U.D.C. 547.23:543.307

Methods for the Cleavage of N-N Bonds in Organic Compounds

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In the review an attempt is made for the first time to give a systematic account of the available extensive literature data on the methods for the dissociation of N-N single bonds in organic compounds. Reductive and acid cleavage, various rearrangements, interaction with oxidants, and thermal and photochemical processes have been examined. In order to account for the characteristics of the dissociation of N-N bonds, data for the energy characteristics of the N-N and N≡N groups are adduced. The bibliography includes 274 references.

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I. INTRODUCTION

Processes involving the dissociation of N–N bonds in both cyclic and acyclic compounds occupy an important place in organic chemistry. They include the classical Fischer, Curtius, and Schmidt reactions, the benzidine rearrangement, and others, each of which has been the subject of serious and thorough reviews. However, there are no reviews giving a general account of different methods for the dissociation of N–N bonds. Even the familiar monograph of Weygand and Hilgetag[1], which constitutes a fairly complete encyclopedia of synthetic methods arranged systematically in accordance with the bond differences in the compounds, contains no section whatsoever dealing with the dissociation of N–N bonds. Other monographs[2-9], in which the general problems of the chemistry of organic compounds with N–N bonds are considered but the reactions involving the dissociation of such bonds are not specified, also fail to fill this gap.

A characteristic feature of a single bond between two nitrogen atoms is the low dissociation energy (37 kcal $mole^{-1}$) compared with other single bonds commonly encountered in organic compounds (for example the dissociation energy is 80 kcal $mole^{-1}$ for C–C, 66 kcal $mole^{-1}$ for C–N, and 64 kcal $mole^{-1}$ for S–S).[10] On the other hand, the linkage with the highest bond multiplicity between nitrogen atoms (N≡N), which is characteristic of molecular nitrogen, has the maximum dissociation energy (225 kcal $mole^{-1}$) compared with the analogous C≡C (198 kcal $mole^{-1}$) and C≡N (209 kcal $mole^{-1}$) bonds[7]. In a saturated system, there is repulsion between the nitrogen *p* orbitals, which makes the N–N bond longer (1.40 Å)[11-13] than the sum of the radii of two nitrogen atoms (2 × 0.53 = 1.06 Å), while a characteristic feature of N≡N is the overlapping of the *p* orbitals, which causes additional bond stabilisation. In particular, the above characteristics are responsible for the behaviour of the relevant substances in chemical reactions. The dissociation of the saturated nitrogen–nitrogen bond takes place very rapidly, much more so than that of the C–C or C–N bonds, and, when competing reactions are possible, the dissociation of the N–N bond takes place preferentially and usually results in the formation of either the corresponding amino-derivative or of unstable products of the nitrene type with an electron sextet at the nitrogen atom. The latter can be stabilised in different ways via addition reactions, rearrangements, etc. The stability of molecular nitrogen noted above, the energy gain in its formation, and its capacity to be removed from the reaction sphere in the form of a gas also have a significant influence. In azides, azines, and other compounds, where the dissociation of N–N bonds with evolution of a nitrogen molecule is possible, this type of process usually takes place preferentially.

The above general features of the cleavage of N–N bonds can be readily traced in different types of reactions discussed in the present review. Naturally, within the framework of a journal article it is impossible to describe all cases of organic reactions involving the dissociation of N–N bonds. Therefore we thought it useful to describe in the review as fully as possible different types of processes at the expense of reducing the number of examples of each.

Together with a description of pioneer investigations, attention was concentrated on a selection of original papers reflecting most fully the scope of the method, the mechanism of the reactions, and their unusual course. The generally known classical reactions are not considered in the review. Whenever possible, references are given in all cases to review articles in which all the remaining literature is quoted.

II. REDUCTIVE CLEAVAGE OF N–N BONDS

The hydrogenolysis of N–N bonds is one of the most familiar methods of converting the various azines, azides, hydrazines, and their derivatives into the corresponding amines. The capacity of zinc in an acid medium to dissociate the N–N bond, observed by Curtius in the

reduction of benzylideneazine and its homologues to mono- and di-benzylamines[14], was subsequently used successfully for the synthesis of aromatic perfluorodiamines from hydrazones[15] in the course of the complete synthesis of sphingosine[16]. Various reducing agents are employed to convert arylhydrazones and hydrazines into amines in the synthesis of aminosugars[17-22] and aminoacids[23,24].

The reduction of arylhydrazones of α-ketoacids constitutes the basis of the synthesis of aminoacids via the mechanism

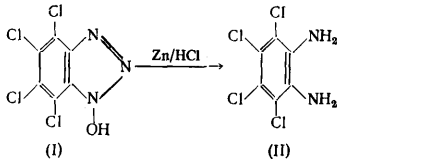
$$RCH(OAc)COOEt \rightarrow R{-}C(=N{-}NHPh)COOH \rightarrow R{-}CH(NH_2)COOH .$$

developed by Feofilaktov and coworkers[25-31].

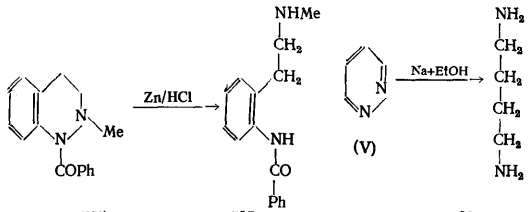
Catalytic methods have found extensive applications in the dissociation of N–N bonds in azines, hydrazines, hydrazides, and hydrazones[32-46]. Catalytic reduction has been used also for the conversion of sulphonyl hydrazides into sulphonamides[47].

Earlier studies on the reductive cleavage of N–N bonds in hydrazines and their derivatives by chemical and catalytic methods have been discussed[48-50] and other reports have dealt with the polarographic reduction of arylhydrazones[51,52].

The N–N bonds in heterocyclic N–N systems have also been successfully cleaved by reductive methods[34,38,53-55] and the conversion of, for example, the benzotriazole derivative (I) into o-phenylenediamine (II),[56] of tetrahydrocinnoline (III) into the o-aminoethylphenylamine derivative (IV),[57] of pyridazine (V) into 1,4-diaminobutane (VI,[58] etc. has been achieved.

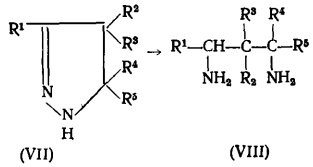


(I) (II)



(III) (IV) (VI)

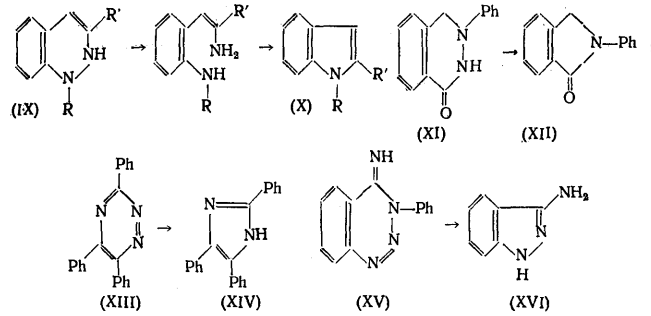
The hydrogenolysis of pyrazolines (VII) over a nickel catalyst constitutes the basis of the preparative synthesis of 1,3-diamines (VIII) developed by Kost and coworkers[59,60]:



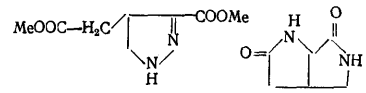
(VII) (VIII)

The hydrogenolysis of cyclic hydrazines derived from 3,5-dioxopyrazolidines over a nickel catalyst was investigated in detail by Moldaver and coworkers[61-63]. The electrochemical reduction of heterocyclic N–N compounds has been described in a review[64].

