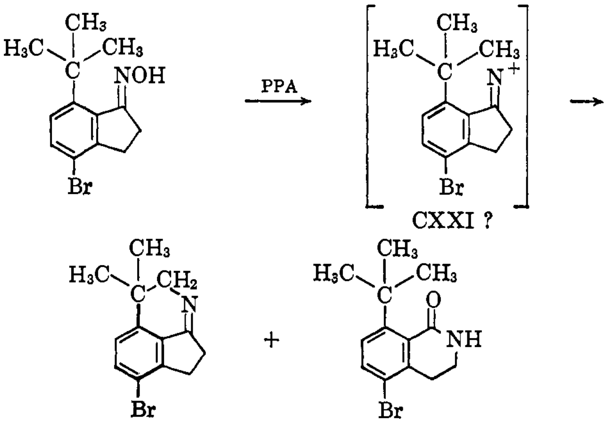


$$2Ph_2C=N—N \rightarrow Ph_2C=N—N=N—N=CPh_2 \xrightarrow{-N_2} \text{CXX}$$

and the photolysis of diphenyl diazomethane to give benzophenone azine (CXX) (177).

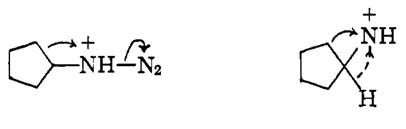
G. IMIDONIUM ION INTERMEDIATES $R\overset{+}{N}R'$

The formation of such intermediates has occasionally been postulated and a few examples have already been mentioned, *e.g.*, the two-electron oxidation product of 1,1-dimethylhydrazine in acid solution, $(CH_3)_2N\text{-}\overset{+}{N}H \longleftrightarrow (CH_3)_2\overset{+}{N}=NH$. The evidence against the intermediacy of such a species in the Beckmann rearrangement has been summarized (275). The isomerization of oximes by polyphosphoric acid observed in some Beckmann rearrangements, however, may best be explained by the suggestion that they occur through an electron-deficient nitrogen $>C=\overset{+}{N}$ (91). Similarly, the formation of imines by electrophilic substitution or insertion at a saturated carbon atom in some Beckmann rearrangements may involve a discrete imidonium ion intermediate (CXXI), though a concerted process (201) is a distinct possibility (182) [see also (23)].

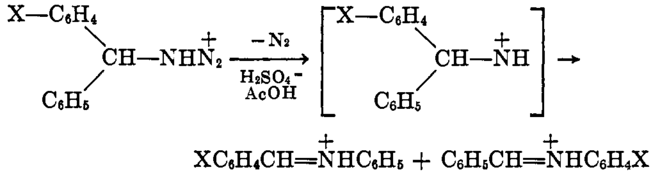


The acid-catalyzed decompositions of azides may be considered to involve either the formation of a protonated imido intermediate, or a concerted elimination of nitrogen from the protonated azido group. The Schmidt reaction has been reviewed (275). In one example in which the formation of an imidonium ion was suggested (28), it has been shown that a concerted process is more likely (24).

When cyclopentyl azide is treated with concentrated sulfuric acid, cyclopentanone imine is obtained in 2.2% yield and piperideine in 79.8% yield (56). This is to be contrasted with the photolysis of cyclopentyl azide in which a 55% yield of imine and a 5% yield of isotripiperideine was reported (35). The predominant formation of piperideine in strong acid might be taken as evidence of participation in the elimination of nitrogen or may reflect a different order of alkyl and hydrogen migratory aptitudes in protonated imido intermediates.

