Chemistry of Heterocyclic Compounds, Vol. 29, No. 11, 1993

SYNTHESIS OF HETEROCYCLIC COMPOUNDS BASED ON TRICHLOROACETONITRILE (REVIEW)

G. A. Shvekhgeimer

The available literature data on the utilization of trichloroacetonitrile in the synthesis of heterocyclic compounds are correlated.

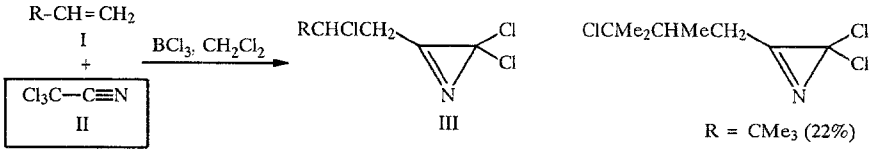
INTRODUCTION

Trichloroacetonitrile is a unique compound in which two groupings that have strong electron-acceptor properties are bonded directly. Both the cyano group and the trichloromethyl group acquire high reactivities as a result of their mutual effect. Among the numerous transformations of trichloroacetonitrile, of special interest are heterocyclization reactions with the participation of the cyano group that lead to various heterocyclic systems.

In this review we examine reactions that lead to the formation of heterocycles from trichloroacetonitrile and compounds that do not contain heterocyclic rings, as well as reactions in which the starting compounds contain a heterocyclic radical and groupings through which, on reaction with trichloroacetonitrile, new heterocyclic rings are formed.

1. Three-Membered Heterocyclic Compounds

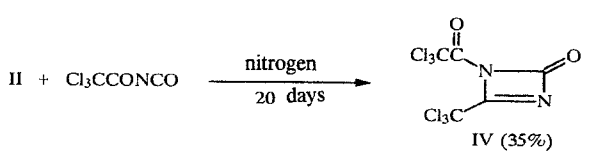
The reaction of olefins I with trichloroacetonitrile (II) in the presence of BCl_3 at −78°C in an argon atmosphere gives azirine derivatives III [1]:



R = *n*-C_6H_{13} (90%); Bu (90%); Me_2CHCH_2 (90%); $EtCHMe_2$ (92%); Me_3C (68%); $PhCH_2$ (44%)

2. Four-Membered Heterocyclic Compounds

Just as for three-membered rings, there is only one paper in which the synthesis of 1,3-diazetinone derivative IV is reported [2]:



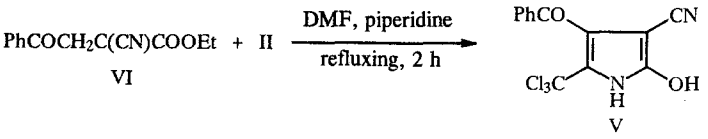
IV (35%)

Moscow State Textile Academy, Moscow 117918. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1443-1471, November, 1993. Original article submitted June 2, 1993.

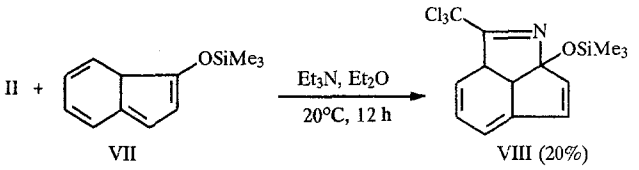
0009-3122/93/2911-1241$12.50

3. Five-Membered Heterocyclic Compounds

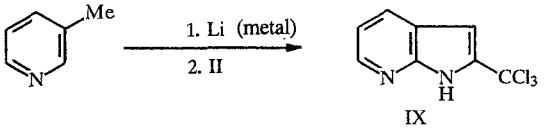
3.1. Syntheses of Nitrogen Heterocycles. Pyrrole derivative V was synthesized from nitrile II and keto acid ester VI [3]:



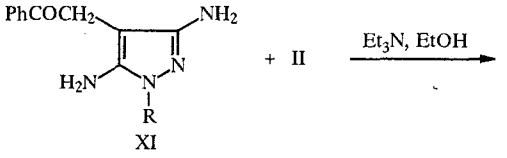
Nitrile II reacts with O-silyl ether VII in the presence of triethylamine to give pyrrole derivative VIII [4]:

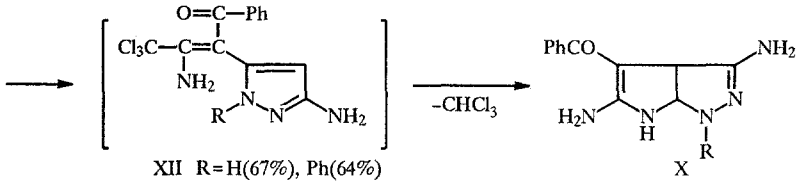


It is interesting that the carbanion obtained by the action of lithium on 3-picoline reacts with nitrile II to give 2-trichloro-methyl[1H]pyrrolo[2,3-b]pyridine (IX) [5]:



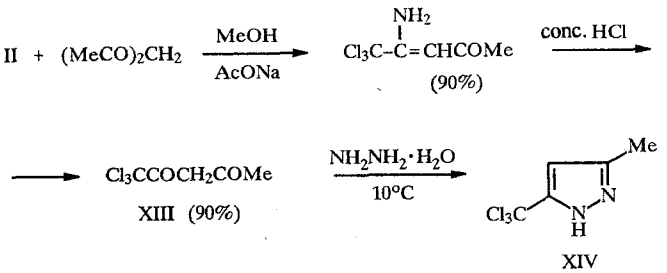
According to the data presented in [6], the formation of pyrrolo[2,3-c]pyrazoles X from nitrile II and pyrazole derivatives XI proceeds through intermediate XII:



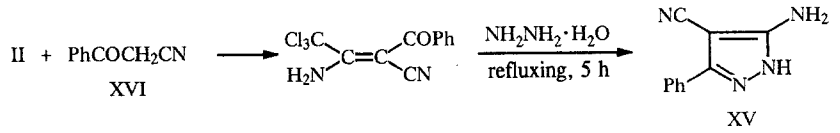


Several approaches to the synthesis of pyrazole derivatives using nitrile II as one of the starting compounds have been developed.

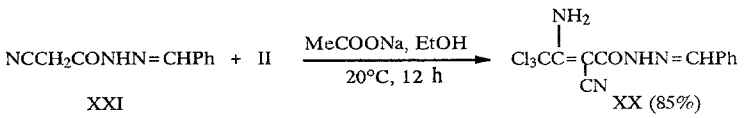
The product of the reaction of nitrile II with acetylacetone was converted to 1,3-diketone XIII, from which substituted pyrazole XIV was obtained by the action of hydrazine hydrate [7]:

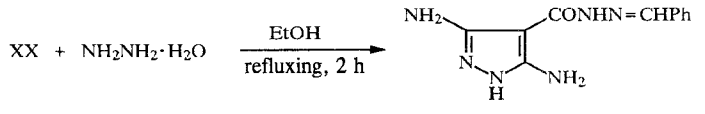


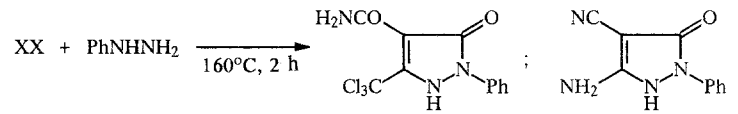
Pyrazole derivative XV was synthesized by the action of hydrazine hydrate on the product of the reaction of nitrile II with keto nitrile XVI [8]:



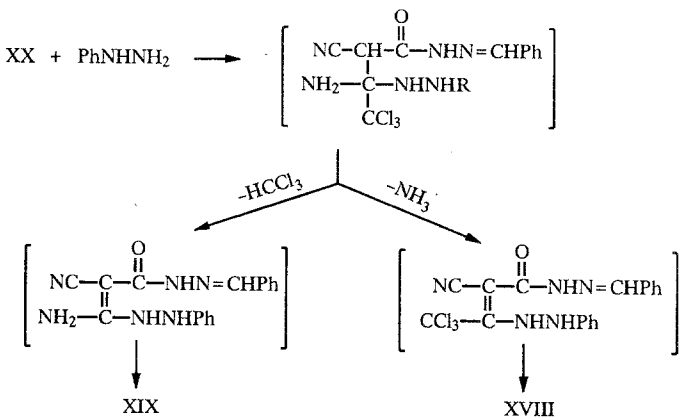
Various pyrazole derivatives XVII-XIX were obtained by treatment of XX — the product of the reaction of nitrile II with N-benzylidene hydrazide (XXI) — with hydrazine hydrate or phenylhydrazine [9]:



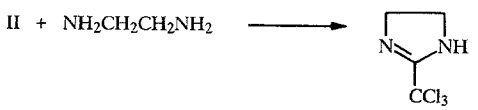




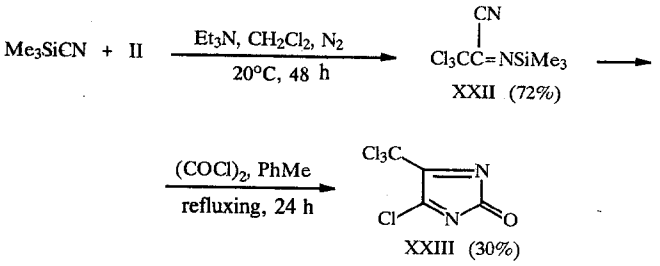
To explain the formation of XVIII and XIX Ibrahim and coworkers [9] propose the following scheme:



