CARBAMOYL AZIDES

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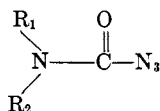
CONTENTS

I. INTRODUCTION

Carbamoyl azides possess the stucture

$$\underset{R_2}{\overset{R_1}{\diagdown}} N - \underset{}{\overset{\overset{O}{\parallel}}{C}} - N_3$$

where R_1 and R_2 may be hydrogen, alkyl, or aryl. This review covers the important articles from about 1910 through December 1963. The shorter name, carbamyl azides, was used by *Chemical Abstracts* until 1952.

The nature and the number of substituents on the amino nitrogen atom of carbamoyl azide exerts considerable influence on the stability and reactivity of these compounds. The preparative methods, spectra, and reactions of carbamoyl azides have been discussed in this review based on the generalizations that are possible.

Caution. Carbamoyl azides are explosive compounds. Investigators planning to work with these compounds should consult the literature and take proper precautions.
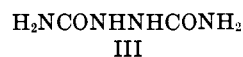
II. PREPARATION OF CARBAMOYL AZIDES

Three general methods have been employed for the preparation of carbamoyl azides: (a) the diazotization of semicarbazide or other compounds containing the carbohydrazide grouping, $RNHCONHNH_2$; (b) the reaction of isocyanates with hydrazoic acid; and (c) the reaction of carbamoyl chlorides with sodium azide.

A. DIAZOTIZATION OF SEMICARBAZIDES

By the action of nitrous acid on semicarbazides, $RNHCONHNH_2$ (R = H, alkyl, or aryl), carbamoyl azides have been prepared.

$$RNHCONHNH_2 + HNO_2 \longrightarrow \underset{II}{RNHCON_3} + 2H_2O$$
$$_{I}$$
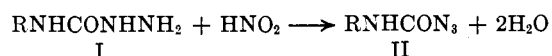
Carbamoyl azide, H_2NCON_3, the parent compound of this series, has been prepared in 70% yield by the treatment of semicarbazide hydrochloride with a solution of sodium nitrite at a low temperature (17). Carbamoyl azide has also been reported to have been prepared by the action of nitrous acid on hydrazodicarbonamide (III) (41). Various values have been reported for the

$$\underset{III}{H_2NCONHNHCONH_2}$$

melting point of carbamoyl azide: 92–94° (15, 41), 95–97° (17), and 97° (8). The azide decomposes on heating with gradual evolution of nitrogen (13).

Several N-monosubstituted carbamoyl azides (II) have been prepared by reacting the N-monosubstituted semicarbazide (I) with nitrous acid: R = $C_6H_5CH_2$, m.p. 94° (18); R = C_6H_5, m.p. 103–104°; $C_6H_4AsO_3H_2$ (14); R = p-BrC₆H₄, m.p. 126° (6). The only N,N-disubstituted carbamoyl azide prepared by the diazotization procedure is the diphenyl derivative (IV), m.p. 78°, starting from N,N-diphenylsemicarbazide (43).
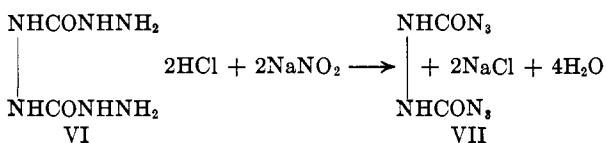
$$\underset{IV}{(C_6H_5)_2NCON_3}$$
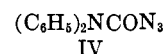
Small quantities of the bisdiphenylamide of hydrazodi-

carbonic acid (V) have also been isolated from this reaction.

$$[(C_6H_5)_2NCONH]_2$$
V
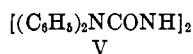
Hydrazidocarbamoyl azide (VII) has been obtained by the action of nitrous acid on dihydrazodicarbonic acid dihydrochloride (VI) in aqueous solution at low temperatures (37). This compound has also been

$$\begin{array}{cc} NHCONHNH_2 & NHCON_3 \\ | & \\ | & 2HCl + 2NaNO_2 \longrightarrow \quad | + 2NaCl + 4H_2O \\ | & \\ NHCONHNH_2 & NHCON_3 \\ \text{VI} & \text{VII} \end{array}$$

obtained in 20% yield as a by-product in the diazotization of carbohydrazide (VIII) (21). Hydrazidocarbamoyl azide explodes on heating and resembles silver or lead azide in explosive properties (21).

$$H_2NNHCONHNH_2$$
VIII

The diazotization of VIII at low temperature in the presence of a solvent yields carbonyl azide (IX; also known as carbonyl nitride)

$$(H_2NNHCONHNH_2) \cdot 2HCl + 2NaNO_2 \longrightarrow$$
VIII
$$CO(N_3)_2 + 2NaCl + 4H_2O$$
IX
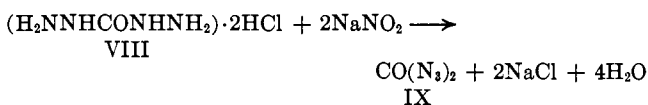
The diazide IX formed an explosive oil and was identified by the formation of sym-diphenylurea when treated with aniline. When the diazotization was carried out by adding a calculated amount of hydrochloric acid to a mixture of the carbohydrazide and sodium nitrite in the absence of solvent, the carbonyl diazide separated out in flocks which, after a period of time, changed into needles. The solid product decomposed with violent explosion even under ice–water (21).