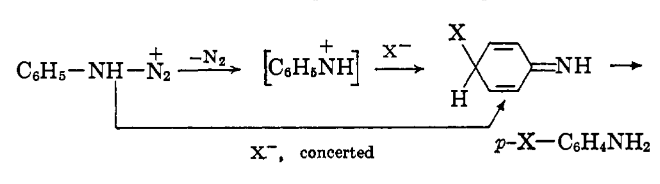


A kinetic study of the acid-catalyzed rearrangement of benzhydryl azides and 1,1-diarylethyl azides led to the conclusion that evolution of nitrogen and migration of an aryl group were not synchronous processes and that, therefore, an imidonium ion intermediate was formed (128). Arguing on the ground that,



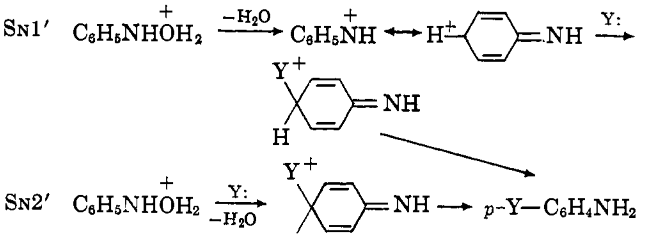
in view of the low basicity of hydrogen azide, one can expect that benzhydryl azides will be protonated to only a small extent by sulfuric acid in acetic acid, and making use of the same rate law as deduced by Gudmundsen and McEwen (128), $d[\text{azide}]/dt = k[\text{azide}]h_0$, Smith reached exactly the opposite view, namely, that migration and nitrogen elimination were concerted (275).

The reactions of aryl azides in acid solution (32, 278) may either be two-step or concerted processes.

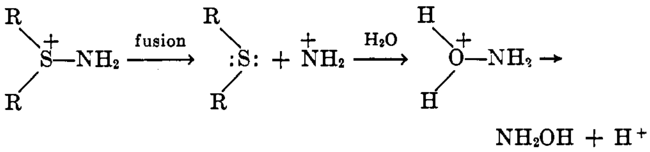


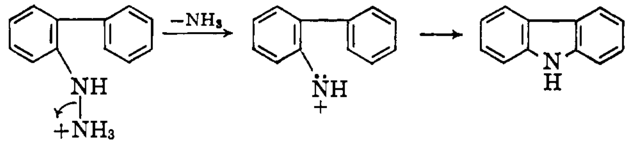
The rearrangement of hydroxylamines (31) may also be regarded an S$_N$1′- or as an S$_N$2′-type process (163b) (see Scheme XXIV). A study of the products which may be obtained (Y = H_2O, C_2H_5OH, CH_3OH, Cl^-, C_6H_5OH, $C_6H_5NH_2$, $NH_2C_6H_4$-p-OH) leads one to assume an active electrophilic intermediate. A kinetic study (137) indicated that a proton was involved in the rate-determining step, and that the rate of the HCl-catalyzed reaction, in which considerable *o*- and *p*-chloroaniline are formed, is independent of the Cl^- concentration. The S$_N$1′ process *via* a discrete phenylimidonium ion intermediate seems the more likely.

Scheme XXIV

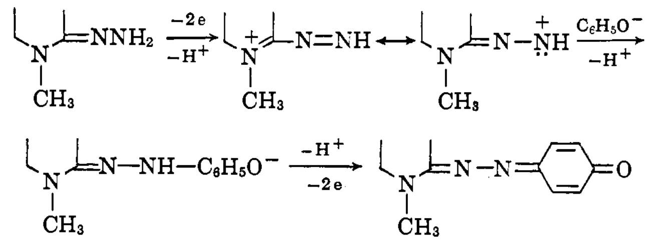


Protonated imidogen itself is thought to result from the fusion of sulfiminium salts (17), and the formation of a phenylimidonium ion has been suggested (174) to account for the formation of carbazole when 2-hydrazinobiphenyl is treated with ethanolic hydrogen chloride (192). It should be noted that no carbazole was formed when 2-azidobiphenyl was treated with HBr (278). A π-complex between a phenylimidonium ion and aniline has been proposed as an intermediate in the benzidine rearrangement (99), but the π-complex hypothesis has been seriously questioned both on kinetic grounds and on the basis of the types of products obtained (162).