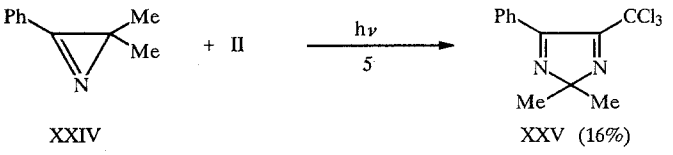
Nitrile II reacts with ethylenediamine at room temperature to give 2-(trichloromethyl)imidazoline [10, 11]:



5-Chloro-4-(trichloromethyl)-imidazol-2-one (XXIII) is formed as a result of treatment of nitrile XXII (the product of the reaction of nitrile II with trimethylcyanosilane) with oxalyl chloride [12]:

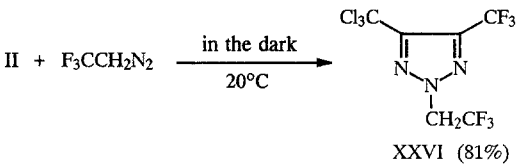


Substituted imidazole XXV was obtained by irradiation with UV light of a mixture of nitrile II and azirine derivative XXIV [13]:

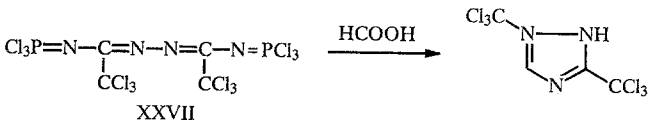


Stegmann and coworkers [13] assume that this is a [2+3]-cycloaddition reaction of nitrile II with benzonitrile isopropylide (formed *in situ* from azirine XXIV).

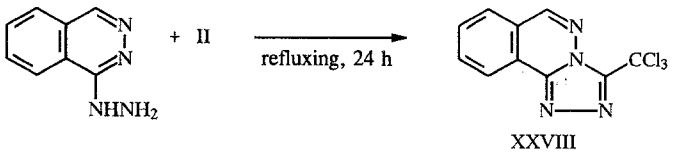
The activated cyano group of nitrile II reacts readily with 2,2,2-trifluorodiazoethane, and 1,2,3-triazole derivative XXVI is formed in high yield [14]:



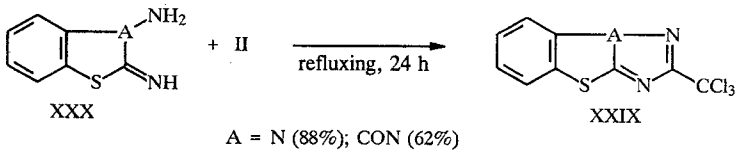
3,5-Bis(trichloromethyl)-1,2,4-triazole was synthesized by treatment with formic acid of XXVII, obtained from nitrile II, PCl_5, and hydrazine [15]:



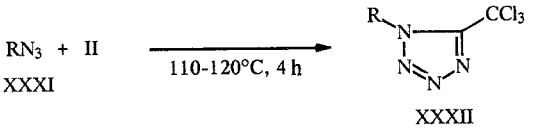
Triazolophthalazine derivative XXVIII is formed as a result of the reaction of nitrile II with 1-hydrazinophthalazine [16]:



Condensed systems XXIX, which contain a 1,2,4-triazole ring, can be synthesized by the reaction of nitrile II with XXX, which has an $-N(NH_2)-C(=NH)-$ fragment [17, 18]:



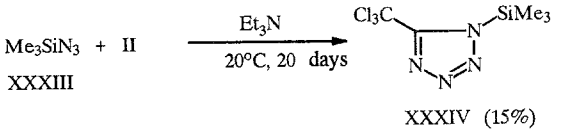
The reaction of nitrile II with azides XXXI, which leads to 1,5-disubstituted tetrazoles XXXII, has been studied in detail [19-21]:



R = C_5H_{11} (87%); CH_2CH_2OH (81%); CH_2CH_2Cl (74%); CH_2COOEt (85%)

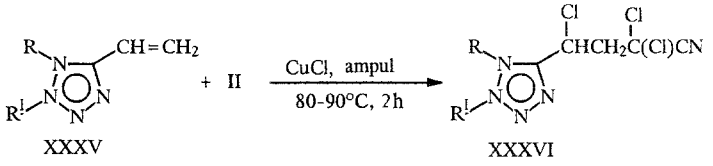
The kinetics of the reaction [R = C_5H_{11}, CH_2CH_2OH, CH_2CH_2Cl, $CH_2CH_2NO_2$, $CH_2CH_2ONO_2$, $CH_2CH(Me)NO_2$, CH_2COOEt] were studied, and it was found that an increase in the electron-acceptor character of R in RN_3 leads to slowing down of the reaction, the activation parameters of which are characteristic for 1,3-dipolar cycloaddition [21].

1-Trimethylsilyl-5-(trichloromethyl)tetrazole (XXXIV) is formed in low yield as a result of the reaction of nitrile II with trimethylsilyl azide (XXXIII) in the presence of triethylamine [22]:



Lazukina and Kukhar' [22] note that the mixture explodes when it is heated to 80-90°C.

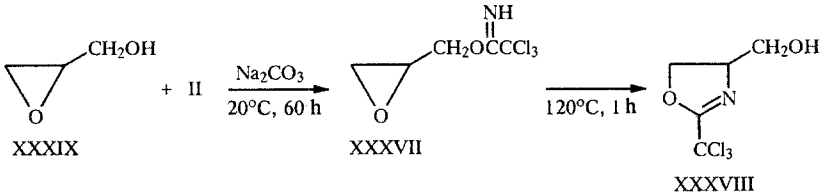
Nitrile II adds smoothly to vinyltetrazoles XXXV, and the corresponding adducts XXXVI are formed in high yields [23]:



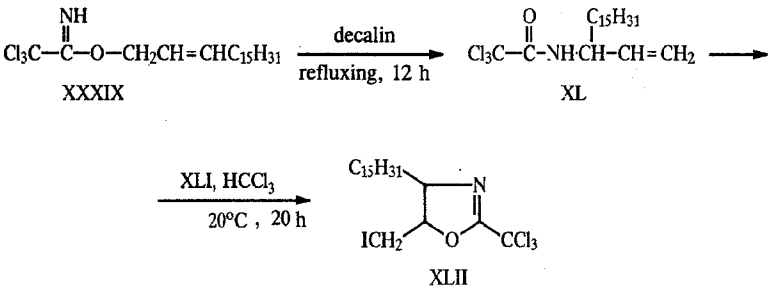
R, R^1 = CH_3, H (86%); H, CH_3 (94%)

1-Trichloromethyltetrazole was synthesized by the 1,3-dipolar cycloaddition of nitrile II with a polymeric Schiff base and a phosphine-palladium complex [24].

3.2. Synthesis of N,O-Heterocycles. Condensation product XXXVII, formed from nitrile II and glycidol, undergoes isomerization to isoxazoline derivative XXXVIII when it is heated [25]:

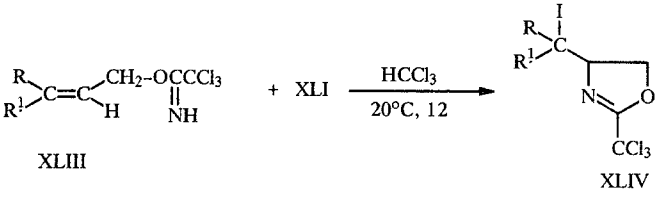


Adduct XXXIX (synthesized from nitrile II and octadec-2-yn-1-ol), on heating in decalin, undergoes isomerization to amide XL, which, under the influence of N-iodosuccinimide (XLI), undergoes cyclization to a mixture of *cis*- and *trans*-5-iodomethyl-4-pentadecyl-2-(trichloromethyl)-4,5-dihydrooxazoles XLII, which are used in the synthesis of (±)-erythro-sphinganine [26]:



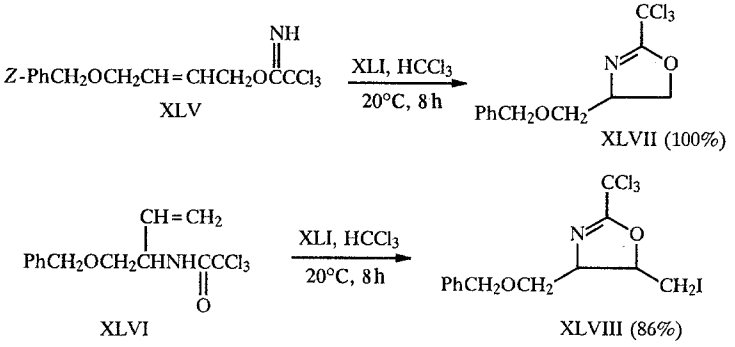
In a study of the reaction of N-iodosuccinimide (XLI) with imino esters XLIII — products of the reaction of nitrile II with unsaturated alcohols — it was established that electronic and steric factors in this process control the preferred cyclization pathway to favor the formation of either oxazoline or dihydro-1,3-oxazine derivatives.