By the reaction of nitrous acid on guanidine carbonylhydrazine hydrochloride (X), guanidine carbonyl azide (XI) has been prepared (42). The product was crystal-

$$H_2NNHCONHC(NH)NH_2 \cdot 2HCl + 2NaNO_2 \longrightarrow$$
X
$$N_3CONHC(NH)NH_2 + 2NaCl + 4H_2O$$
XI
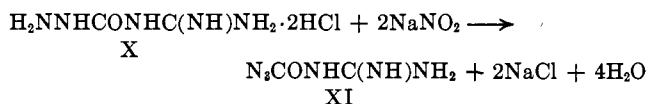
line and exploded on rapid heating. Allophanic acid azide (XII) has been prepared by the diazotization of amidobiuret hydrochloride (42)

$$H_2NNHCONHCONH_2 \cdot HCl + NaNO_2 \longrightarrow$$
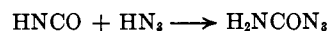$$N_3CONHCONH_2 + NaCl + 2H_2O$$
XII
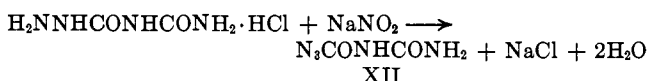
B. REACTION OF ISOCYANATES WITH HYDRAZOIC ACID

Carbamoyl azides (II) have been prepared in good yields by the reaction of isocyanates, RNCO (R = hydrogen, alkyl, or aryl), with hydrazoic acid

$$RNCO + HN_3 \longrightarrow RNHCON_3$$
II
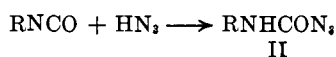
Carbamoyl azide itself was obtained starting from isocyanic acid and hydrazoic acid (15)

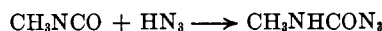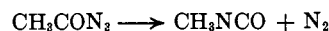$$HNCO + HN_3 \longrightarrow H_2NCON_3$$

The yields were poor owing to the equilibrium nature of the reaction and the hydrolysis of isocyanic acid. A number of N-monosubstituted carbamoyl azides (II) have been prepared by the interaction of the isocyanate with hydrazoic acid at low temperatures in a nonaqueous solvent such as ether (25, 28, 29). Some of the carbamoyl azides (II) prepared by this method are: R = CH_3, m.p. 46–47°; $ClCH_2$, unstable; $BrCH_2$, unstable; C_2H_5, m.p. 12°, b.p. 90° (28 mm.); n-C_3H_7, b.p. 86° (28 mm.); i-C_3H_7, m.p. 44°; i-C_4H_9, b.p. 94° (22 mm.) (28, 29, 34); C_6H_5, m.p. 102–103° (28), 107° (36); α-naphthyl, m.p. 119–120° (25); and 4-bromo-1-naphthyl, m.p. 150° (25).
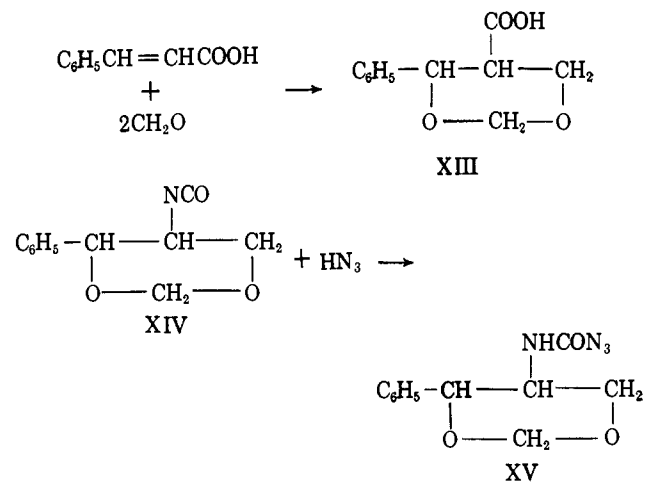
The reaction of ketenes with hydrazoic acid has been employed for the preparation of methylcarbamoyl azide and diphenylmethylcarbamoyl azide, m.p. 122° (27).