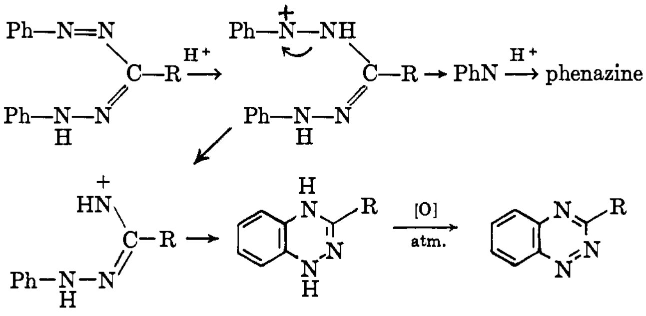


The formation of aminoimidonium and imidonium ion intermediates has been proposed to explain the mechanism of the formation of heterocyclic azo dyes by the oxidation coupling of hydrazones and of unsymmetrical hydrazines (157, 158).



Imidonium ions have also been suggested as possible intermediates in the thermolysis of silylated tetrazoles (46) and the hydrolytic ring opening of diaziridines (307).

The Bamberger synthesis of 1,2,4-benzotriazines from formazans (11, 33) may well also involve imidonium ion intermediates and a possible mechanism might be



III. ELECTRONIC STRUCTURE AND SPECTRA

The evidence presented so far indicates that imido intermediates can exhibit the properties either of triplet diradicals $R-\ddot{N}\cdot$ or of singlet electrophilic reagents $R-\ddot{N}$, and the question as to whether they behave as one or the other in individual reactions has been much discussed in recent literature, *e.g.*, (5, 19, 22, 164, 211, 262, 289, 290, 292, 327), to refer but to a few. The ground state for imido intermediates is expected to be the triplet state (*vide infra*), but, provided a low-lying singlet state exists and conditions for singlet → triplet transitions are suitable (*e.g.*, in the presence of paramagnetic ions), the species might be expected to react in either form. For example, if a singlet imido intermediate is formed in the primary step but finds no suitable substrate with which to react, it might persist long enough to decay to the triplet state, in which form it might be able to react readily. It would be very difficult to predict exactly in which state the imido intermediate generated in the primary step should be. Application of the Wigner spin-conservation rule would suggest that reactions such as the thermal decomposition of azides should lead *initially* to a singlet imido intermediate, whereas a triplet imidogen could arise from the photolysis of azides. In general, one has to be contented with deductions based on the nature of the final products formed, at least until the possibility of trapping the intermediates and studying their spectra *under the reaction conditions* is realized. In some cases, direct chemical evidence has been obtained. For example, the radical character of NH in aqueous solution is said to have been demonstrated unequivocably by the polymerization of acrylonitrile (19), but this work, like that on the benzenesulfonyl azide decomposition, does not appear to have been published yet. When benzoyl azide is irradiated in the presence of acrylonitrile, about 1% of polyacrylonitrile is formed, and this has been taken as evidence that the triplet state cannot be intercepted. A similar result was obtained with phenyl azide (146). The formation, to a small extent, of radicals is, however, indicated.

A. THEORETICAL CALCULATIONS

The electronic structure of imidogen has been calculated both by MO and valence-bond methods. Molecular orbital methods of various degrees of refinement have been used [LCAO–SCF method (138, 245), self-consistent field MO calculations allowing for electron-correlations (160), and configuration interaction (54, 181)] with varying degrees of success to calculate electronic structures of ground and excited states, the dissociation energy, dipole moments, electron populations (117), and the energies of the various states. The ground state is the triplet $^3\Sigma^-$, the lowest excited state the $^1\Delta$, and then the $^1\Sigma^+$. The dissociation energy has also been calculated by a semiempirical valence-bond method (90) and found to be in quite good agreement with the experimental value. The π-electron spin densities for a number of imido intermediates have apparently been computed (296).

B. INFRARED ABSORPTION AND ULTRAVIOLET ABSORPTION AND EMISSION SPECTRA

The ultraviolet and infrared spectra of NH and ND have been measured and analyzed often both for the free species and for the intermediates trapped in a solid matrix at low temperatures. Only some of the more recent work is referred to (101, 114, 127, 237, 238, 304). The effect of the nature of the solid matrix upon the positions of the electronic and vibrational bands of NH has been studied and discussed (173, 199, 255, 256).