In many cases the diamines formed on reduction of cyclic hydrazine derivatives can recyclise, becoming converted during the reaction into other heterocycles. Indoles (X) from cinnolines (IX),[65-69] phthalimidine (XII) from dihydrophthalozolone (XI),[70] imidazole (XIV) from triazine (XIII),[71] and indazole (XVI) from benzotriazine (XVI)[72] have been obtained in this way:

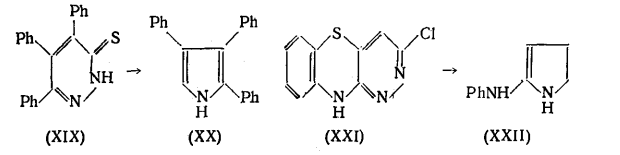


An interesting reaction was observed in the catalytic reduction of methyl 3-methoxycarbonylpyrazoline-4-acetate (XVII) where the diamine formed in the hydrogenation reaction is cyclised into a dilactam (XVIII):[73]



(XVII) (XVIII)

Unexpected results were obtained on heating 3-mercapto-4,5,6-triphenylpyridazine (XIX) with Raney nickel, when 2,3,4-triphenylpyrrole (XX) was isolated as the desulphurised product[74] and in the reduction of 5-chloro-3,4-diazaphenothiazine (XXI) in the presence of the same catalyst where the elimination of sulphur and the halogen was accompanied by the dissociation of the N–N bond, the elimination of ammonia, and the closure of the pyrroline ring with formation of compound (XXII):[75]



(XIX) (XX) (XXI) (XXII)

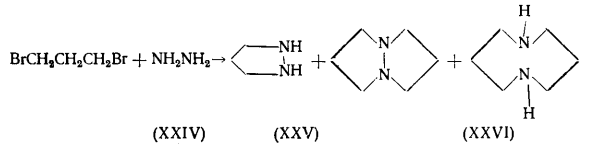
The cleavage of the N–N bond in 1-(2′-diethylaminoethyl)-2-phenylisopropylhydrazine (XXIII) on refluxing with hydrochloric acid without the addition of reducing agents was described by Elslager et al.[76]:

$$PhCH_2CH(Me)\underset{(XXIII)}{NHNH(CH_2)_2NEt_2} \longrightarrow$$
$$\rightarrow PhCH_2CH(Me)NH_2 + H_2N(CH_2)_2NEt_2 .$$

Probably a molecule of the initial compound (XXIII) behaves in this case as a reducing species; this mechanism is supported by the detection of phenylacetone in the reaction products.

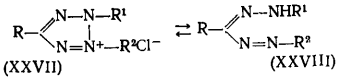
A mechanism involving a diarylnitrenium ion has been proposed for the cleavage of tetra-arylhydrazines under the influence of acids to diarylamines and a stable radical-cation[77] and the homolytic cleavage of N–N bonds in tetra-arylhydrazines has been discussed in two reports[79,80]. The oxidation–reduction reaction involving the initial compound evidently takes place when hydrazine interacts with 1,3-dibromopropane, which results in the formation,

together with pyrazolidine (XXIV) and a bicyclic hydrazine (XXV), also of bistrimethylenedi-imine (XXVI):[81]



(XXIV) (XXV) (XXVI)

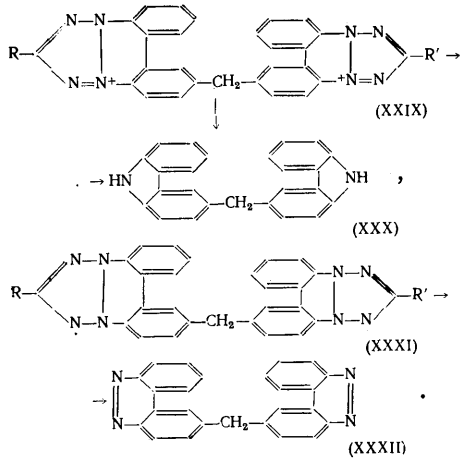
The reduction of quaternary tetrazolium salts (XXVII) with dissociation of the N–N bond and the formation of the formazan (XXVIII) takes place under the influence of bacteria, yeasts, germinating seeds[82], and also on treatment with ammonium sulphide[83] or on a cation-exchange resin treated with sodium dithionite[84]:



(XXVII) (XXVIII)

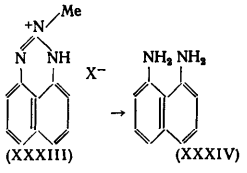
In the oxidation of formazan, quaternary tetrazolium salts are readily reformed[83]. The ease of the interconversion by a similar mechanism of substituted triazolium salts and 2-phenylamino-1-phenylazonaphthalenes made it possible to employ compounds of this kind as oxidation–reduction indicators of cobalt ions[85].

The conversion of quaternary bis-(2,3-*o*-diphenylenetetrazolium) salts (XXIX) into the corresponding carbazole (XXX) under the influence of zinc dust has been described; in the presence of sodium dithionite or hydrazine in an alkaline medium, free N-radicals (XXXI) are formed and reduced by nickel to phenazone (XXXII):[86]



(XXIX) (XXX) (XXXI) (XXXII)

The tendency of quaternary tetrazinium salts to undergo hydrogenolysis at N–N bonds has served as a basis for the preparation of 1,8-diaminonaphthalene (XXXIV) from 2-methyl-1*H*-naphtho[1,8-*de*]triazinium halides (XXXIII):[87]



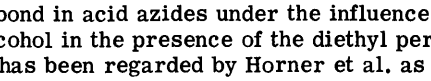
(XXXIII) (XXXIV)

The reduction of azides to the corresponding amines with cleavage of N–N bonds by both chemical and catalytic methods has been used to synthesise aminosugars[88–91] and aminosteroids[92]; methyl *p*-azidosulphonylcarbanilate is reduced by zinc in acetic acid to the corresponding sulphonamide[93].

When aryl azides are treated with hydrogen bromide, the N–N bonds are cleaved with simultaneous ring bromination; the following mechanism has been proposed to account for this process[94]:

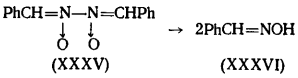


The reductive elimination of nitrogen with dissociation of the N–N bond in acid azides under the influence of isopropyl alcohol in the presence of the diethyl peroxydicarbonate has been regarded by Horner et al. as a radical reaction proceeding via the formation of radicals, and isopropyl alcohol followed by their interaction with azides via the following mechanism[95]:



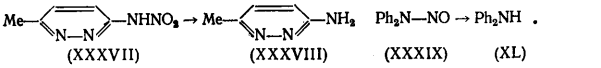
The reduction of acid azides by tributyltin hydride in the presence of azobisisobutyronitrile probably also proceeds via a radical mechanism[96].

There is an interesting case of the dissociation of the N–N bond in the reduction of benzaldehyde azine *NN'*-dioxide (XXXV) by ammonium sulphide in alcohol which gives a 78% yield of benzaldehyde oxime (XXXVI):[97]



(XXXV) (XXXVI)

Reductive cleavage of the N–N bond is also known for *N*-nitro- and *N*-nitroso-compounds: 6-methyl-3-nitraminopyridazine (XXXVII) is reduced in the presence of palladium to 3-amino-6-methylpyridazine (XXXVIII)[98] and *N*-nitrosodiphenylamine (XXXIX) is reduced by lithium aluminium hydride to diphenylamine (XL):[99,100]

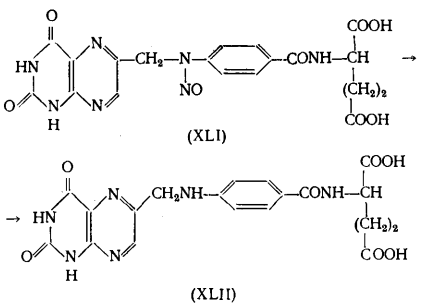


(XXXVII) (XXXVIII) (XXXIX) (XL)

III. ACID CLEAVAGE OF *N*-NITROSO- AND *N*-NITRO-DERIVATIVES

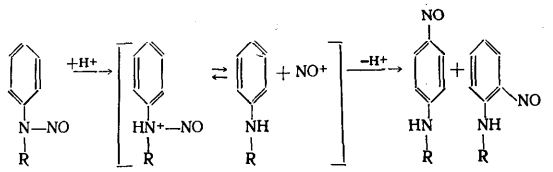
Together with the reductive cleavage of N–N bonds in *N*-nitro- and *N*-nitroso-compounds, the cleavage of compounds of this type by inorganic and organic acids, frequently in the presence of additives binding the nitro-groups and also binding or oxidising the nitroso-groups, has been described[101–105].