$$CH_2=C=O + 2HN_3 \longrightarrow CH_3NHCON_3 + N_2$$
$$(C_6H_5)_2C=C=O + 2HN_3 \longrightarrow (C_6H_5)_2CHNHCON_3 + N_2$$
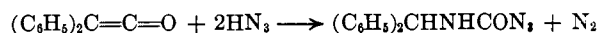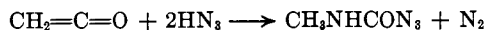
This reaction proceeds through the stage of the isocyanate. Ketene reacts with 1 mole of hydrazoic acid to form an azide intermediate which is unstable, decomposing to nitrogen and methyl isocyanate which in turn reacts with a second mole of hydrazoic acid to yield methylcarbamoyl azide.

$$CH_2=C=O + HN_3 \longrightarrow CH_3CON_3$$
$$CH_3CON_3 \longrightarrow CH_3NCO + N_2$$
$$CH_3NCO + HN_3 \longrightarrow CH_3NHCON_3$$

A dioxane derivative of carbamoyl azide (XV) has been prepared from trans-cinnamic acid and paraformaldehyde using the Prins reaction (4). The procedure involves preparing 4-phenyl-5-isocyanato-1,3-dioxane (XIV) from 4-phenyl-5-carboxy-1,3-dioxane (XIII), by

$$\begin{array}{cc} & COOH \\ C_6H_5CH=CHCOOH & | \\ + & \longrightarrow \quad C_6H_5-CH-CH-CH_2 \\ 2CH_2O & | \quad\quad | \\ & O-CH_2-O \\ & \text{XIII} \end{array}$$

$$\begin{array}{c} NCO \\ | \\ C_6H_5-CH-CH-CH_2 \quad + HN_3 \longrightarrow \\ | \quad\quad\quad | \\ O-CH_2-O \\ \text{XIV} \end{array}$$

$$\begin{array}{c} NHCON_3 \\ | \\ C_6H_5-CH-CH-CH_2 \\ | \quad\quad\quad | \\ O-CH_2-O \\ \text{XV} \end{array}$$

way of the acid chloride and the acid azide. 4-Phenyl-5-azidocarbamido-1,3-dioxane (XV) melts at 158°.

TABLE I

IMPORTANT GROUP FREQUENCIES (CM.$^{-1}$) OF CARBAMOYL AZIDES,[a] $R_1R_2NCON_3$

R_1	R_2	$2\nu_4$ or $(\nu_4 + \nu_5)$	ν_1	ν_2	ν_3	ν_4	ν_5	ν_x
H	H	...	2160	1715	1585	1217	1135	...
H	CH₃	2440	2150 / 2275[b]	1710	1525	1225	1165	1045 / 910
H	C₆H₅	2400 / 2340	2141 / 2164[b] / 2195[b]	1725	1525	1212	1175	948
CH₃	CH₃	2460	2160 / 2200[b]	1700	...	1225	1175	1065 / 968
C₆H₅	C₆H₅	2450 / 2400	2162 / 2200[b]	1695	...	1220	1150	1070 / 1030 / 975

[a] ν_1, asymmetric N_3 stretching; ν_2, amide I band (carbonyl stretching); ν_3, amide II band; ν_4, symmetric N_3 stretching; ν_5, C-N stretching (?); ν_x, other bands. [b] These bands are generally weaker than the main N_3 asymmetric stretching band and often appear as shoulders on the main bands.

## C. REACTION OF CARBAMOYL CHLORIDES WITH SODIUM AZIDE

Several N,N-disubstituted carbamoyl azides (XVI) have been prepared by the reaction of carbamoyl chlorides with sodium azide

$$R_1R_2NCOCl + NaN_3 \longrightarrow R_1R_2NCON_3 + NaCl$$
XVI

The yields of XVI are in the range of 60–80% (33, 35, 39, 40). The substituents R_1 and R_2 may be alkyl or aryl. However, N,N-diethylcarbamoyl azide could not be prepared by this procedure (20). The various N,N-disubstituted carbamoyl azides prepared by this method are: $R_1 = R_2 = CH_3$, m.p. 59°; i-C₄H₉, m.p. 113–115°; and i-C₅H₁₁, m.p. 146–149° (40); $R_1 = CH_3$ and $R_2 =$ C₆H₅, liquid; o-tolyl, oil (39); $R_1 = C_2H_5$ and $R_2 =$ C₆H₅, m.p. 43°; o-tolyl, oil; p-tolyl, oil; α-naphthyl, m.p. 100° (39, 40); $R_1 = C_6H_5$ and $R_2 = C_6H_5CH_2$, oil (40); C₆H₅, m.p. 75–76° (33), 86° (35); α-naphthyl, m.p. 89°; β-naphthyl, oil (40); $R_1 = R_2 = p$-tolyl, m.p. 78°; and β-naphthyl, m.p. 124° (40). α-Phenyl-β-benzalhydrazocarbonyl azide (XVI, $R_1 = C_6H_5$ and $R_2 = N=CHC_6H_5$) and α-phenyl-β-o-chlorobenzalhydrazocarbonyl azide (XVI, $R_1 = C_6H_5$ and $R_2 = N=CHC_6H_4Cl$) have been prepared in greater than 90% yield by refluxing the corresponding carbamoyl chlorides with sodium azide (40).