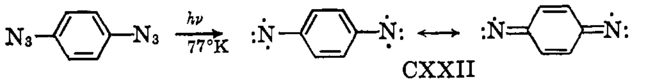
The dissociation energy D (N–H) = 3.7–3.8 e.v. and D (N–D) = 3.4 e.v. could be calculated from the electronic spectra (87, 236, 237, 247). The ionization potential I (NH) = 13.10 ± 0.05 e.v. was measured by electron impact (247).

The emission spectrum of NBr has been measured and the bands assigned (107, 214). The infrared spectra of NCl, NBr, and NF have been studied (207, 210).

C. ELECTRON SPIN RESONANCE SPECTRA

The e.s.r. spectra of imido intermediates generated at 77°K. in a fluorolube matrix by ultraviolet irradiation of the corresponding azide were detected and assigned to the triplet ground state, or to a state just above the ground state, for the following species: $C_6H_5\ddot{N}\cdot$, o-$CF_3C_6H_4\ddot{N}\cdot$, $C_6H_5SO_2\ddot{N}\cdot$, and p-$CH_3C_6H_4SO_2\ddot{N}\cdot$. No resonance was observed for the following: $C_6H_{11}N$, $C_6H_5CH{=}CHN$, C_2H_5OCON, and C_6H_5OCON, probably because they react further too quickly to permit a sufficient stationary concentration to be detected (295). The intensity of the signal for $C_6H_5\ddot{N}\cdot$ was stable at 77°K. for at least 18 hr. after irradiation was discontinued, but disappeared on warming the glass. In addition to $\Delta m = 1$ transitions,

$\Delta m = 2$ (half-field) transitions were observed for C_6H_5N and o-$CF_3C_6H_4N$. The absorptions were observed at considerably higher fields than those observed for phosphorescent states, presumably due to the interaction of unpaired electrons on the same atom (339). A theoretical correlation of substituent effects in ground-state triplet imidogen e.s.r. spectra has been carried out and compared with the $\Delta m = 1$ line positions observed for 11 aromatic imido intermediates (294). The e.s.r. spectrum of a diimido intermediate (CXXII) has been measured at 77°K. (313).



CXXII

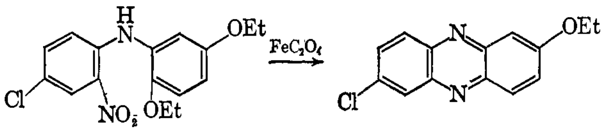
An e.s.r. examination of Smith's solid imido derivative (XLVII) failed to detect the presence of a triplet state (284) so that the electrons must be presumed paired.

IV. SYNTHETIC APPLICATIONS

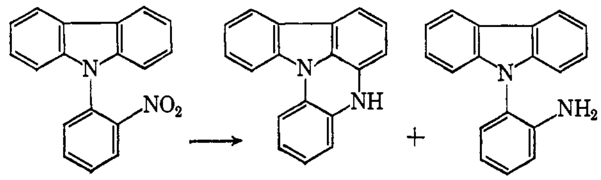
The synthetic possibilities of imido intermediates, including the preparation of azobenzene derivatives and of fluorinated compounds, have been briefly mentioned throughout section II. Only a few of the more recent and interesting applications and general principles will be emphasized in this section.

A. HETEROCYCLIC COMPOUNDS

Intramolecular cyclizations to yield carbazoles, carbolines, phenazines, benzimidazoles, indazoles, triazoles, and related systems have been studied very extensively, are very versatile, and one can visualize many extensions to new ring systems. A few limitations have been noted in these reactions. Thus, in the phenazine synthesis, an alkoxyl group is eliminated in preference to a hydrogen atom whenever both are in the appropriate position for reaction (319, 321). Since an ethoxyl group *meta* to the position of cyclization is never eliminated this might indicate some form of complexing between the imido group and the 2′-alkoxyl group, leading to the elimination. Advantage has been taken of this fact in the selective synthesis

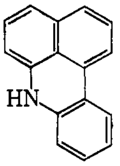


of 2-phenazinols (321). In some cases, 2′-chloro compounds give phenazines in which the chlorine atom has been lost (320). A 2′-amino group may also be eliminated (322). No cyclization occurred with 2-nitrodiphenyl sulfide or the sulfone. In the former case, the only product isolated was the azo compound; in the latter, the amine (323). The cyclization of CXXIII gave only a small amount of CXXIV, the main product being the amine (CXXV) (12). Limitations in the synthesis of carboline derivatives by this method have also been discussed (3).