The formation of oxazoline derivatives is favored by the development of more stable intermediate carbonium ions, as well as by the Z configuration of the starting allyl imidates (5-exo ring closing) [27]:

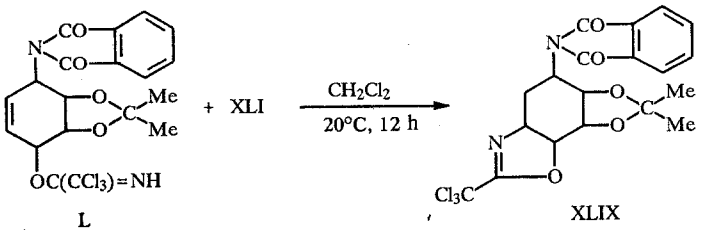


$R, R^1 = C_{15}H_{31}$, H (90%); H, Et (88%); H, $C_{15}H_{31}$ (90%); H, Ph (92%); H, CH_2OMe (87%); H, CH_2O- CH_2O-tetrahydro-2,H-pyranyl -2 (81%); H, CH_2OCH_2Ph (98%); CH_2OMe, H (61%); CH_2O-tetrahydro-2-pyramyl-2, H (55%)

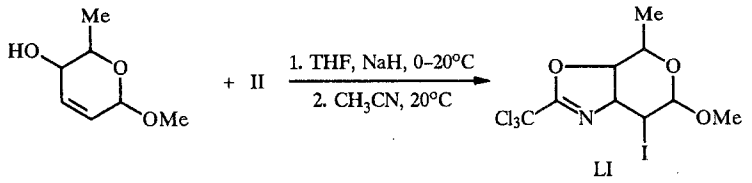
Benzyl alcohol derivatives XLV and XLVI undergo cyclization to substituted oxazolines XLVII and XLVIII on treatment with N-iodosuccinimide (XLI) [28]:



The synthesis of XLIX was accomplished via a similar scheme from imino ester L [29]:

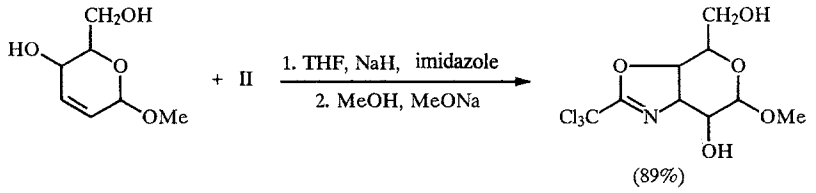


3-Hydroxy-6-methoxy-2-methyldihydropyran reacts with nitrile II in the presence of iodoniadicollidine perchlorate to give bicyclic LI, in which the configuration of the starting pyran derivative is retained [30-33]:



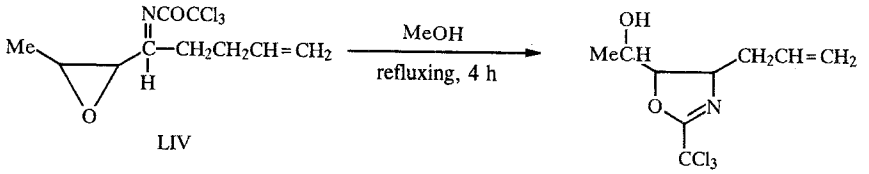
LI

3-Hydroxy-6-methoxy-2-hydroxymethyldihydropyran undergoes an interesting transformation on reaction with nitrile II [34]:



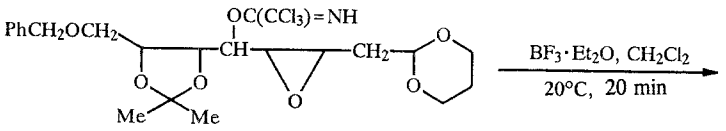
(89%)

Oxazoline derivatives LII and LIII are formed as a result of rearrangement of epoxides LIV and LV, obtained on the basis of nitrile II [35, 36]:

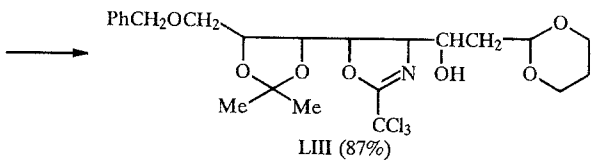


LIV

LII (96%)



LV

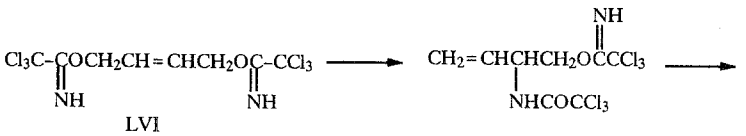


LIII (87%)

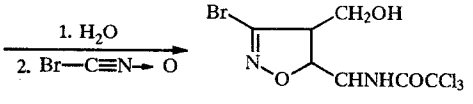
A series of compounds containing condensed oxazoline and tetrahydropyran rings was synthesized by the reaction of nitrile II with epoxides of the monosaccharide series in the presence of imidazole and sodium hydride in THF at 0-20°C [34].

Under the influence of boron trifluoride etherate, the formation of an oxazolidine ring may proceed through the —OC(CCl$_3$)=NH and —NHAc groupings with removal of a trichloroacetonitrile fragment, which functions as an activator [37].

Bis(imino ester) LVI, obtained by the reaction of nitrile II with 2-but-ene-1,4-diol, was, after rearrangement, subjected to reaction with cyanogen bromide N-oxide BrC ≡ N → O, and isoxazoline derivative LVII was obtained in this way [38]:

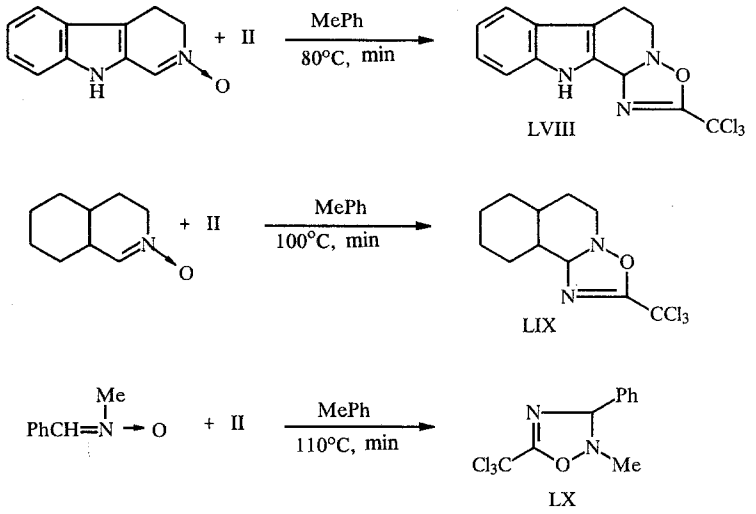


LVI



LVII

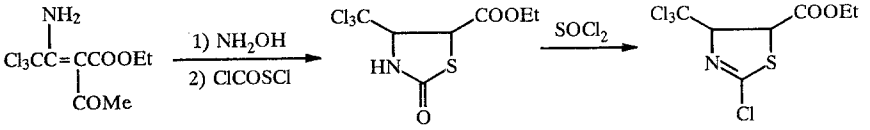
1,2,4-Oxadiazole derivatives LVIII-LX were synthesized in quantitative yields by 1,3-dipolar cycloaddition of nitrile II with compounds containing the C=N → O grouping [39]:



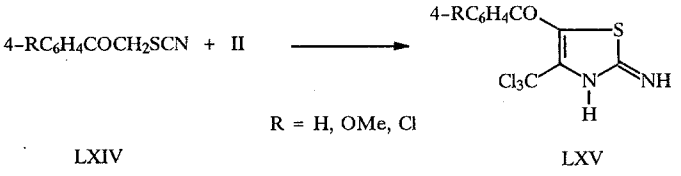
3.3. Synthesis of N,S-Heterocycles. A method for obtaining 3,4-dichloro-5-cyanoisothiazole, which consists in heating elementary sulfur with nitrile II at 200-300°C, has been patented; the yield was 48% [40].

2-Trichloromethyl-4,5-dihydrothiazole, obtained from nitrile II and 2-thioxyethylamine by refluxing in methanol, is completely nontoxic for grain cultures vis-à-vis high effectiveness against common weeds [41].