III. INFRARED SPECTRA

The infrared spectrum of phenylcarbamoyl azide was reported by Scott (30). Lieber and co-workers (22a) have recently studied the infrared spectra of carbamoyl azides in detail. The important group frequencies are summarized in Table I. All the carbamoyl azides show characteristic azide group frequencies around 2150 and 1220 cm.$^{-1}$, thus eliminating the possibility of the 5-substituted 1,2,3,4-oxatriazole structure (XVII). This is interesting in view of the fact that thiocarbonyl

$$\begin{array}{c} -C-O \\ \| \\ N \diagdown \diagup N \\ N \end{array}$$
XVII
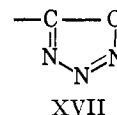
azides do not exhibit the azide frequencies and possess the cyclic 1,2,3,4-thiatriazole structure (22b). None of the compounds show indication of any O–H band. Some of the azides show bands around 2400 cm.$^{-1}$ probably due to the first overtone of the N_3 symmetric stretching band or a combination band of ν_4 and ν_5. The carbonyl stretching (amide I) band and the amide II band (only NH bending in the case of carbamoyl azide) are found in the expected regions (29a). Secondary carbamoyl azides show the NH stretching as a doublet (3460, 3340 cm.$^{-1}$), the weak characteristic secondary amide band around 3070 cm.$^{-1}$, and the amide III band around 1300 cm.$^{-1}$. Anomalous splitting of the asymmetric stretching band of the azide group is found in the case of a few compounds. The splitting has been explained as due to Fermi interaction of ν_1 with a combination tone of ν_4 or ν_5 with one of the bands (ν_x) in the 1070–910-cm.$^{-1}$ region listed in Table I (22a). The origin of ν_x is not understood.
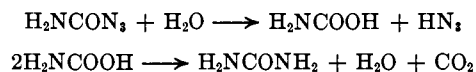
IV. REACTIONS

A. REACTIONS INVOLVING THE DISPLACEMENT OF THE AZIDE GROUP (DECOMPOSITION OF CARBAMOYL AZIDES)

All the carbamoyl azides decompose on heating with evolution of nitrogen, some with explosive violence. If the decompositions are carried out in solvents, the nature of the decomposition and products depend on the solvent employed and the substituents on the carbamoyl azide.
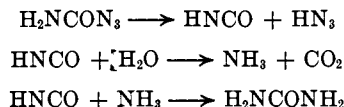
Carbamoyl azide decomposes readily when heated in aqueous solution evolving carbon dioxide and forming ammonium azide (13)

$$H_2NCON_3 + H_2O \longrightarrow CO_2 + NH_4N_3$$
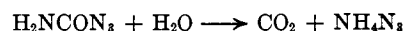
Small quantities of urea have also been isolated. It is postulated that the urea arises from carbamic acid

$$H_2NCON_3 + H_2O \longrightarrow H_2NCOOH + HN_3$$

$$2H_2NCOOH \longrightarrow H_2NCONH_2 + H_2O + CO_2$$

The urea may also result from a sequence of reactions in which the primary step is the decomposition of carbamoyl azide into isocyanic and hydrazoic acids (15)

$$H_2NCON_3 \longrightarrow HNCO + HN_3$$

$$HNCO + {}^\cdot H_2O \longrightarrow NH_3 + CO_2$$

$$HNCO + NH_3 \longrightarrow H_2NCONH_2$$

On heating an aqueous solution of carbamoyl azide with 2 moles of carbon dioxide-free sodium hydroxide and barium chloride solution, a white precipitate of barium carbonate was found. The formation of isocyanic acid has been confirmed by the development of a deep blue color of sodium cobalticyanate when a solution of carbamoyl azide is warmed with sodium acetate and cobalt acetate (15).

A comparison of carbamoyl azide with guanyl azide is of interest. Guanyl azide is known to decompose to cyanamide and hydrazoic acid (15)

$$H_2NC(NH)N_3 \longrightarrow H_2NCN + HN_3$$
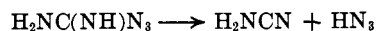
Guanyl azide readily cyclizes to the isomeric 5-aminotetrazole (XVIII) while carbamoyl azide does not undergo this cyclization (16, 22a).