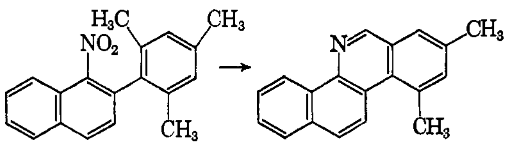


CXXIII CXXIV CXXV

The cyclizations of alkyl and aryl azides through imido intermediates nearly always produce five-membered rings when a choice is possible. The Barton "rule of six" has already been discussed. In a few cases where the structures force the formation of a six-membered ring, yields are low (279). Whereas 2-o-azidophenylnaphthalene cyclized readily to 1,2-benzocarbazole, cyclization of 1-o-azidophenylnaphthalene gave 3,4-benzocarbazole exclusively, no attack at the *peri* position to give CXXVI occurring (280). Insertion by imido intermediates into aliphatic C–H groups has been taken advantage of in the synthesis of the benzo[*c*]phenanthridine ring system (CXXVII) present in a number of alkaloids (7).

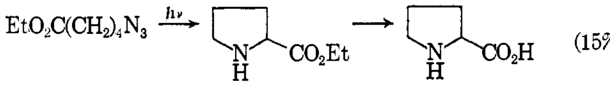


CXXVI



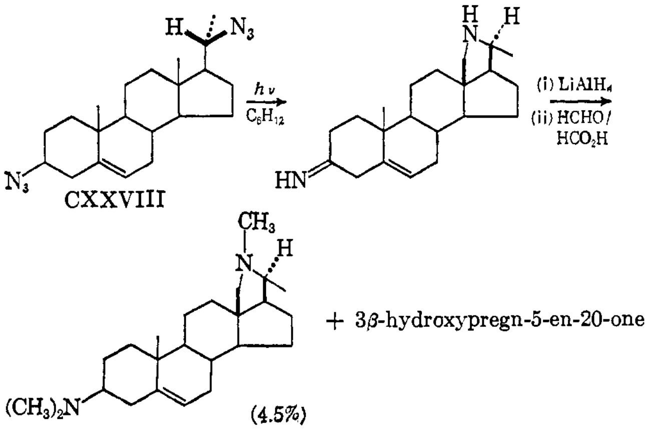
CXXVII

Proline has been synthesized by the photolysis of ethyl δ-azidovalerate (35).



B. DITERPENE AND STEROIDAL ALKALOIDS

An elegant synthesis of conessine (CXXIX) from 3β-20α-bisazidopregn-5-ene (CXXVIII) has been achieved (34, 35).



CXXVIII

+ 3β-hydroxypregn-5-en-20-one

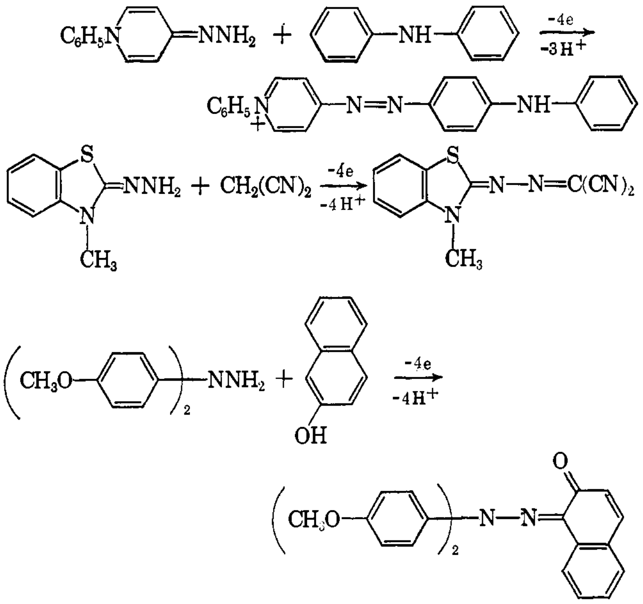
CXXIX

The synthesis of LXXXIX from podocarpic acid methyl ether (LXXXVIII) served to complete the structure proof of the atisine family of alkaloids, the Garrya alkaloids, and related diterpenes, and proved the absolute stereochemistry of these substances (22). The use of the photolytic cyclization of acid azides in the synthesis of diterpene alkaloids has been discussed (204). Such a cyclization followed by a study of the n.m.r. spectra of the products has permitted the determination of the position of the double bond in isopimaric acid (13).