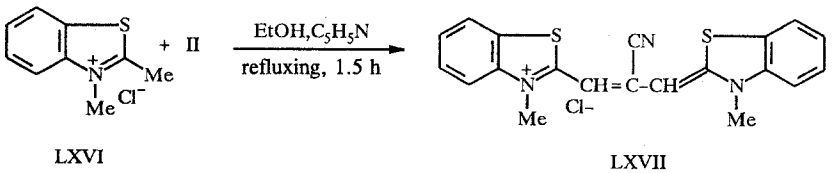
The product (LXI) of the reaction of nitrile II with acetoacetic ester, on treatment with hydroxylamine and ClCOSCl, is converted to thiazole derivative LXII, and the latter reacts with thionyl chloride to give 2-chloro-4-trichloromethyl-5-ethoxycarbonylthiazoline (LXIII) [42]:



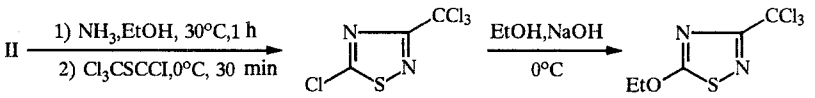
According to the data in [43], the products of the reaction of nitrile II with isothiocyanates LXIV are thiazole derivatives LXV:



The reaction of nitrile II with 2,3-dimethylbenzothiazolium chloride (LXVI) was used in the synthesis of cyanine dye LXVII [44]:

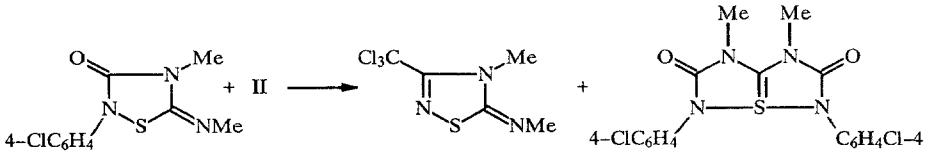


5-Ethoxy-3-(trichloromethyl)-1,2,4-thiadiazole was obtained by the successive treatment of nitrile II with ammonia and Cl_3CSCl and treatment of the resulting 5-chloro-3-(trichloromethyl)-1,2,4-thiadiazole (LXVIII) with alcoholic sodium hydroxide [45]:



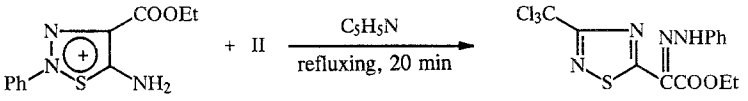
LXVIII

When LXIX is heated with nitrile II, it gives two compounds — one is the one-ring compound LXX, while the other is the two-ring compound LXXI, which contain a sulfur atom and two nitrogen atoms in five-membered rings [47]:



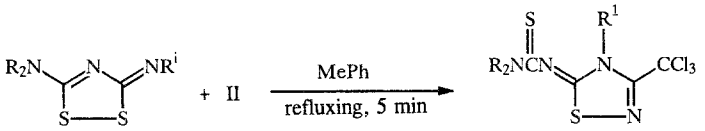
LXIX LXX LXXI

Recyclization occurs when 1,2,3-thiadiazolium salt LXXII is treated with nitrile II in refluxing pyridine, and 1,2,4-thiadiazole derivative LXXIII is formed [48]:



LXXII LXXIII (82%)

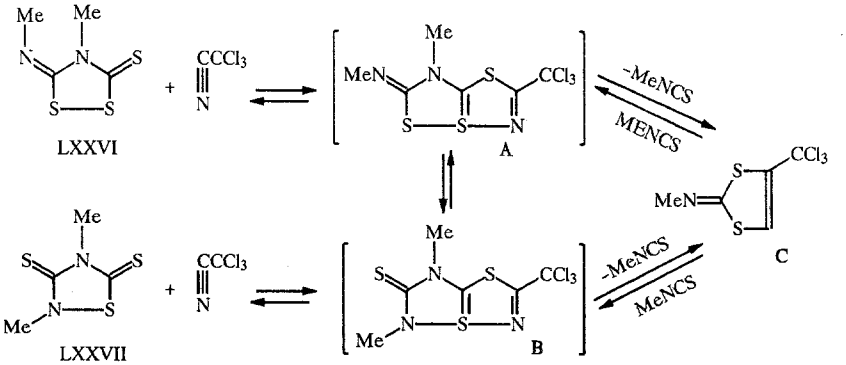
The conversion of compounds of the 1,2,4-dithiazole series LXXIV to 1,2,4-thiadiazole derivatives LXXV by refluxing in dry toluene with nitrile II has been described [49]:



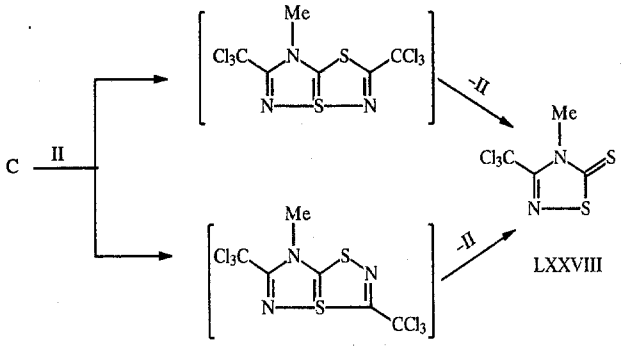
LXXIV LXXV (97%)

L'Abbe and co-workers [50] have established that the very same compound — 3-(trichloromethyl)-4-methyl-1,2,4-thiadiazolidine-5-thione (LXXVIII) — is formed in the reaction of nitrile II with both 3-methylimino-4-methyl-1,2,4-dithiazolidine-5-thione (LXXVI) and with 2,4-dimethyl-1,2,4-thiazolidine-3,5-dithione (LXXVII).

The examined transformations can be represented by the following scheme:

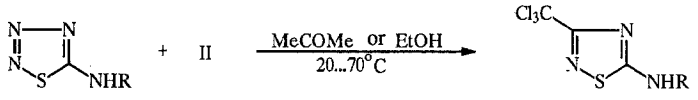


LXXVI LXXVII



As L'Abbe and co-workers assumed [50], under the influence of nitrile II, the reversible isomerization LXXVI ⇄ LXXVII proceeds through intermediates A and B, and the S—S or S—NMe bonds are cleaved. This is not a thermal process, since, in the absence of nitrile II, LXXVI and LXXVII are stable at 90°C. Compound C probably exists in the form of *syn* and *anti* conformers, which are capable of reacting with nitrile II.

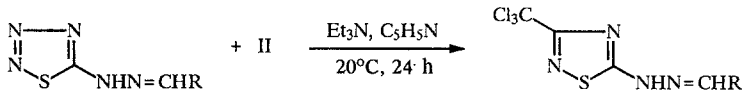
The 1,2,3,4-thiatriazole ring of LXXIX, which contains an amino group in the 5 position, undergoes recyclization to a 1,2,4-thiadiazole ring on reaction with nitrile II to give LXXX [51]:



LXXIX LXXX

R = H (92%); Me (72%); Ph (42%)

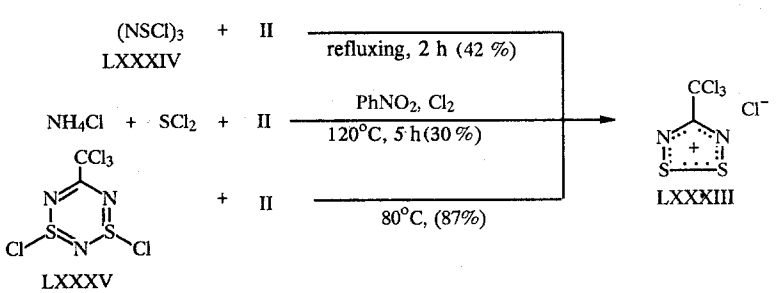
A similar recyclization takes place in the reaction of nitrile II with hydrazones LXXXI in pyridine in the presence of triethylamine; the reaction products are thiadiazoles LXXXII [52]:



LXXXI LXXXII

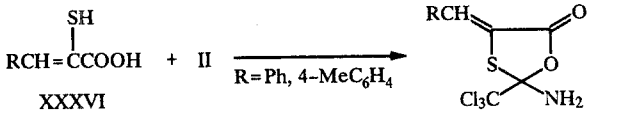
R = 4-ClC$_6$H$_4$ (88%); HO-C$_6$H$_4$ (89%); 2-furyl-2 (74%)

Three approaches have been described to obtain 1,2,3,5-dithiadiazolium chloride LXXXIII: the reaction of nitrile II with 1,3,5-trichloro-1,3,5,2,4,6-cyclotrithiazene (LXXXIV), with $NH_4Cl + SCl_2$, or with 1,3-dichloro-5-(trichloromethyl)-1,3,2,4,6-dithiatriazene (LXXXV) [54]:



LXXXIV LXXXV LXXXIII

Compounds that contain oxygen and sulfur atoms in a five-membered heteroring — 1,3-oxothiolane derivatives LXXXVII — are formed as a result of the reaction of nitrile II with α-mercaptocinnamic acids LXXXVI [55]:



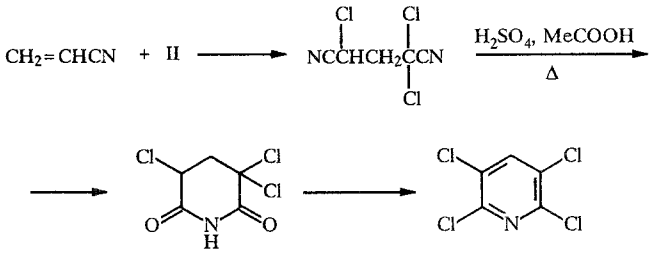
XXXVI

LXXXVII (75%...80%)

4. Six-Membered Heterocyclic Compounds

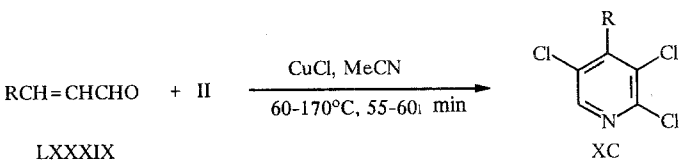
4.1. Formation of Pyridine Rings. The products of the addition of nitrile II to acrylonitrile or to α,β-unsaturated aldehydes and ketones are convenient starting compounds for the synthesis of chlorine-substituted pyridine bases.