XVIII
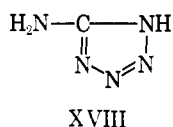
N-Alkylcarbamoyl azides decompose in the presence of cold alkali to carbamic and hydrazoic acids, the carbamic acid subsequently decomposing to the amine and carbon dioxide (27, 29)

$$CH_3NHCON_3 \xrightarrow[H_2O]{OH^-} CH_3NHCOOH + HN_3$$

$$CH_3NHCOOH \longrightarrow CH_3NH_2 + CO_2$$
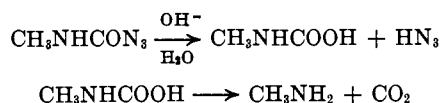
Phenylcarbamoyl azide decomposes at high temperature in solution to yield phenyl isocyanate and hydrazoic acid (26)

$$C_6H_5NHCON_3 \longrightarrow C_6H_5NCO + HN_3$$
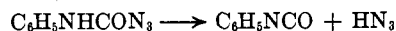
When phenylcarbamoyl azide was heated with water in a sealed tube, sym-diphenylurea, hydrazoic acid, and carbon dioxide were produced (6)

$$2C_6H_5NHCON_3 + H_2O \longrightarrow$$
$$C_6H_5NHCONHC_6H_5 + 2HN_3 + CO_2$$

When treated with hot sulfuric acid, phenylcarbamoyl azide gives rise to aniline, hydrazoic acid, and carbon dioxide (27).

Hydrazidocarbamoyl azide (VII) is hydrolyzed by boiling water forming hydrazoic acid, hydrazine, and carbon dioxide (37)

$$N_3CONHNHCON_3 + 2H_2O \longrightarrow 2HN_3 + N_2H_4 + 2CO_2$$
VII
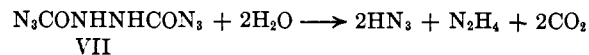
Guanidine carbonyl azide (XI) decomposes to guanidine, hydrazoic acid, and carbon dioxide (42) in hot water. Allophanic acid azide (XII) similarly gives urea, hydrazoic acid, and carbon dioxide, on heating with water (42).

The azide group in carbamoyl azides is readily replaced by other functional groups, forming hydrazoic acid as one of the products. Carbamoyl azides on refluxing with ethanol eliminate the azide group and form esters of carbamic acid (urethanes) (6, 13)

$$R_1R_2NCON_3 + C_2H_5OH \longrightarrow R_1R_2NCOOC_2H_5 + HN_3$$
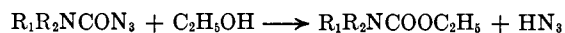
The only exception to this general reaction is the reported Curtius rearrangement of diphenylcarbamoyl azide to 1,1-diphenyl-2-carbethoxyhydrazine (XIX) in 90% yield (33)

$$(C_6H_5)_2NCON_3 + C_2H_5OH \longrightarrow (C_6H_5)_2NNHCOOC_2H_5 + N_2$$
XIX
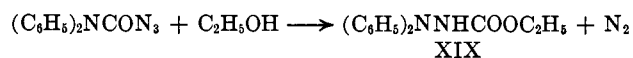
Carbamoyl azides react with ammonia forming the urea and hydrazoic acid (24, 27, 29)

$$RNHCON_3 + NH_3 \longrightarrow RNHCONH_2 + HN_3 \text{ (R = alkyl)}$$

Primary amines, such as aniline, react with carbamoyl azide to form hydrazoic acid and the urea derivative (32). Alkylcarbamoyl azides and aniline react to yield alkylphenylurea (27, 29)

$$RNHCON_3 + C_6H_5NH_2 \longrightarrow$$
$$RNHCONHC_6H_5 + HN_3 \text{ (R = alkyl)}$$

Similarly, phenylcarbamoyl azide yields sym-diphenylurea and hydrazoic acid on reaction with aniline (25). α-Naphthylcarbamoyl azide as well as its 4-bromo derivative behave in an analogous manner (25). Dimethylcarbamoyl azide reacts with excess of aniline or cyclohexylamine to yield sym-diphenylurea or dicyclohexylurea (31). The replacement of the azide group as well as the diphenylamino group has also been reported in the reaction with diphenylcarbamoyl azide (33). The action of amines in ethanolic or pyridine solutions on diphenylcarbamoyl azide does not result in the replacement of the azide group; instead, rearrangement occurs forming N,N-diphenyl-4-substituted semicarbazides. With large excess of amines whose pK_a values range from 9.7 to 11.2 and whose boiling points are below 110°, the replacement of the azide group has been observed (31, 33). This reaction has been studied with allylamine, amylamines, piperidine, and pyrrolidine. If the boiling points of the amines are above 185°, replacement of both the azide and the diphenylamino groups takes place with the formation of sym-disubstituted ureas. This reaction has been observed with benzylamine, β-phenylethylamine, n-decylamine,

and phenetidine (33). Carbonyl diazide also reacts with aniline giving *sym*-diphenylurea and hydrazoic acid (9).