As an example, one may quote the denitrosation of *N*-[4-{[(2,4-dihydroxy-6-pteridyl)methyl]-*N*-nitrosoamino}benzoyl]glutamic acid (XLI) by hydrochloric acid in the presence of phenol in the course of the synthesis of the desaminohydroxy-analogue of folic acid (XLII)[105] and the cleavage of the N–N bond in *N*-nitro-compounds by hydrofluoric acid in the presence of anisole[106] or sulphuric acid with acetanilide[107]:

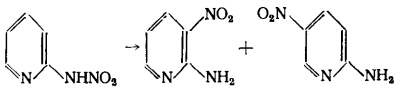


(XLI) (XLII)

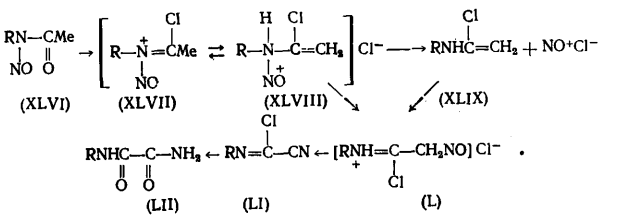
In certain cases the dissociation of the N–N bonds is accompanied by nitration or nitrosation of the denitrosated (or denitrated) compound itself and not of specially added substances with enhanced nucleophilic properties such as phenol, anisole, etc. Such rearrangements have been observed for the first time by Fischer and Hepp in the conversion of *N*-alkyl(aryl)-*N*-nitrosoanilines into the corresponding *p*-nitroso-derivatives [108]. Subsequently it was established that the nitroso-group can migrate not only to the *para*- but also to the *ortho*-position; it has been suggested that such rearrangement has a cationotropic mechanism [109–111]:



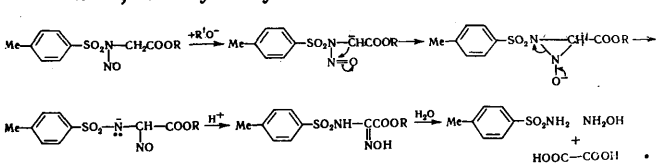
The isomerisation of 2-nitroaminopyridine (XLIII) into 2-amino-3-nitropyridine (XLIV) and 2-amino-5-nitropyridine (XLV): [112]



as well as rearrangements of the Fischer–Hepp type in many other aromatic nitramines [113–117] probably take place similarly. A different type of cleavage of the N–N bond was observed in the rearrangement of *N*-alkyl-*N*-nitrosamides (XLVI) to substituted oxalyldiamides under the influence of phosphorus pentachloride [118]. The mechanism of the rearrangement was associated with the formation of an intermediate iminochloride (XLVII) which isomerises to α-chlorovinylamine (XLVIII) with subsequent migration of the *N*-nitroso-group to the β-carbon atom of the vinyl residue either as a result of the elimination of nitrosyl chloride and its electrophilic addition to the double bond in compound (XLIX) or via an intramolecular shift with subsequent dehydration of compound (L) to the nitrile (LI). The final stage is the hydrolysis of (LI) to the *N*-substituted oxalyldiamide (LII):

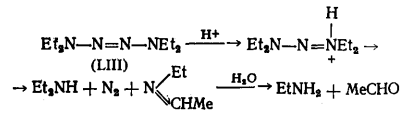


Under the influence of bases, the esters of *N*-nitroso-*N*-tosylglycine are cleaved into toluene-*p*-sulphonamide, oxalic acid, and hydroxylamine [119,120]:

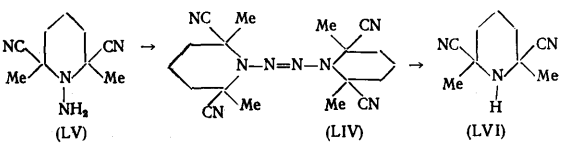


IV. THE CLEAVAGE OF AZINES

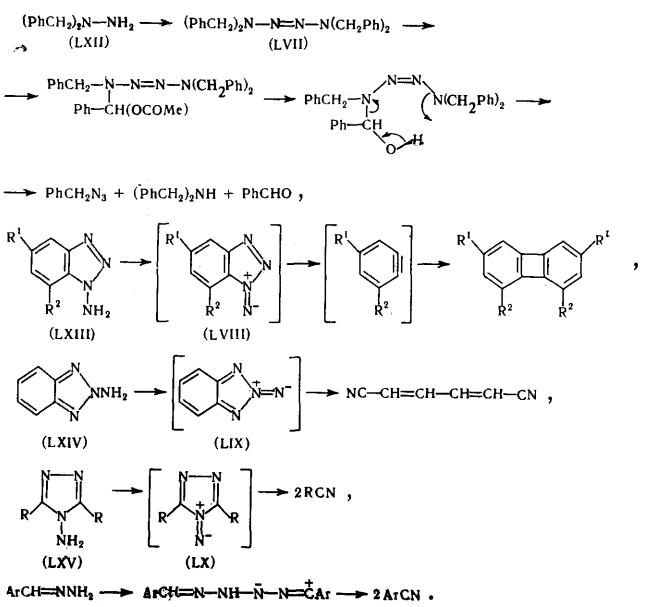
A common reaction involving the dissociation of N–N bonds is the cleavage of azines. For example, in acid tetraethyltetrazine (LIII) is converted into ethyl- and diethyl-amines, nitrogen, and acetaldehyde, the formation of which can be represented as follows [121]:



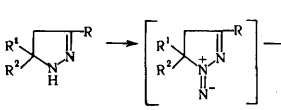
A similar acid cleavage of azines can be used in the synthesis of many carbohydrates [122] and some phenhomazine derivatives [103]. The oxidative deamination of *N*-aminopiperidine (LV) by potassium permanganate with subsequent treatment by hydrobromic acid probably also proceeds via the tetrazine (LIV); the final product of this reaction is 2,6-dicyano-2,6-dimethylpiperidine (LVI): [123]



Another reagent frequently used to deaminate heterocyclic *N*-amino-compounds is nitrous acid [123,124]. The oxidation of 1,1-disubstituted hydrazines of type (LVII), [125,126] 1-aminobenzotriazole (LXIII) and 2-aminobenzotriazole (LXIV), [127] 1-amino-1,3,4-triazoles (LXV), [128] and also arylhydrazones (LXVI) [129] by lead tetra-acetate proceeds via the corresponding tetrazines (LVII)–LXI):

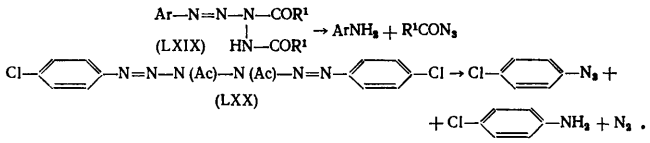


The triazine (LXVII) has been postulated as an intermediate in the nitrile cleavage of pyrazolines (LXVIII) under the influence of difluoroamine [130]:



Azines can be decomposed not only in acid [121–124] but also in alkaline media, as can be observed in the formation of acyl azides and aromatic amines [131] from the products of the reaction of 1,2-diacylhydrazines and arenediazonium

salts (LXIX) or in the alkaline cleavage of the hexaazadiene (LXX):[132]

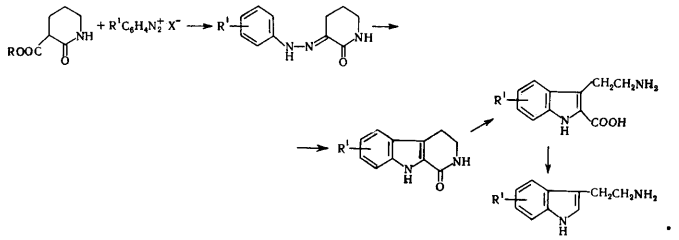


The thermal decomposition of azines with dissociation of N–N bonds has also been described[133–135].

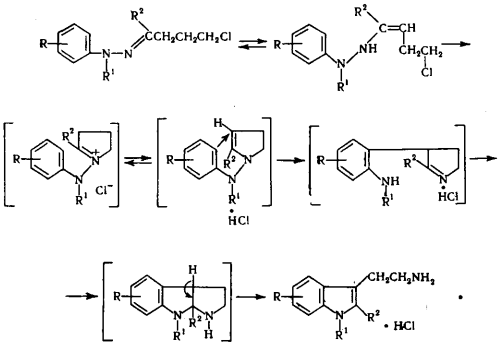
V. REACTIONS OF ARYLHYDRAZONES ANALOGOUS TO THE FISCHER REACTION

The very familiar Fischer reaction involving the synthesis of indole derivatives with dissociation of N–N bonds has been discussed in fine detail in many recent reviews[136–139], which obviates the necessity to analyse in the present report the extensive literature on this question. At the same time, one should mention that the great interest in the Fischer reaction and the detailed study of this method in various systems have led to the development of many other reactions analogous to the Fischer cyclisation and also involving the dissociation of N–N bonds.