By heating with sulfuric acid in acetic acid, the adduct of nitrile II with acrylonitrile was converted to cyclic imide LXXXVIII, from which 2,3,5,6-tetrachloropyridine was obtained by the action of $POCl_3$ or PCl_5 [56]:



LXXXVIII

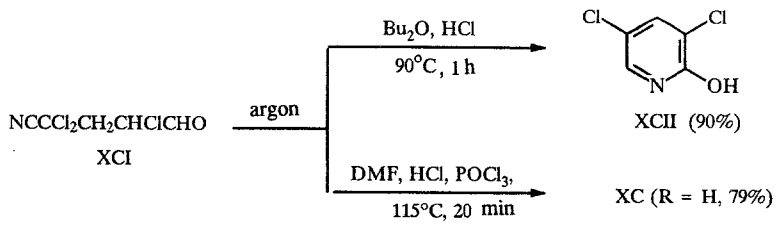
Chlorine-substituted pyridine bases can be obtained from nitrile II and α,β-unsaturated aldehydes with or without isolation of the products of addition of the starting compounds. Thus pyridine derivatives XC were isolated when nitrile II was heated with α,β-unsaturated aldehydes LXXXIX in benzene or acetonitrile in the presence of CuCl or Cu in sealed ampuls [57]:



LXXXIX XC

R = H (72%), R = Me (51%), R = Ph (38%)

If the reaction of nitrile II with acrolein is carried out at 90°C for 6 h in a sealed ampul, only addition product XCI can be isolated in 68% yield; the cyclization of XCI under the influence of hydrogen chloride leads to different compounds under different conditions: dihydropyridine derivative XCII is formed in dibutyl ether, while the reaction product is 2,3,5-trichloropyridine XC (R = H) when the reaction is carried out in DMF in the presence of $POCl_3$ [58]:

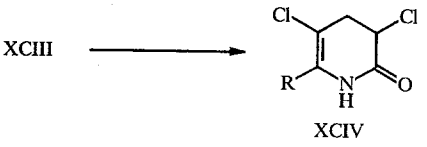


XCI XCII (90%)

XC (R = H, 79%)

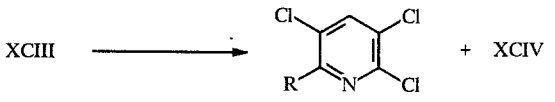
Interesting results were obtained in a study of the cyclization of $RCOCHClCH_2CCl_2CN$ (XCIII) — products of the addition of nitrile II to vinyl ketones [59, 60].

Dihydro-2-pyridone derivatives XCIV are formed in high yields when hydrogen chloride is passed through solutions of adducts XCII (R = Me, Et, Pr) in diethyl or dibutyl ether at 5-90°C [59, 60]. In the case of adduct XCIII (R = 1-adamantyl), however, cyclization can be realized only when the reaction is carried out in a sealed ampul — the yield is 41-52% [60]:



XCIV

If the reaction is carried out in DMF by passing hydrogen chloride for 10-15 min, the principal reaction products are pyridine derivatives XCV, while dihydro-2-pyridone derivatives XCIV are formed in 5-8% yields [60]:

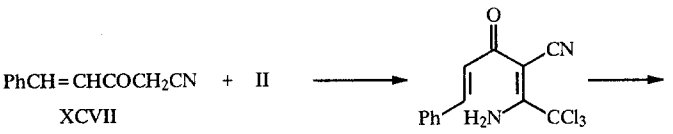


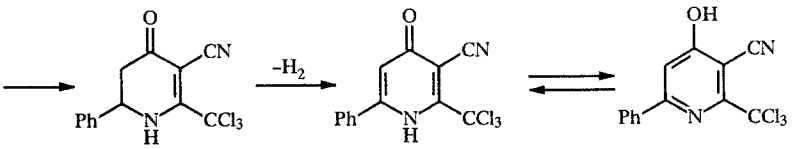
XCV

R = Me (86%); Et (79%); Pr (81%)

Only dihydro-2-pyridone derivatives XCIV are formed in up to 90% yields when the reaction is carried out for a longer time (45-60 min) [60].

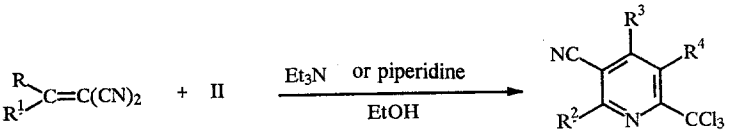
2-(Trichloromethyl)-3-cyano-6-phenyldihydro-4-pyridone (XCVI), which is formed in the reaction of nitrile II with keto nitrile XCVII, is converted under the reaction conditions to 2-(trichloromethyl)-3-cyano-4-hydroxy-6-phenylpyridine [61]:





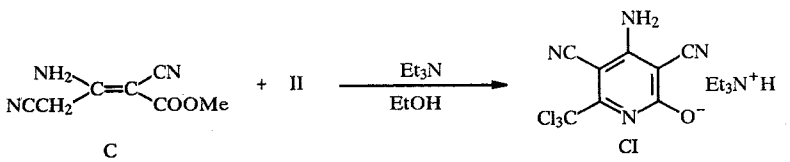
XCVI

In a number of studies [62-66] the synthesis of trichloromethyl-substituted amino nitriles XCVIII of the pyridine series is accomplished by the reaction of nitrile II with XCIX, which contain a $C{=}C(CN)_2$ grouping; the yields range from 55% to 80%:



XCIX XCVIII

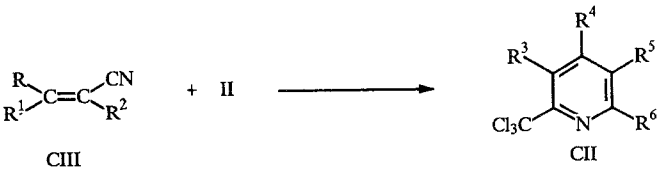
Salt CI was obtained under similar conditions from nitrile II and dinitrile CI [65]:



C CI

50%

Pyridine derivatives CII were synthesized by the reaction of nitrile II with unsaturated CIII, which contain various functional groups, one of which must be a cyano group [67-70]; the yields range from 50% to 85%:



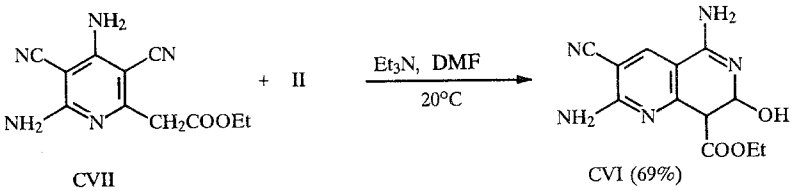
CIII CII

In these studies the researchers used various solvents (DMF, dioxane, ethanol) and catalysts (triethylamine, piperidine, sodium acetate). When the reaction of nitrile II with CIII (R = Me, R^1 = PhNHNH, R^2 = $PhNHCOCH_2$) in refluxing EtOH in the presence of piperidine, the reaction product (in 68% yield) was the corresponding ethoxy derivative, which is formed due to nucleophilic substitution of the CCl_3 group for an OCH_2H_5 group [71].

Pyridine derivative CV is formed as a result of the reaction of nitrile II with unsaturated ketone CIV [72]:

CIV CV

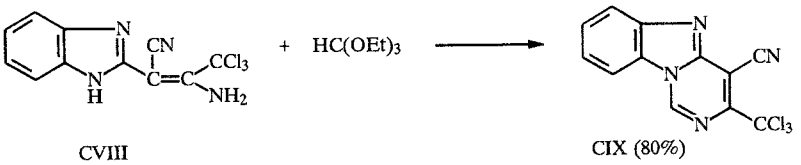
Two-ring system CVI, which contains one nitrogen atom in each of the six-membered rings, was synthesized from nitrile II and pyridine derivative CVII [73]:



CVII CVI (69%)

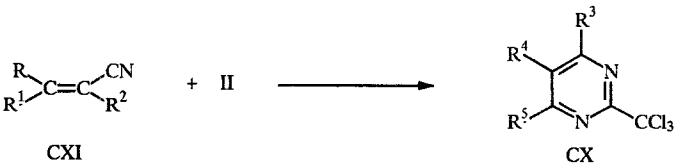
4.2. Formation of Pyrimidine Rings. A method for obtaining pyrimidine derivatives from unsaturated compounds that contain cyano groups has been developed in quite some detail.