Carbamoyl azides react with hydrazine in a manner analogous to primary amines. Thus, carbamoyl azide reacts with hydrazine to yield hydrazodicarbonamide (32)

$$2NH_2CON_3 + N_2H_4 \longrightarrow NH_2CONHNHCONH_2 + 2HN_3$$

Similarly, dimethylcarbamoyl azide reacts with hydrazine to form the dimethylamide of hydrazodicarbonamide (31)

$$2(CH_3)_2CON_3 + N_2H_4 \longrightarrow$$
$$(CH_3)_2NCONHNHCON(CH_3)_2 + 2HN_3$$
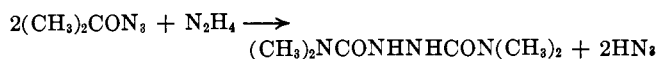
Phenylhydrazine reacts with α-naphthylcarbamoyl azide to produce 1-α-naphthyl-4-phenylsemicarbazide (25). With glycine in aqueous medium, phenylcarbamoyl azide gives rise to phenyl ureidoacetic acid (XX) (12)

$$C_6H_5NHCON_3 + H_2NCH_2COOH \longrightarrow$$
$$C_6H_5NHCONHCH_2COOH + HN_3$$
$$XX$$
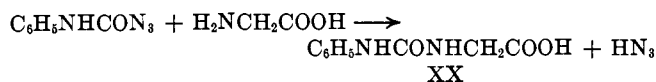
Grignard reagents react with carbamoyl azides in two ways: (a) by displacing the azido group, or (b) by adding to the azido group to form triazenes. Phenyl- and ethylcarbamoyl azides react with phenylmagnesium bromide giving benzanilide and ethylbenzamide, respectively (25).

$$RNHCON_3 + C_6H_5MgBr \longrightarrow$$
$$RNHCOC_6H_5 \ (R = C_6H_5 \text{ or } C_2H_5)$$

Carbamoyl azide and hydrazocarbonazide react with phenylmagnesium bromide to form benzazourea (XXI; phenyltriazenecarbonamide) and the secondary hydrazide of phenyltriazenecarbonic acid (XXII), respectively (2)

$$\begin{array}{cc} H_2NCONHN{=}NC_6H_5 & NHCONHN{=}NC_6H_5 \\ XXI & | \\ & NHCONHN{=}NC_6H_5 \\ & XXII \end{array}$$
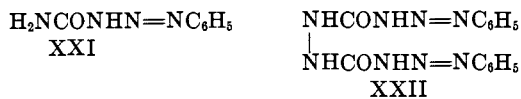
B. REACTION INVOLVING IMIDO INTERMEDIATES (1a): THE CURTIUS REARRANGEMENT

Bertho (3), in reviewing the work of Curtius on azides, included carbamoyl azides under the class of *rigid azides*. According to Bertho, organic acid azides can be broadly divided into two types: (a) the acid azides where the carboazido group, $-CON_3$, is attached to a carbon atom, and (b) the *rigid azides*. The former class of azides is characterized by their tendency to undergo the Curtius rearrangement while the rigid azides are indifferent to such rearrangement. In the latter class of azides Bertho included the aliphatic and aromatic sulfonazides, RSO_2N_3, and the carbonazides where the $-CON_3$ group is linked to a nitrogen or oxygen atom. Bertho's inclusion of carbamoyl azides under rigid azides was based on the observation (6, 10) that

phenylcarbamoyl azide does not undergo any rearrangement. However, it is now well established that some carbamoyl azides do undergo rearrangements.
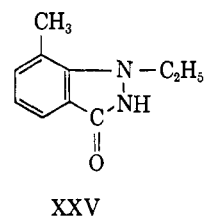
Diphenylcarbamoyl azide, when refluxed in xylene or tetralin, decomposes to give nitrogen and 1-phenylindazolone (XXIII) (35, 39)
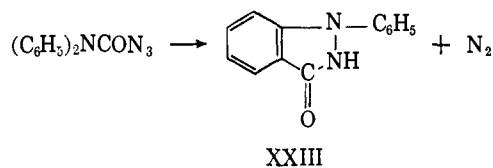

XXIII

It was suggested that the intermediate is the imido radical, $(C_6H_5)_2NCO\ddot{N}$, which rearranges to the isocyanate, $(C_6H_5)_2NNCO$. The isocyanate then cyclizes to form the indazolone (XXIII). Similar reactions have been found in the case of other N,N-diaryl- and N,N-arylalkylcarbamoyl azides (38–40). In addition to indazolone derivatives, appreciable quantities of the isocyanate dimers XXIV have been isolated in some