Here mention must be made in the first place of the reaction of Abramovitch and Shapiro which has found extensive application in the synthesis of tryptamines and which consists in the interaction of diazonium salts and 3-alkoxycarbonylpiperidine-2-ones with subsequent cyclisation, opening of the piperidinone ring, and decarboxylation[140]:

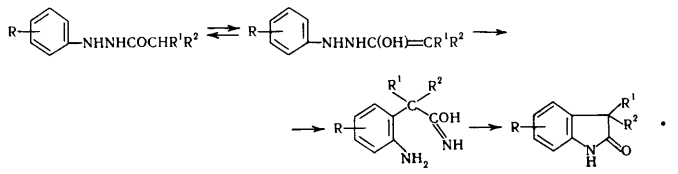


A novel method of synthesising tryptamines and homotryptamines in one step from arylhydrazones of γ- and δ-halogenocarbonyl compounds has been described by Grandberg and coworkers[141–145]:

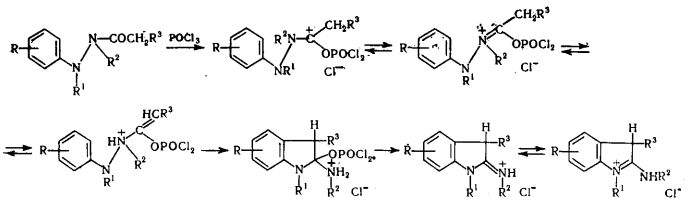


Cyclic enamines have been introduced into the reaction with hydrazines instead of halogenocarbonyl compounds[146]; the use of α-substituted γ-halogenoketones leads to eseroline derivatives[147,148].

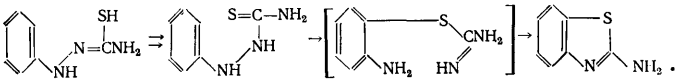
The synthesis of oxindoles from carboxylic acid arylhydrazides has been developed by Bruner[149–153]:



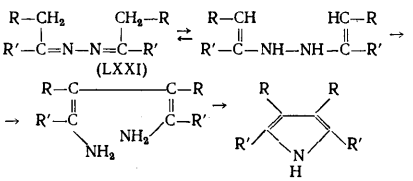
Kost and coworkers suggested a method for the synthesis of 2-aminoindoles based on the interaction with phosphoryl chloride of the arylhydrazides of carboxylic acids containing a methylene group in the α-position in the acid residue[154]:



Even earlier, Fischer and Besthorn[155] and then other workers[156] showed that phenylthiosemicarbazide formed from phenylhydrazine and thiocyanate readily cyclises to 2-aminobenzothiazole when acted upon by acids:

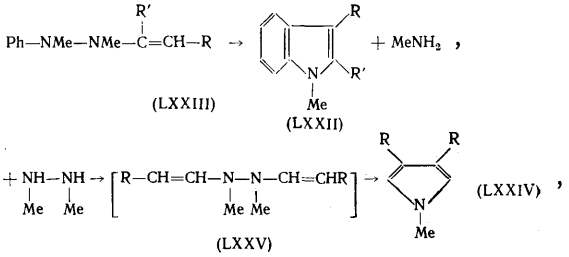


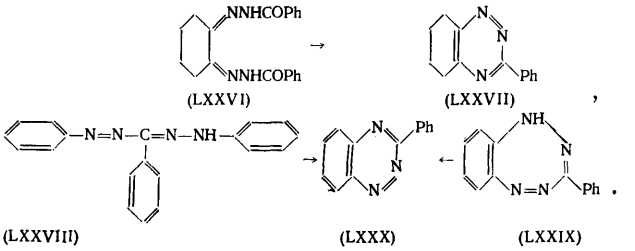
The synthesis of pyrrole derivatives by treating tetrasubstituted azines (LXXI) with acid catalysts has been developed by Piloty[157]:



A similar reaction has been used also to prepare octahydrocarbazole from cyclohexanone azine[158,159].

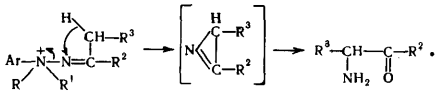
Other processes involving the dissociation of N–N bonds in *N*-substituted hydrazines, hydrazones, and their cyclic analogues are also closely related to the Fischer cyclisation: the synthesis of indoles (LXXII) from *NN'*-dimethylene-*N*-phenylhydrazines (LXXIII),[160] of symmetrical *N*-methylpyrroles (LXXIV) from 1,2-dimethylhydrazines (LXXV),[161] the rearrangement of the bisbenzoylhydrazone of cyclohexane-1,2-dione (LXXVI) to 3-phenyl-5,6-cyclohexeno-1,2,4-triazine (LXXVII),[162] and the rearrangement of 1,3,5-triphenylformazan (LXXVIII) and *C*-phenyl-*NN'*-*o*-phenyleneformazan (LXXIX) to 3-phenyl-5,6-benzo-1,2,4-triazine (LXXX):[163,164]





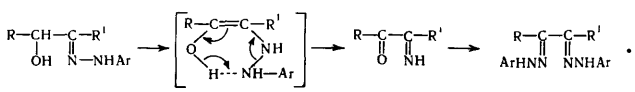
(LXXVI) (LXXVII) (LXXVIII) (LXXX) (LXXIX)

The dissociation of the N–N bond with the Neber rearrangement has been described for quaternary derivatives of arylhydrazones of ketones with an α-hydrogen atom [compounds (LXXXI)] [165-167] which, in contrast to the analogous aldehyde derivatives, are incapable of the nitrile rearrangement. It has been shown that the process is stereospecific, probably proceeds via a three-membered cyclic transition state (LXXXII), [168-170] and leads to the formation of α-aminoketones (LXXXIII):



(LXXXI) (LXXXII) (LXXXIII)

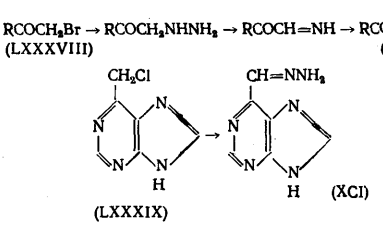
Many studies have been made on the dissociation of the N–N bond in the arylhydrazone of α-hydroxycarbonyl compounds (LXXXIV) with their conversion into osazones (LXXXV). [171-175] The mechanism of this reaction, which is important in sugar chemistry, has been investigated by Shemyakin and coworkers using labelled nitrogen [174]. It was shown that the arylamine is split off initially via a six-membered transition state, for which the authors postulate the structure (LXXXVI), and the monoimine of the α-diketone (LXXXVII) is formed and then converted into compound (LXXXV) under the influence of the arylhydrazine:



(LXXXIV) (LXXXVI) (LXXXVII) (LXXXV)

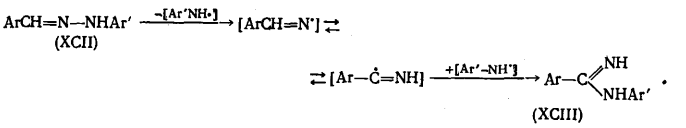
The monoimines of α-diketones (LXXXVII) can be isolated in the form of *N*-acetyl derivatives when compounds (LXXXIV) are cleaved in acetic acid; the addition of *o*-phenylenediamine leads to the formation of substituted quinoxalines [176,177].