C. HETEROCYCLIC AZO DYES

The literature on the interesting new dyestuffs that can be obtained by the oxidative coupling of suitable hydrazones and unsymmetrically substituted hydrazines has been summarized (157). Only a few examples will be given here to illustrate the type of reactions involved and products formed (see Scheme XXV).

SCHEME XXV



D. DEAMINATIONS

Difluoramine has been used to convert primary aliphatic amines to alkanes (70). The active species is presumed to be NF, formed from the amine and HNF_2. The mechanism proposed is

$$RNH_2 + HNF_2 \rightarrow [R\overset{+}{N}H_3 \cdot \overset{-}{N}F_2] \rightarrow R\overset{+}{N}H_3F^- + NF$$

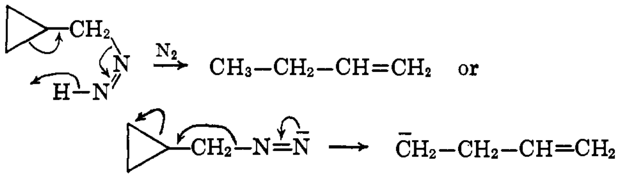
$$RNH_2 + NF \rightarrow R\overset{+}{N}H_2NF^- \rightarrow R\overset{+}{N}H{=}NH \leftrightarrow RNH\overset{+}{N}H$$

$$R\overset{+}{N}H{=}NH + RNH_2 \rightarrow [R\overset{+}{N}H{=}\overset{-}{N} \leftrightarrow RNH\ddot{N}]$$

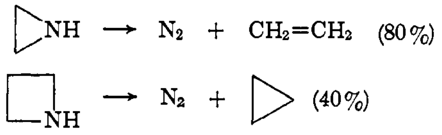
or

$$[RN{=}NH] \rightarrow RH + N_2$$

which is equivalent to $3RNH_2 + HNF_2 \rightarrow 2R\overset{+}{N}H_3F^- + N_2 + RH$. A number of primary aliphatic and aromatic amines have been deaminated in this way in good yield. The final step is similar to that proposed for the deamination of primary amine sulfonamides by the action of hydroxylamine-O-sulfonic acid in basic solution (219). Cyclopropylmethyl amine, however, gives a 46% yield of 1-butene.

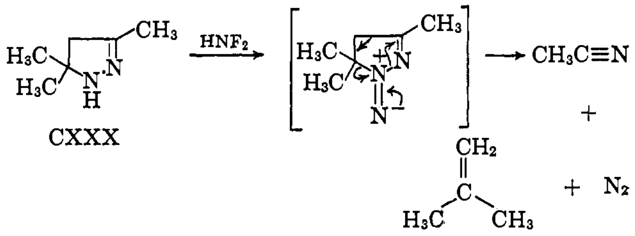


Secondary amines are also deaminated.

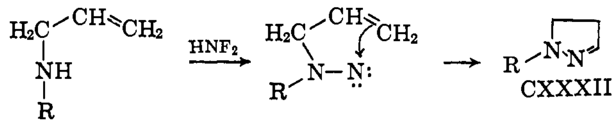


$(C_6H_5CH_2)_2NH \rightarrow N_2 + C_6H_5CH_2CH_2C_6H_5 + C_6H_5CHO$

Formation of an aminoimido intermediate, similar to the one proposed for the oxidation of 1,1-disubstituted hydrazines, is suggested. An interesting fragmentation of CXXX was observed. The secondary amine (CXXXI) reacted with HNF_2 to give the pyrazoline (CXXXII) (67).



CXXX



CXXXI

CXXXII

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