XXIV
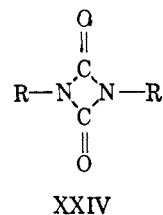
cases. By heating the corresponding isocyanate dimer with sodium hydroxide, the indazolone derivative XXV was obtained (39). On heating the isocyanate dimer


XXV

with aniline, 1-ethyl-*o*-tolyl-4-phenylsemicarbazide (XXVI) is formed. If diphenylcarbamoyl azide is re-
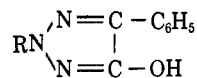

XXVI
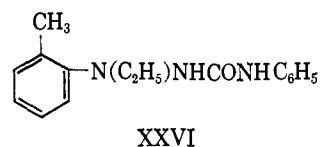
fluxed with ethanol, 1,1-diphenyl-2-carbethoxyhydrazine (XIX) is obtained in good yield (33). Reactions of diphenylcarbamoyl azide with certain amines show evidence for competition between the Curtius rearrangement and the displacement of the azide group (33). Thus, in the reaction with cyclohexylamine a mixture of 1,1-diphenyl-4-cyclohexylsemicarbazide and 1,1-diphenyl-3-cyclohexylurea was obtained. Apparently, the basicity of the reacting amine and the reaction temperature are important factors.

α-Phenyl-β-benzalhydrazocarbonyl azide (XVI, R_1 = C_6H_5; R_2 = N=CHC$_6$H$_5$) and α-phenyl-β-o-chloro-benzalhydrazocarbonyl azide yield nitrogen on refluxing in xylene. The other products isolated were first believed to be the indazolone derivatives XXVII (40).
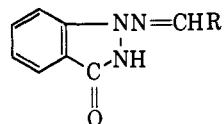

XXVII, R = C_6H_5 or o-ClC$_6$H$_4$

Since these products did not split off the benzal residue, even under drastic hydrolytic conditions (38, 40), the alternate structure XXVIII was suggested (40). It

XXVIII

was later found that no rearrangement had actually taken place in these decompositions and the 1,2,4-tri-azole structure XXIX was therefore suggested (38). This structure was confirmed by comparison with
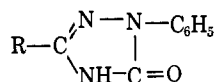

XXIX

authentic specimens of the compounds prepared by independent routes (1b).

The failure of carbamoyl azide and N-monosubstituted carbamoyl azides to undergo the Curtius rearrangement has been explained on the basis of structure (20), as well as on the basis of the electronic requirements of the transition states necessary to bring out the change (32). It has been suggested that these azides exist in the enol form, HN=C(OH)N$_3$ (20). However, recent infrared studies do not support this structure (22a). It has been proposed that the velocity of anionotropic migration (M_v) should be greater than the cyclization velocity (C_v) or the replacement velocity (R_v) in order for reactions of the Curtius type to occur (32). Another explanation based on the lack of electrophilic requirements of the transition state has also been postulated (31, 33).

If carbamoyl azide is heated with benzene or toluene in a sealed tube at 120°, it decomposes forming nitrogen, hydrazoic acid, ammonium azide, cyanuric acid (XXX), and urazole (XXXI) (13). Traces of hydrazodicar-
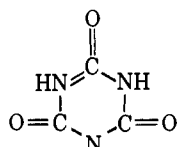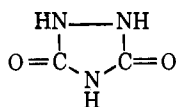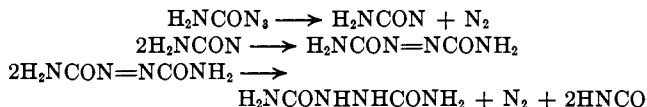

XXX   XXXI

bonamide (III) have also been isolated. After complete removal of the solvent, small quantities of sym-diaryl-urea (the aryl group depending on the solvent) have also been found. The formation of cyanuric acid is simply due to the trimerization of the isocyanic acid which, along with hydrazoic acid, is the primary decomposition product of carbamoyl azide. Ammonium azide could result from the decomposition of hydrazoic acid. Hydrazodicarbonamide (III) most probably results from the dimerization of the imidogen followed by disproportionation

$$H_2NCON_3 \longrightarrow H_2NCON + N_2$$
$$2H_2NCON \longrightarrow H_2NCON=NCONH_2$$
$$2H_2NCON=NCONH_2 \longrightarrow$$
$$H_2NCONHNHCONH_2 + N_2 + 2HNCO$$