Reactions of hydrazine with phenylacyl halides (LXXXVIII) [178] and 6-chloromethylpurine (LXXXIX) [179] apparently also proceed via intermediate amino-derivatives and lead to the formation of the corresponding hydrazones (XC) and (XCI):



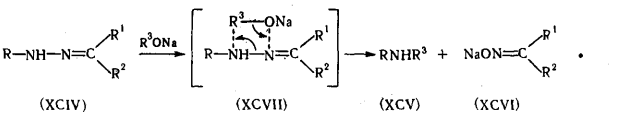
(LXXXVIII) (XC) (LXXXIX) (XCI)

Together with the well known benzidine rearrangement [180-186], it is appropriate to mention in this section the amidine rearrangement discovered by Robev [187-190], which is observed when the arylhydrazones of aldehydes (XCII) are heated with strong bases; it is initiated by atmospheric oxygen, probably has a radical mechanism [191,192], and leads to the formation of *N*-substituted amidines (XCIII):



(XCII) (XCIII)

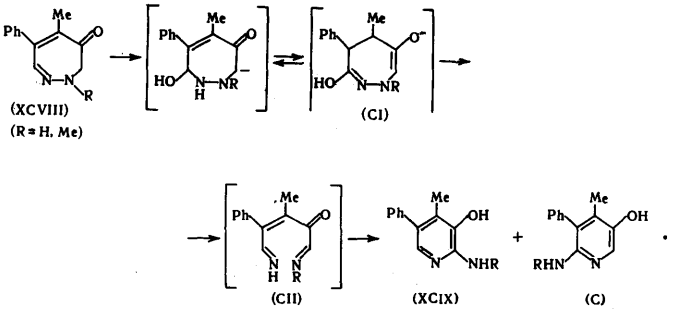
A new type of cleavage of the N–N bond in pyridyl-(aryl)hydrazones (XCIV) under the influence of alkali metal alkoxides has been described by Yakhontov and Marshalkin [193-195]. The reaction products are *N*-monoalkylpyridyl-(or aryl)amines (XCV) and the sodium derivatives of the *syn*-oximes of the carbonyl component (XCVI). The reaction takes place particularly smoothly with (4-pyridyl)- and (3-pyridyl)-hydrazones of aromatic aldehydes. Under these conditions, the corresponding pyridylhydrazines are cleaved only to the aminopyridines and *N*-alkylation products are not formed. It has been suggested that the reaction of alkoxides with compounds (XCIV) proceeds via a four-membered cyclic transition state (XCVII) with simultaneous dissociation of the N–N bond in the hydrazone and the C–O bond in the attacking alkoxide:



(XCIV) (XCVII) (XCV) (XCVI)

VI. REARRANGEMENT OF HETEROCYCLIC 1,2-DIAZA-SYSTEMS

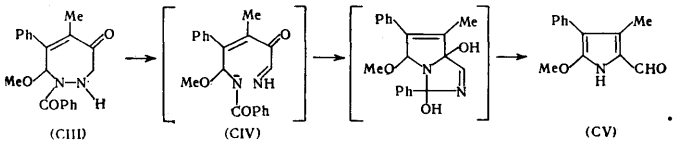
The rearrangements of heterocyclic 1,2-diaza-systems investigated in recent years are related to the methods of synthesising α-imino- and α-hydrazino-ketones described in the preceding section. An example of this type of rearrangement is the conversion of 2,3-dihydro-5-methyl-6-phenyl-1,2-diazepin-4-one (XCVIII) under the influence of alkali to substituted α-aminopyridines (XCIX) and (C), which probably takes place as a result of the nucleophilic attack on compound (XCVIII) by the hydroxide ion in the 3- and 7-positions with formation of the enolate (CI); the β-elimination processes involving the last product lead to the di-iminoketone (CII), which can cyclise in two ways with conversion into the isomers (XCIX) and (C): [176,196]



(XCVIII) (R = H, Me) (CI) (CII) (XCIX) (C)

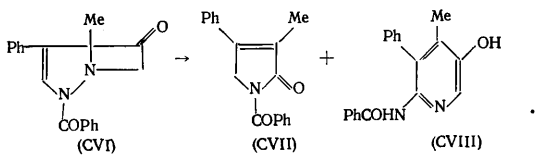
β-Elimination does not occur in the case of 1-benzoyl-7-methoxy-5-methyl-6-phenyltetrahydrodiazepin-4-one (CIII), since the anion (CIV) formed after the dissociation of the N–N bond is stabilised by the amide carbonyl and

a retro-Michael condensation takes place with formation of the pyrrole (CV):[197]



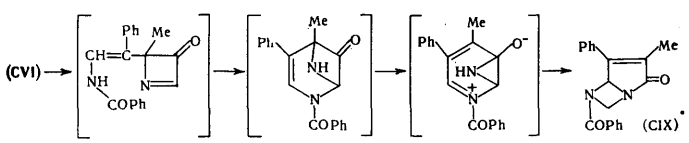
(CIII) (CIV) (CV)

It is suggested that the rearrangement of the substituted 2-benzoyl-1,2-diazabicyclo[3,2,0]hept-3-en-6-one (CVI) on refluxing in methanol to derivatives of pyrrole (CVII) and α-aminopyridine (CVIII) also proceeds via a derivative of 2,3-dihydro-1,2-diazepin-4-one[198,199]:



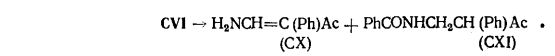
(CVI) (CVII) (CVIII)

Compound (CVI) undergoes a more complex rearrangement in boiling benzene, where 6-benzoyl-3-methyl-4-phenyl-1,6-diazabicyclo[3,2,0]hept-3-en-3-one (CIX) is formed by a mechanism analogous to the cleavage of α-hydrazinocarbonyl compounds[198]:



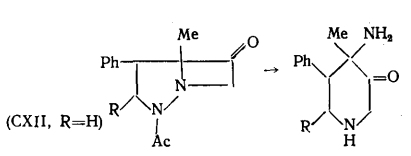
(CIX)

In an alkaline medium compound (CVI) is cleaved with formation of an acyclic enaminoketone (CX) and a saturated benzoylaminoketone (CXI):[198,199]



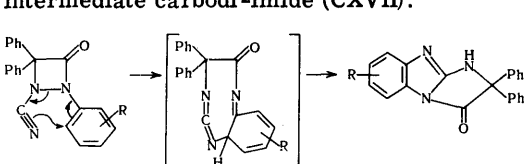
(CX) (CXI)

When bases act on 2-acetyl-5-methyl-4-phenyl-1,2-diazabicyclo[3,2,0]heptan-6-one (CXII) and its 3-methoxy-derivative (CXIII), a rearrangement takes place with dissociation of the N–N bond and the formation of substituted 4-aminopiperidin-3-ones (CXIV):[176,198]



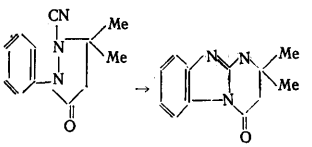
(CXII, R=H) (CXIII, R=OMe) (CXIV)

An interesting thermal rearrangement takes place in 1-aryl-2-cyano-3,3-diphenyldiazetidin-4-ones (CXV), which are converted in high yields into imidazo[1,2-a]-benzimidazole derivatives (CXVI), probably via the cleavage of the N–N bond and subsequent transannular cyclisation of the intermediate carbodi-imide (CXVII):[200]

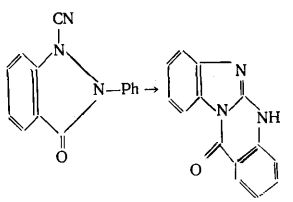


(CXV) (CXVII) (CXVI)

Probably 2-cyano-3,3-dimethyl-1-phenylpyrazolidin-5-one (CXVIII) is converted via a similar mechanism into 1,2,3,4-tetrahydro-2,2-dimethyl-4-oxopyrimido[1,2-a]-benzimidazole (CXXI)[201] and 1-cyano-2-phenyl-3-indazolone (CXX) is likewise converted into benzimidazo-[2,1-b]-12-quinazolone (CXXI):[201]

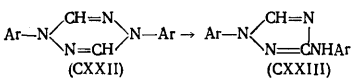


(CXVIII) (CXIX)

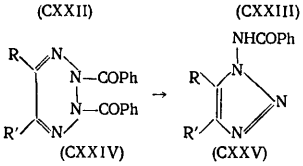


(CXX) (CXXI)

Tetrazine-triazole rearrangements, which also involve the dissociation of N–N bonds, constitute another type of rearrangement of heterocyclic 1,2-diaza-systems. They include the conversion of 1,4-diaryl-1,4-dihydro-1,2,4,5-tetrazines (CXXII) by sodium ethoxide into 3-arylamino-1,2,4-triazoles (CXXIII)[202] and of C-substituted 2,3-dibenzoyl-2,3-dihydro-1,2,3,4-tetrazines (CXXIV) in acid or neutral media into benzamido-1,2,3-triazoles (CXXV):[203–205]



(CXXII) (CXXIII)



(CXXIV) (CXXV)

The conversion of 1-arylalkylindazoles on treatment with sodamide into 2-aryl-4-quinazolones discovered by Simonov et al.[206] can also be formally regarded as a rearrangement of heterocyclic 1,2-diazasystems.[206] However, this reaction has the mechanism of the nitrile rearrangement and can be more usefully considered in the next section of the review.