Substituted benzo[g]imidazo[1,2-c]pyrimidine CIX is formed in high yield when amino nitrile CVIII, obtained from 2-cyanomethylbenzimidazole and nitrile II, is treated with ethyl orthoformate [74]:



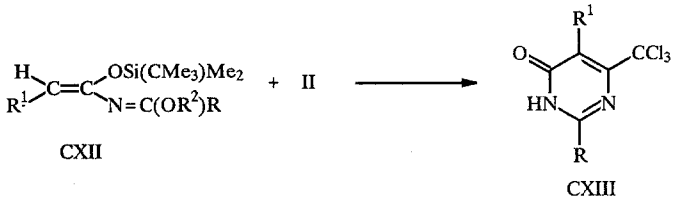
CVIII CIX (80%)

A large number of pyrimidine derivatives CX were synthesized by the reaction of nitrile II with unsaturated nitriles CXI; the yields ranged from 60% to 80% [8, 75, 76]:



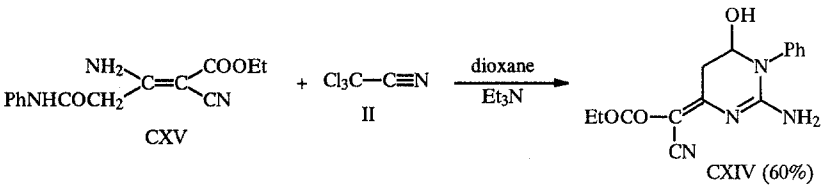
CXI CX

6-Pyrimidinone derivatives CXIII were obtained as a result of the reaction of nitrile II with polyfunctional compounds CXII [77]:



CXII CXIII

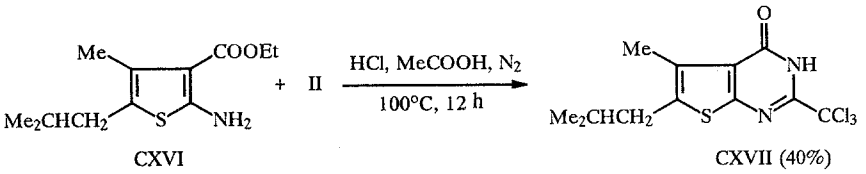
Substituted dihydropyrimidine CXIV, which does not contain a CCl_3 group, is formed as a result of the reaction of nitrile II with CXV [78]:



CXV II CXIV (60%)

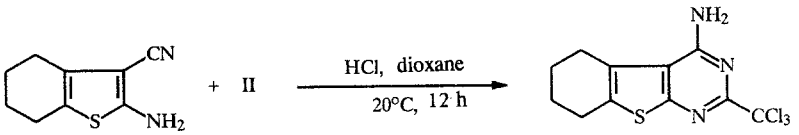
A convenient and frequently used method for the synthesis of pyrimidine derivatives is the reaction of carboxylic acid nitriles with amines that contain an alkoxycarbonyl, amido, or cyano group attached to the adjacent carbon atom.

Amino ester CXVI of the thiophene series reacts with nitrile II in the presence of hydrogen chloride in acetic acid to give thieno[2,3-d]pyrimidine derivative CXVII [79]:



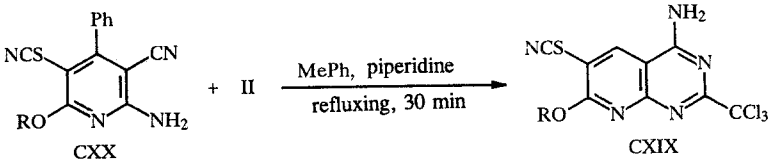
CXVI CXVII (40%)

Under the influence of hydrogen chloride, 2-amino-3-cyano-4,5,6,7-tetrahydrobenzo[b]thiophene and nitrile II are converted to three-ring system CXVIII [80]:



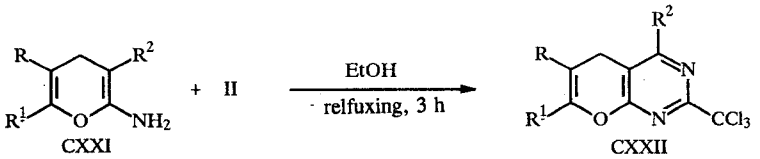
CXVIII (50%)

Compound CXIX, which contains condensed pyridine and pyrimidine rings, is formed from pyridine derivatives CXX and nitrile II by refluxing a mixture of them in toluene in the presence of piperidine [81]:



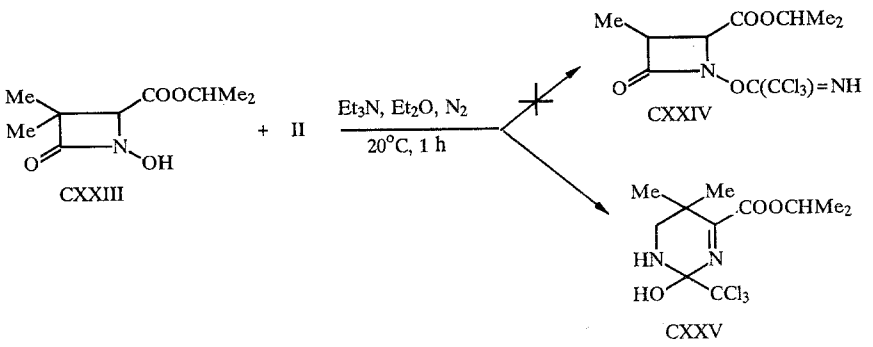
CXX CXIX

The reaction of nitrile II with γ-pyran derivatives CXXI gave CXXII, which contain condensed pyran and pyrimidine rings [82, 83]; the yields range from 53% to 85%:

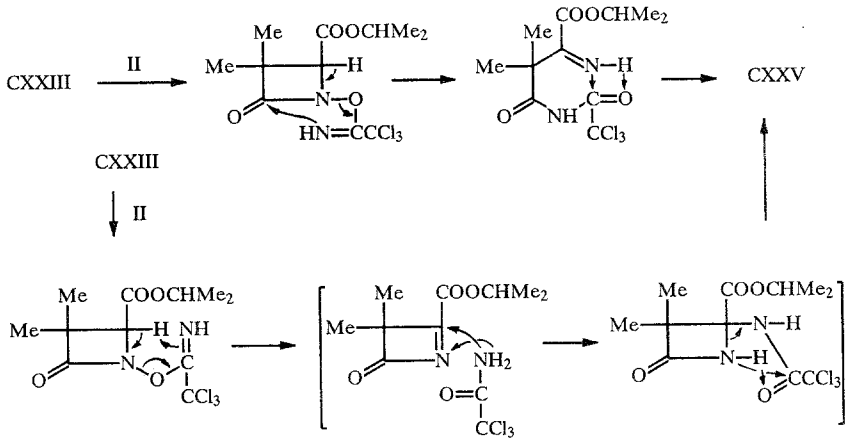


CXXI CXXII

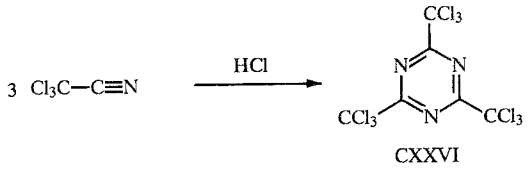
The results of the treatment of 1-hydroxy-4-isopropoxycarbonyl-3,3-dimethyl-2-azetidinone (CXXIII) with nitrile II in the presence of triethylamine were unexpected — instead of the expected imino ester CXXIV, compound CXXV of the pyrimidine series was obtained [84]:



In the opinion of Biswas and co-workers [84], the reaction may proceed via one of two pathways:

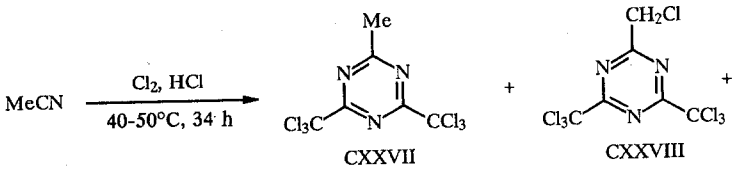


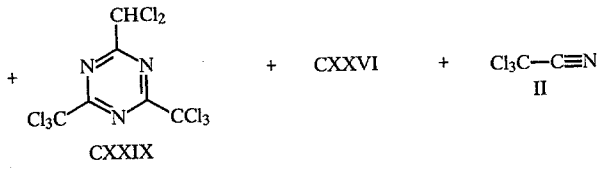
4.3. Formation of Triazine Rings. The cyclotrimerization of nitrile II under pressure to 1,3,5-triazine derivative CXXVI was described for the first time in 1947 [85]:



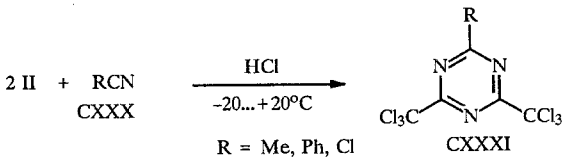
A method for the cyclotrimerization of nitrile II in the presence of HCl—$AlCl_3$ and HBr—$AlBr_3$ systems at −40°C in sealed vessels was patented; the yield of trimer CXXVI ranges from 80% to 93%. It is pointed out that, without a Lewis acid ($AlCl_3$), cyclotrimerization proceeds with considerably greater difficulty and does not take place at all in the absence of HCl [86]. In a later patent [87] it is noted that the cyclotrimerization of nitrile II proceeds in the presence of Bi, Pb, Sn, Ti, Zn, Ba, and Cd at 0-400°C. Wakabayashi and co-workers [88] made a detailed study of the cyclotrimerization of nitrile II in the presence of HCl or HBr and Lewis acids at 20°C for 12 h. The following results [HX, Lewis acid, and yield (%) of CXXVI] were obtained: HCl, —, 1.6; HBr, —, 34; HCl, AlF_3, 67.2; HCl, $AlCl_3$, 35.9; HCl, $AlBr_3$, 95.3; HBr, $AlBr_3$, 95.3; HCl, BF_3·MeCOOH, 62.5; HCl, BF_3·Et_2O, 93.8; HCl, $FeCl_3$, 43.8; HCl, $ZnCl_2$, 42.2; HCl, $SnCl_4$, 51.6; HCl, $SbCl_3$, 46.9; HCl, $TiCl_4$, 40.5; HCl, $TiBr_4$, 24.9.

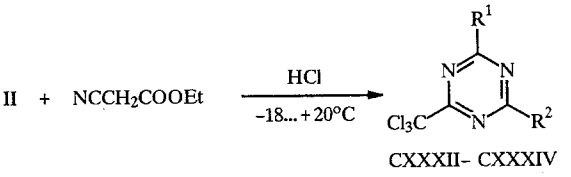
Trimer CXXVI was obtained in high yield with high purity by treatment of acetonitrile saturated with HCl and chlorine at 60-65°C for 12 h with irradiation of the mixture with UV light and subsequent saturation of the reaction mixture with HCl at 15°C for 30 min and by the action of chlorine at 60-65°C for 40 h [89]. Aliev and co-workers [90] carried out the same process under different conditions. According to their data, four 1,3,5-triazine derivatives CXXVI-CXXIX and nitrile II are formed from acetonitrile:





Grundmann and co-workers [91] studied the cocyclomerization of nitrile II with nitriles RCN CXXX and observed that when R = Me, Ph, and Cl, the same compound (CXXXI) is formed; if, however, R = CH_2COOEt, three compounds (CXXXII-CXXXIV) are formed:





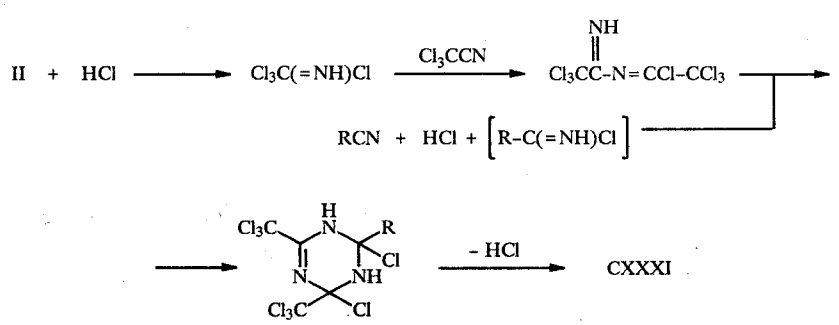
R^1, R^2 = CH_2COOEt, CCl_3 (CXXXII); CH_2COOEt, CH_2COOEt (CXXXIII); CCl_3, CCl_3 (CXXXIV)

The cocyclotrimerization of nitrile II with other nitriles was studied most thoroughly and systematically by Wakabayashi and co-workers [88]. The following results [Lewis acid, yield of CXXXI (%), R = Me] were obtained as a result of the cyclotrimerization of nitrile II with MeCN (in a ratio of 1:2) in the presence of HCl and a Lewis acid at 20°C for 2-3 h: AlF_3, 95; $AlCl_3$, 85; $AlBr_3$, 95; $BF_3 \cdot MeCOOH$, 95; $BF_3 \cdot Et_2O$, 95; BBr_3, 88; $FeCl_3$, 83; $ZnCl_2$, 78; $SnCl_4$, 83; $SbCl_5$, 76; $TiCl_4$, 90; $TiBr_4$, 90; $CuCl_2$, 58; $MgCl_2$, 50.

The following results [R in RCN and in CXXXI, yield of CXXXI (%)] were obtained under similar conditions from nitrile II and nitriles RCN (in a ratio of 2:1) in the presence of HBr and $AlBr_3$ [88]: Me, 95; Ph, 94; 2-ClC_6H_4, 91; 3-ClC_6H_4, 93; 4-ClC_6H_4, 92; 2,4-Cl_2-C_6H_3, 88; 3,4-$Cl_2C_6H_3$, 90; 2,4,5-$Cl_3C_6H_2$, 85; 4-BrC_6H_4, 92; 4-MeC_6H_4, 95; 3-$NO_2C_6H_4$, 74; 4-$MeOC_6H_4$, 90; 1-naphthyl, 83; 2-naphthyl, 78.

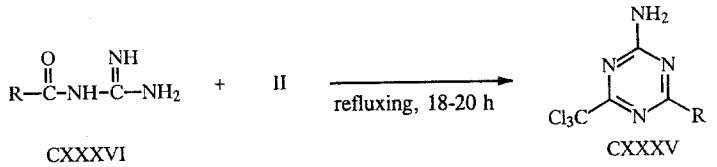
The cyclotrimerization of nitrile II and nitriles RCN was also carried out in the presence of HCl at 20°C for 12 h with subsequent heating of the reaction mixture at 150-200°C [88], and the following compounds [R in CXXXI, yield of CXXXI (%)] were obtained: Et, 92; Pr, 93; Me_2CH, 87; Bu, 90; Me_2CHCH_2, 82; sec-C_4H_9, 81; Me_3C, 56; C_5H_{11}, 95; C_9H_{19}, 78; $C_{17}H_{35}$, 92; $ClCH_2CH_2$, 69; Cl_3CCH_2, 87.

Wakabayashi and co-workers [88] propose the following scheme for the formation of 1,3,5-triazine derivatives CXXXI:



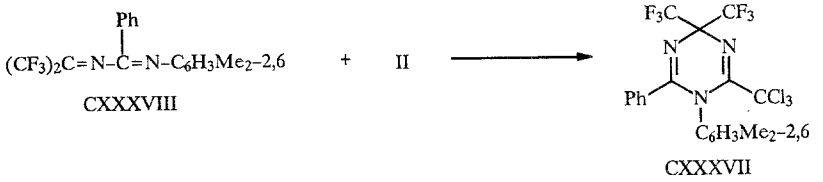
There is yet another series of studies of the cyclotrimerization of nitrile II with carboxylic acid nitriles RCN in which the production of either only CXXXI (R = 2-thienyl, 1-methyl-2-pyrrolyl [92], $CH_2CH_2CH_2Cl$ [93], 4-MeC_6H_4 [94], 3-MeC_6H_4, 4-MeC_6H_4, 3-FC_6H_4 [95], 4-$MeOC_6H_4$ [96]) or mixtures of CXXXI and CXXVI (R = CH_2CH_2Cl, CH_2CH_2F, CH_2CH_2OEt, CH_2CH_2OPr, 1-indolylethyl [98], Me [99], C_5H_{11}, $C_{10}H_{21}$, $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{15}H_{31}$, $C_{17}H_{35}$ [100]) is reported.

1,3,5-Triazine derivatives CXXXV were synthesized in good yields from nitrile II and N-acylguanidines CXXXVI [101-103]; the yields ranged from 67% to 92%:



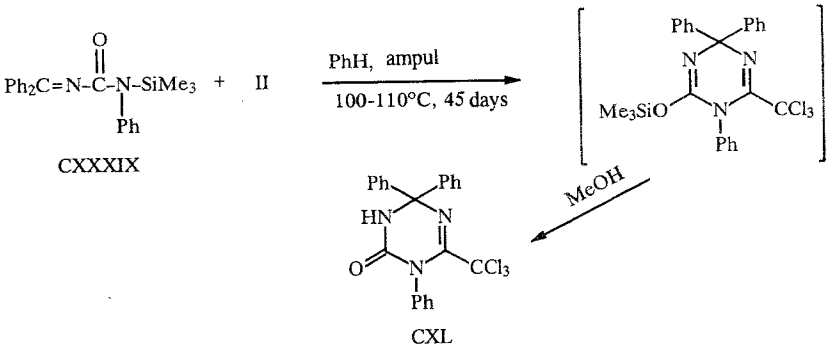
CXXXVI CXXXV

An unusual method for the synthesis of 1,3,5-triazine derivative CXXXVII — the reaction of nitrile II with CXXXVIII — was described in [104].