Urazole (XXXI) probably results from the interaction of the imido radical with isocyanic acid (23)

$$H_2NCON + HNCO \longrightarrow (H_2NCONHNCO) \longrightarrow XXXI$$
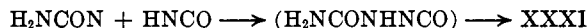
There are other reactions of carbamoyl azide which probably proceed through the imido radical intermediate. Thus, carbamoyl azide when heated with benzene forms phenylurea, evolving nitrogen (3,13). At higher temperatures diarylureas are also formed, the aryl group depending on the solvent employed. Xylene yields sym-dixylylurea. Carbamoylazide reacts with compounds containing active methylene groups releasing nitrogen. Ethyl malonate yields diethyl ureido-malonate (XXXII) and diethyl diureidomalonate (XXXIII) along with nitrogen, ammonium azide, cyanuric acid, and urazole (5). A similar reaction takes place with barbituric acid yielding XXXIV and nitrogen (5). Ethyl fumarate yields ethyl aminocarbonyl-iminosuccinate (XXXV) in 40% yield (7). A small quantity of ethyl carbonyldiaminosuccinate (XXXVI) is also obtained. Compound XXXV has also been ob-
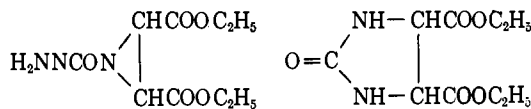
H$_2$NCONHCH(COOC$_2$H$_5$)$_2$
XXXII
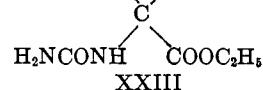
XXIII
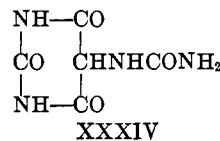

XXXIV

XXXV   XXXVI

tained in low yields from the reaction of carbamoyl azide with ethyl maleate (7).

c. cyclization of carbamoyl azides

Although carbamoyl azide resembles guanyl azide in many of its properties (15), it does not undergo cycliza-

tion to the isomeric tetrazole derivative (16). It had been reported earlier that carbamoyl azide readily cyclized into 5-hydroxytetrazole (44). Subsequent studies failed to verify this observation (16, 32). Recently,

$$H_2NCON_3 \longrightarrow \begin{array}{c} N=C-OH \\ | \quad | \\ N_{\diagdown N}\text{-}NH \end{array}$$
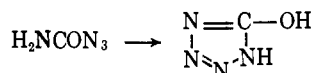
1-aryl-5(4H)-tetrazolinones (XXXVII) have been prepared by the reaction of aluminum azide with aryl iso-

$$\begin{array}{c} R-N-C=O \\ | \quad | \\ N_{\diagdown N}\text{-}NH \end{array}$$
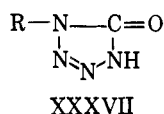
XXXVII

cyanates (19) or phenylcarbamoyl azide (22) in boiling tetrahydrofuran.

Carbamoyl azide reacts with dimethyl acetylenedicarboxylate at 110° to form 1-amido-4,5-carbomethoxy-1,2,3-triazole (XXXVIII) in poor yields (11). This reaction probably proceeds by 1,3-dipolar cycloaddition.

$$\begin{array}{c} H_2NCO-N-C-COOCH_3 \\ | \quad \| \\ N_{\diagdown N}\text{-}C-COOCH_3 \end{array}$$

XXXVIII
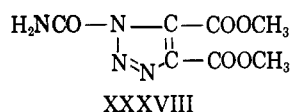
D. OTHER REACTIONS OF CARBAMOYL AZIDES

With a solution of silver nitrate, carbamoyl azide forms a silver salt which is insoluble in water, but readily dissolves in ammonia and dilute nitric acid. The silver salt is highly explosive. On reaction with concentrated nitric acid it decomposes to silver azide, carbon dioxide, and ammonia (15).

On passing hydrogen sulfide into a solution of carbamoyl azide, urea is formed accompanied by the evolution of nitrogen and precipitation of sulfur (15). Hydrogen cyanide adds to carbamoyl azide to form an unstable urea azocyanide (XXXIX) (15)

$$H_2NCON_3 + HCN \longrightarrow H_2NCONHN=NCN$$
XXXIX

It has been reported that carbamoyl azide reacts with nitrous acid forming a diazonium salt (XL) (17)

$$H_2NCON_3 + HNO_2 \longrightarrow \overset{+}{N}_2CON_3 + OH^- + H_2O$$
XL
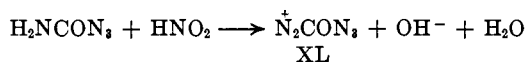
The action of bromine on phenyl- and α-naphthylcarbamoyl azides results in the bromination of the aromatic nucleus (6,25). The reaction of carbamoyl azide with diazomethane is reported to yield the O-methyl derivative XLI (32). Diphenylcarbamoyl azide reacts

$$HN=C(OCH_3)N_3$$
XLI
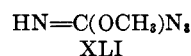
with triphenylphosphine to form N-(diphenylcarbamoyl)triphenylphosphinimine (21a) which slowly decomposes to nitrogen and phosphinimine.

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