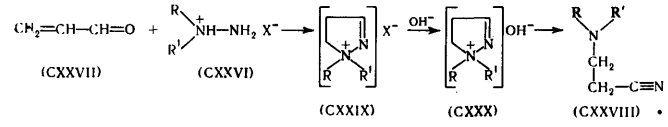
VII. THE NITRILE REARRANGEMENTS

In 1910 Arbuzov observed that, on heating with Lewis acids, the phenylhydrazones of aliphatic aldehydes undergo a rearrangement with dissociation of the N–N bond, the elimination of aniline, and the formation of a nitrile[207]:



Subsequently Kost, Grandberg and coworkers showed that this reaction is common to compounds of the type $RCH{=}N{-}N(R^1)R^2$ and suggested that it proceeds via the formation of a complex of the hydrazone with the Lewis acid, a far shift of the electron pair of the N–N bond, the formation of a δ^+ charge on the neighbouring carbon atom, and subsequent deprotonation with dissociation of the N–N bond[208–211]. A similar rearrangement takes place also when the hydrochlorides of pyrazoline derivatives are heated[212,213].

Ioffe and Zelenin observed that the condensation of asymmetric dialkylhydrazines (CXXVI) with acrolein (CXXVII) involves a rearrangement with formation of β-dialkylaminopropionitriles (CXXVIII) for which it has been established that the process proceeds via the quaternary pyrazolinium derivatives (CXXIX) and (CXXX) according to the mechanism [214-216]:

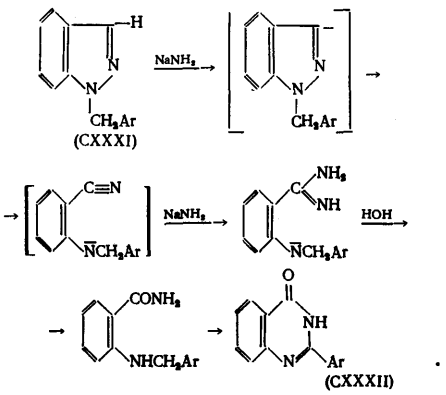


(CXXVII) (CXXVI) (CXXIX) (CXXX) (CXXVIII).

A similar nitrile cleavage of quaternary hydrazinium derivatives was observed in other instances also [217-221] and Grandberg and Naumov showed that the N–N bonds in compounds of this type are more labile than the C–N bond in quaternary ammonium bases [217].

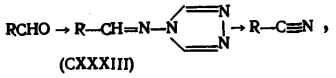
The nitrile rearrangement of hydrazones can be achieved not only under the influence of Lewis acid but also in reactions in the presence of various nucleophilic agents (sodamide, alkalies, etc.) [208,209,222-226] and apparently proceeds via a β-elimination mechanism: the nucleophilic agent attacks the hydrogen atom at the C=N double bond and the highly polarised N–N bond in the anion formed after deprotonation is readily dissociated under the influence of heat [209].

In many reactions this process does not stop at the nitrile stage, the nitrile being converted further into an amidine and an amide capable of cyclising into 4-quinazolone derivatives, as happens in the conversion, mentioned above, of 1-arylalkylindazoles (CXXXI) in the presence of sodamide into 2-aryl-4-quinazolones (CXXXII):[206,225]



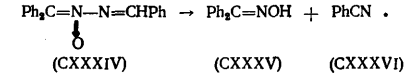
(CXXXI) (CXXXII).

The nitrile rearrangement is probably the final stage of the cleavage reactions of the azines (LXIV), (LXV), (LXVI), (LXVII), etc., described above (Section IV) and constitutes the basis of the method for the conversion of aldehydes into nitriles via 1-amino-1,2,4-triazoles derivatives (CXXXIII) proposed by Becker and Timpe [227]:



(CXXXIII)

as well as the conversion of aldehydes into nitriles via hydrazonium salts [220,228,229]. The polarisation of N–N bonds in the conversion from azines and hydrazones into their *N*-monoxides also promotes the cleavage of these compounds via a mechanism of the nitrile rearrangement type [230,231], as happens, for example, in the thermal decomposition of the azine *N*-monoxide (CXXXIV) to the corresponding oxime (CXXXV) and nitrile (CXXXVI): [230]

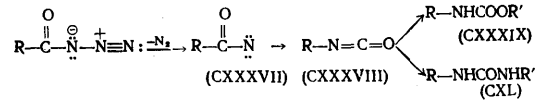


(CXXXIV) (CXXXV) (CXXXVI)

The thermal cleavage of non-oxidised azines and hydrazones, in which the polarisation of the N–N bond is less marked, proceeds with greater difficulty and the products of the nitrile rearrangement are obtained in lower yields [233-234]. It has been suggested that in such cases the reactions have a radical mechanism.

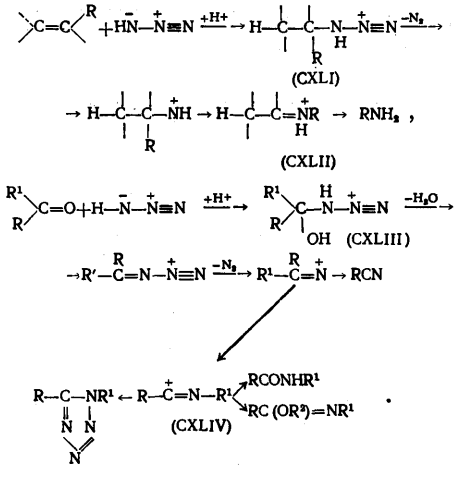
VIII. SEXTET REARRANGEMENTS OF THE TYPE OF THE CURTIUS AND SCHMIDT REACTIONS

The conversion of acid azides into isocyanates with cleavage of the N–N bond and the evolution of a nitrogen molecule, called the Curtius reaction, proceeds via the intermediate formation of a product (CXXXVII) with an electron sextet, the rearrangement of which takes place owing to the tendency of nitrogen to acquire the missing electrons from the adjacent carbon atom. As a result of the migration of the alkyl or aryl residue from compound (CXXXVII), the isocyanate (CXXXVIII) is formed and can be isolated from non-polar solvents; in the presence of alcohols it is converted into carbamic acid esters (CXXXIX) and on treatment with ammonia or amines it gives rise to substituted ureas (CXL):



(CXXXVII) (CXXXVIII) (CXXXIX) (CXL).

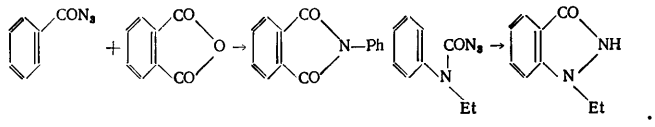
The Schmidt reaction, which consists in the interaction of equivalent amounts of hydrazoic acid and a carbonyl compound or an olefin in the presence of strong inorganic acids, has a similar mechanism. After the scission of nitrogen and the rearrangement, protonated *N*-substituted ketimines (CXLI) are formed from the adducts with olefins (CXLII) and can be readily hydrolysed to the corresponding amines. In the adducts with aldehydes (CXLIII, R′ = H), the sextet is usually stabilised via deprotonation with formation of a nitrile and the interaction of HN_3 with ketones entails a rearrangement with migration of the alkyl or aryl group, the resulting carbonium ion (CXLIV) being converted into amides on reaction with water, into iminoethers on reaction with alcohols, and into tetrazoles on reaction with an excess of HN_3:



(CXLI) (CXLII) (CXLIII) (CXLIV).

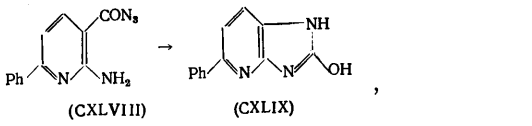
The Curtius and Schmidt reactions constitute important preparative methods for the synthesis of different classes of compounds: amines, amides, urethanes, substituted ureas, etc., which have been thoroughly investigated in a large number of instances and have been discussed in detail in many reviews [235-237]. This makes it unnecessary to consider them in detail here. Probably attention should be concentrated on sextet rearrangements of the type of the Curtius and Schmidt reactions, not included in the above reviews, which takes place with dissociation of N–N bonds and lead to the formation of more complex products.

As examples of reactions of this type, one may quote the formation of *N*-phenylphthalimide (CXLV) on heating benzoyl azide with phthalic anhydride [238] or the rearrangement of *N*-ethyl-*N*-phenylcarbamoyl azide (CXLVI) in boiling xylene to 1-ethyl-3-indazolone (CXLVII): [239]

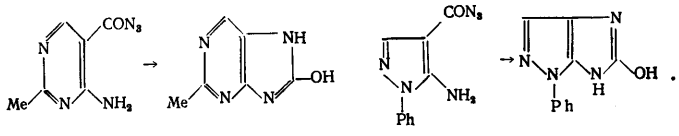


(CXLV) (CXLVI) (CXLVII)

When 2-amino-6-phenylnicotinoyl azide (CXLVIII) is heated in xylene, a quantitative yield of 2-hydroxy-6-phenylimidazo[4,5-*b*]pyridine (CXLIX) is obtained [240]. The thermal cleavage of the azides of 4-amino-2-methylpyrimidine-5-carboxylic (CL) and 5-amino-1-phenylpyrazole-4-carboxylic (CLI) acids takes place similarly [241]:

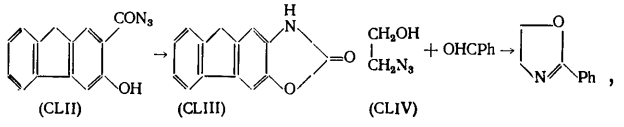


(CXLVIII) (CXLIX)

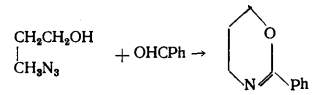


(CL) (CLI)

The rearrangement of the azides of 3-hydroxyfluorene-2-carboxylic acid (CLII) also leads to the closure of a new ring: the formation of 5*H*-fluoreno[2,3-*d*]oxazolidin-2-one (CLIII). [242] The closure of the oxazolidine or dihydrooxazine ring takes place also on heating of β- and γ-hydroxyalkyl azides, (CLIV) and (CLV), with benzaldehyde in the presence of sulphuric acid [243]. Probably this process proceeds via the mechanism of the Schmidt reaction with dehydration at the imino-derivative stage. Aliphatic and alicyclic carbonyl compounds do not enter into this reaction, in contrast to aromatic aldehydes:

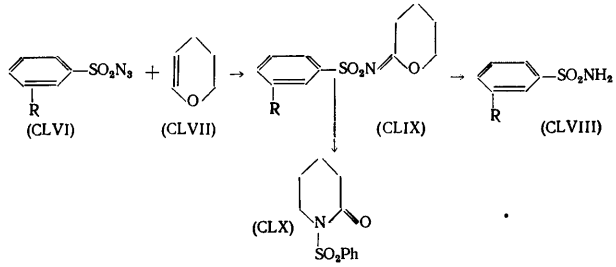


(CLII) (CLIII) (CLIV)



(CLV)

Sulphonylazides usually do not undergo the Curtius rearrangement. However, high yield of *m*-nitrobenzenesulphonamide (CLVIII, R = NO_2) was obtained on heating in alcohol *m*-nitrobenzenesulphonylazide (CLVI, R = NO_2) and dihydropyran (CLVII). [244] Evidently the sextet formed after the dissociation of the N–N bond and evolution of nitrogen is in this case stabilised by the addition of a molecule of (CLVII) and the formation of 2-(*m*-nitrobenzenesulphonylimino)tetrahydropyran (CLIX, R = NO_2), which is cleaved in alcohol to compound (CLVIII, R = NO_2). [245] Similar reactions with dissociation of the N–N bond have been observed also for unsubstituted benzenesulphonyl azide (CLVI, R = H), where the hydrolysis of compound (CLIX, R = H) results in the formation of benzenesulphonamide (CLVIII, R = H) and the thermal rearrangement of (CLIX, R = H) yields *N*-phenylsulphonylpiperidin-2-one (CLX): [245]



(CLVI) (CLVII) (CLIX) (CLVIII)

(CLX)

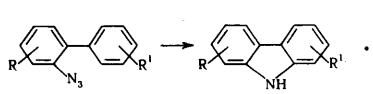
One should probably also include among sextet rearrangements the conversion of hydrazones into amides under the influence of sodium nitrite and concentrated sulphuric acid [246,247]:

$$R_2C{=}NNH_2 \rightarrow RCONHR + N_2 ,$$

and also the rearrangement of 1-acetylimino-1-methyl-2-phenylpyrrolidine (CLXI), discovered by Wawzonek, which results in the formation of methyl isocyanate (CLXII) and 1-methyl-2-phenylpyrrolidine (CLXIII). [248]

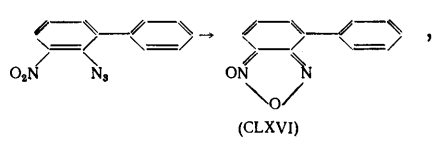
IX. THERMAL CYCLISATION OF AZIDES

The thermal cyclisation of azides discovered by Smith and Brown, which takes place with dissociation of the N–N bond [249], constitutes an important method for the synthesis of heterocyclic systems and merits special discussion. Initially this reaction was developed for the synthesis of carbazoles (CLXIV) from 2-azidobiphenyls (CLXV) and it was found that with 5-nitro- or 4′-5-dinitro-derivatives (CLXV) the yields of the tricyclic derivatives were appreciably higher than in the cyclisation of the 5-bromo- and 3,5-dibromo-derivatives or the unsubstituted compound (CLXV): [249]

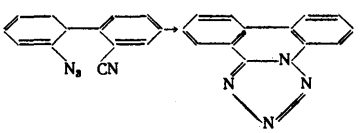


(CLXV) (CLXIV)

The 3-nitro-derivative of compound (CLXV) is converted into 4-phenylbenzofuroxan (CLXVI), i.e. the cyclisation involves the nitro-group, while with 2-azido-2′-cyanobiphenyl the process takes place without the evolution of nitrogen with formation of tetrazolophenanthridine (CLXVII): [250]

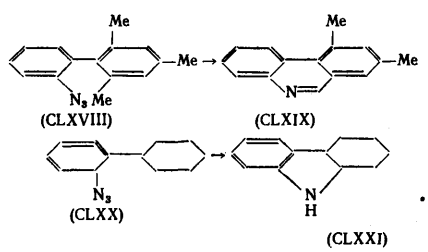


(CLXVI)



(CLXVII)

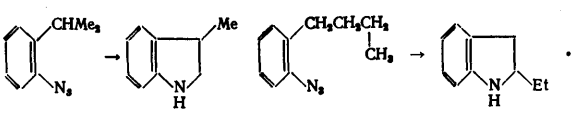
Subsequently the thermal cyclisation of azides were extended to aza- and thia-analogues of compound (CLXV) [251] and it was also shown that an analogous reaction with dissociation of the N–N bond can occur with participation of aliphatic residues. Thus the cyclisation of 2-azido-2′,4′,6′-trimethylbiphenyl (CLXVIII) yielded phenanthridine (CLXIX) [252] and hexahydrocarbazole (CLXXI) was obtained from *o*-azidophenylcyclohexane (CLXX): [252]



(CLXVIII) (CLXIX)

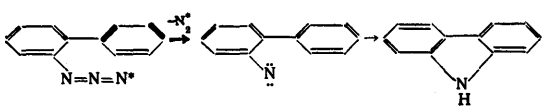
(CLXX) (CLXXI)

The application of the same reaction to *o*-azidoisopropylbenzene (CLXXII) and *o*-azidobutylbenzene (CLXXIII) permitted a new synthesis of indolines (CLXXIV) and (CLXXV), [252,253] in which tetrahydroquinolines and products of the reductive cleavage of the N–N bonds in the azides (CLXXII) and (CLXXIII) (*o*-alkylanilines) were obtained as side products:



(CLXXII) (CLXXIV) (CLXXIII) (CLXXV)

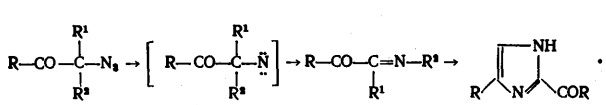
It was established with the aid of labelled nitrogen that the cyclisation of azides proceeds via a nitrene (CLXXVI) stage [250,254] with evolution of molecular nitrogen containing the label:



(CLXXVI)

This mechanism is supported also by the formation of phenyl isocyanate on thermal decomposition of phenyl azide in carbon monoxide and of carbazole and 2-biphenylyl isocyanate from 2-azidobiphenyl [255]. A similar mechanism for the decomposition of azides was proposed for the process catalysed by iridium salts [258].

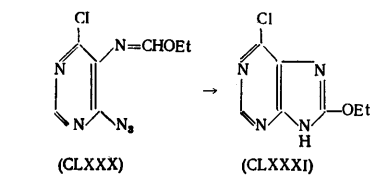
A radical process with formation of intermediate nitrenes has also been postulated for the thermal cleavage of α-azidocarbonyl compounds (CLXXVII), where the substituent R^2 was found to migrate after the elimination of the nitrogen molecule (the ease of migration increases in the sequence $CH_3 < C_6H_5 < H$) and a monoimino-derivative (CLXXVIII) of the α-dicarbonyl compound was formed:



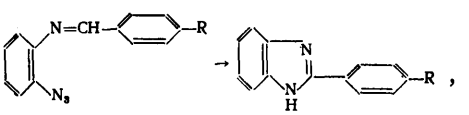
CLXXVII) (CLXXVIII) (CLXXIX)

This reaction has been used for the synthesis of substituted imidazoles (CLXXIX) from α-azidocarbonyl compounds (CLXXVII, $R^1 = R^2 = H$) via (CLXXVIII, $R^1 = R^2 = H$) by dimerisation of the latter with elimination of water [257].

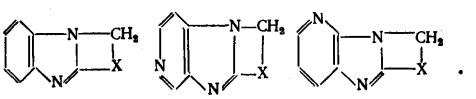
Another method for the synthesis of the imidazole ring via the thermal cyclisation of azides has been described in connection with a new synthesis of purines, whereby 6-chloro-8-ethoxypurine (CLXXXI) was obtained on heating 4-azido-6-chloro-5-ethoxymethyleneiminopyrimidine (CLXXX). [258] 2-Arylbenzimidazoles (CLXXXIII) were obtained similarly in almost quantitative yields from 2-azidobenzylideneanilines (CLXXXII) [259] and tricyclic derivatives of benzimidazole (CLXXXIV) and pyridoimidazole, (CLXXXV) and (CLXXXVI), were obtained from *N*-(*o*-azidophenyl)- or *N*-(3-azido-4-pyridyl)-derivatives of pyrrolidines, piperidines, and morpholines [260]:



(CLXXX) (CLXXXI)



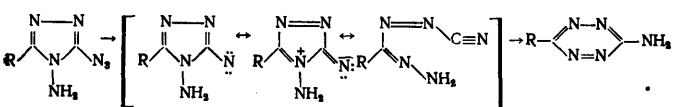
(CLXXXII) (CLXXXIII)



(CLXXXIV) (CLXXXV) (CLXXXVI)

(X=(CH$_2$)$_2$; (CH$_2$)$_3$; —CH$_2$OCH$_2$—)

On heating with chlorobenzene, the corresponding 4-amino-3-azido-s-triazoles (CLXXXVII) are converted in almost quantitative yields into 3-amino-1,2,4,5-tetrazines (CLXXXVIII), [261] which constituted a convenient method for the synthesis of symmetrical tetrazines. The process probably proceeds via a stage in which a nitrene is formed and exists in one of the canonical forms—the acylic nitrile (CLXXXIX) — which cyclises to (CLXXXVIII):



(CLXXXVII) (CLXXXIX) (CLXXXVIII)

Various reactions of nitrenes are considered in greater detail in special reviews [254,262–265].

X. PHOTOCHEMICAL DISSOCIATION OF N–N BONDS

In the last decade publications on the photochemical dissociation of N–N bonds in organic compounds have appeared with increasing frequency. One of the first reports in this field concerned the photochemical cleavage of acetaldehyde azine and benzaldehyde azine to the corresponding nitriles [266,267]. The photolysis was achieved in the presence of benzophenone and proceeded via the mechanism

$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2\dot{C}{-}O^{\bullet},$$

$$Ph_2\dot{C}{-}O^{\bullet} + PhCH{=}N \cdot N{=}CHPh \rightleftarrows Ph\dot{C}{=}N \cdot N{=}CHPh + Ph_2\dot{C}{-}OH,$$

$$Ph\dot{C}{=}N \cdot N{=}CHPh + Ph_2C{=}O \rightarrow 2PhCN + Ph_2\dot{C}{-}OH.$$

The photochemical decomposition of aliphatic and aromatic *N*-nitrosoamines (CXC) leads to the corresponding amines (CXCI) and amidoximes (CXCII):[268]

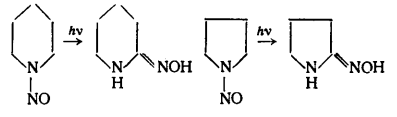
$$\underset{\text{(CXC)}}{PhCH_2N(NO)CH_2Ph} \xrightarrow[-NO^{\cdot}]{h\nu} \underset{\text{(CXCII)}}{PhCH_2\dot{N}CH_2Ph},$$

$$\text{(CXCII)} + \text{(CXC)} \rightarrow PhCH_2NHCH_2Ph + \underset{\text{(CXCI)}}{PhCH_2N(NO)\dot{C}HPh},$$

$$PhCH_2N(NO)\dot{C}HPh \rightarrow PhCH_2N{=}CHPh + NO^{\cdot},$$

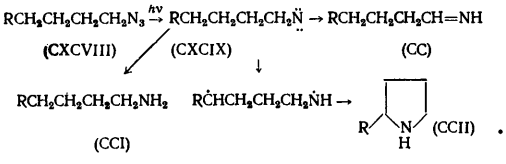
$$\text{(CXCII)} \xrightarrow{+^{\cdot}NOH} PhCH_2NH{-}\overset{+}{C}H(\overset{+}{N}OH)Ph \xrightarrow{-H^+} \underset{\text{(CXCII)}}{PhCH_2NHC(=NOH)Ph}.$$

When *N*-nitrosopiperidine (CXCIV) or *N*-nitrosopyrrolidine (CXCV) is irradiated with ultraviolet light in aqueous methanol containing hydrochloric acid, the amidoximes (CXCVI) and (CXCVII) are formed in high yields[269]:



(CXCIV) (CXCVI) (CXCV) (CXCVII)

The photolysis of the non-aromatic azides (CXCVIII) results in the formation of the nitrenes (CXCIX) which can then react in three different ways: (a) they can isomerise to the imines (CC); (b) they can split off hydrogen from solvent molecules and be converted into amines (CCI); (c) they can undergo 1,5-deprotonation with cyclisation to pyrrolidines (CCII):[264,270]

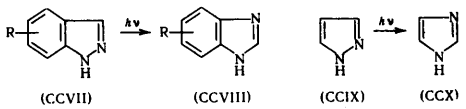


On direct irradiation in isopropyl alcohol, particularly in the presence of added benzophenone, sulphonyl azides (CCIII) are converted via a radical chain mechanism into the sulphonamides (CCIV). The process is catalysed by iron(III) chloride and is accelerated by heat[271].

On irradiation in cyclohexane, the azides of aliphatic carboxylic acids (CCV) are converted into the amides (CCVI). The reaction is sensitised by acetophenone[272]:

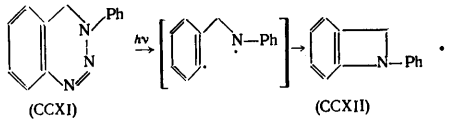
$$\underset{\text{(CCV)}}{C_nH_{2n+1}CON_3} \xrightarrow{h\nu} \underset{\text{(CCVI)}}{C_nH_{2n+1}CONH_2}.$$

Unexpected reactions are observed when certain heterocyclic 1,2-diaza-compounds are irradiated with ultraviolet light. For example, unsubstituted and monosubstituted indazoles (CCVII) undergo photoisomerisation under these conditions into the corresponding benzimidazoles (CCVIII).[273] The introduction of 3-phenyl-, 5-methoxy-, and 5- or 6-chloro-substituents into compounds (CCVII) inhibits the process, while an increase of temperature favours the rearrangement. A similar photoisomerisation has been observed with the unsubstituted pyrazole (CCIX), which is converted into imidazole (CCX) in 12% yield on irradiation with ultraviolet light[273]:



(CCVII) (CCVIII) (CCIX) (CCX)

The irradiation of 3-phenyl-1,2,3-benzotriazine (CCXI) sensitises the radical process, which is accompanied by the dissociation of the N–N bond and evolution of molecular hydrogen, resulting in the formation of *N*-phenylbenzazetine (CCXII):[274]



(CCXI) (CCXII)

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