CXXXVIII CXXXVII

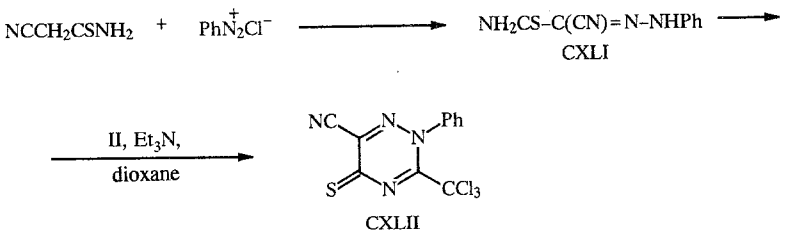
Compound CXL was obtained as a result of the reaction of nitrile II with urea derivative CXXXIX and subsequent treatment of the reaction product with methanol [105]:



CXXXIX CXL

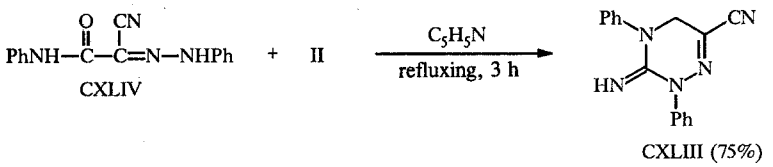
Several methods for obtaining 1,2,4-triazine derivatives on the basis of nitrile II have been described.

Compound CXLI, obtained by condensation of benzenediazonium chloride with cyanothioacetamide, reacts with nitrile II in the presence of triethylamine to give substituted 1,2,4-triazine CXLII [106]:

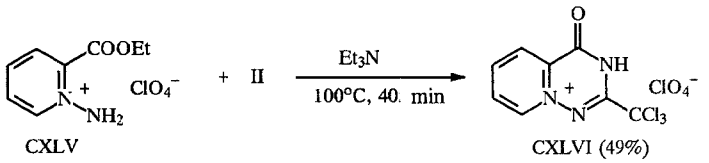


CXLI CXLII

In the opinion of El-Bannany and co-workers [107], the formation of 6-cyano-3-imino-2,4-diphenyl-1,2,4-triazin-5-one (CXLIII) from nitrile II and CXLIV proceeds through an intermediate product of addition of CXLIV to the —C≡N group of nitrile II:

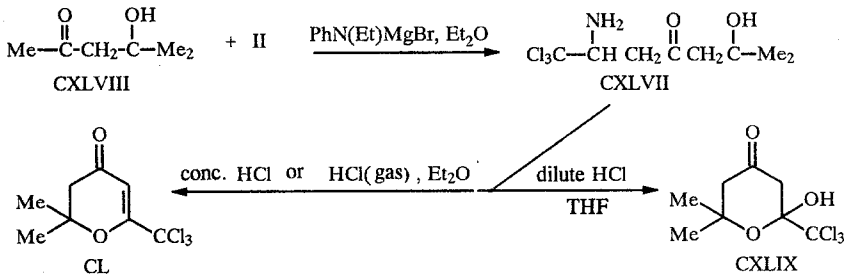


Heating of a mixture of nitrile II with perchlorate CXLV in the presence of triethylamine leads to salt CXLVI [108]:

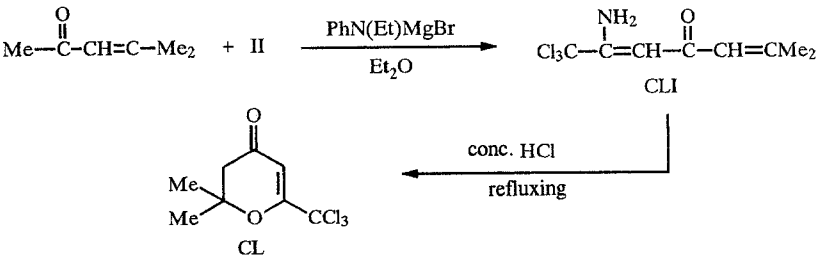


1,3,5-Triazine derivatives that contain a CCl_3 grouping, which were obtained by the cocyclotrimerization of nitrile II with other carboxylic acid nitriles, are patented as components of herbicidal compositions [109] or components of light-sensitive compositions [94, 96, 109-113].

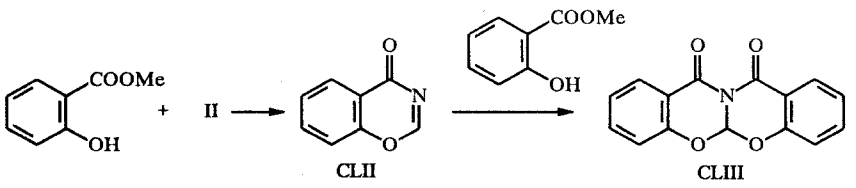
4.4. Formation of O-, N,O-, N,O,S-, and N,P-Heterocycles. When CXLVII, formed from nitrile II and keto alcohol CXLVIII, is treated with dilute hydrochloric acid, it is converted to tetrahydro-γ-pyrone derivative CXLIX, while it is converted to substituted dihydro-γ-pyrone CL by the action of concentrated hydrochloric acid or gaseous hydrogen chloride [114]:



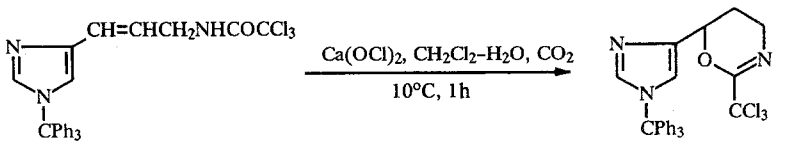
Dihydro-γ-pyrone derivative CL is also formed by treating CLI — the product of the reaction of nitrile II and 2-methylpent-2-en-4-one — with concentrated hydrochloric acid [114]:



Compound CLII, which does not contain a CCl_3 group, is formed as a result of the reaction of nitrile II with methyl salicylate; CLII reacts with yet another molecule of methyl salicylate to give four-ring system CLIII [11]:

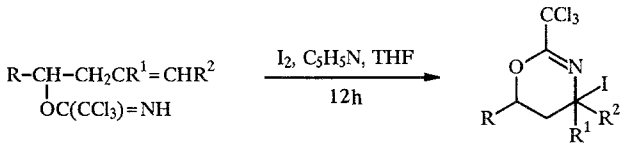


N-Substituted trichloroacetic acid amide CLIV, obtained by the reaction of nitrile II and 1-[1-(triphenylmethyl)-4-imidazolyl]allyl alcohol with subsequent rearrangement of the initially synthesized imidate, was converted to 2,6-disubstituted dihydrooxazine CLV [115]:



CLIV CLV (55%)

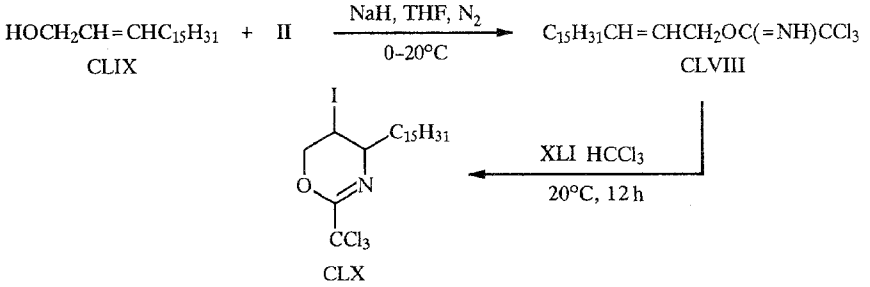
The reaction of nitrile II and the corresponding allyl alcohols gave imidates CLVI, which were converted to dihydro-1,3-oxazine derivatives CLVII by the action of iodine [116]; the yields ranged from 65% to 90%:



CLVI CLVII

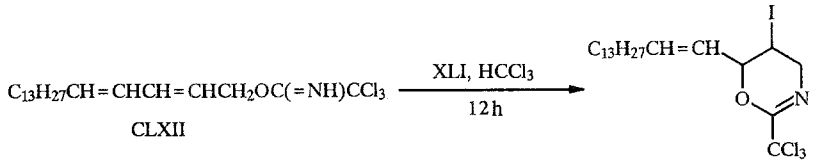
CLVII R, R^1, R^2, (%): H, Me, H, (90%); H, H, Et, (80%); Me, H, H, (65%)

The cyclization of imidate CLVIII, formed from nitrile II and alcohol CLIX, to 5-iodo-6-pentadecyl-2-(trichloromethyl)-5,6-dihydro-4H-1,3-oxazine (CLX) was accomplished by the action of N-iodosuccinimide (XLI) [26]:



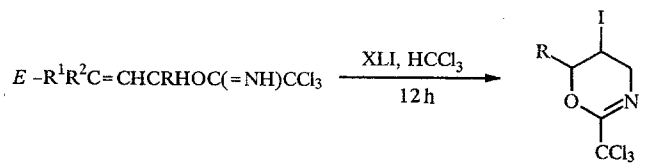
CLIX CLVIII CLX

Dihydrooxazine derivative CLXI is formed in excellent yield as a result of the cyclization of imidate CLXII — the product of the reaction of nitrile II with the corresponding dienic alcohol — by the action of iodosuccinimide (XLI) [117]:



CLXII CLXI (95%)

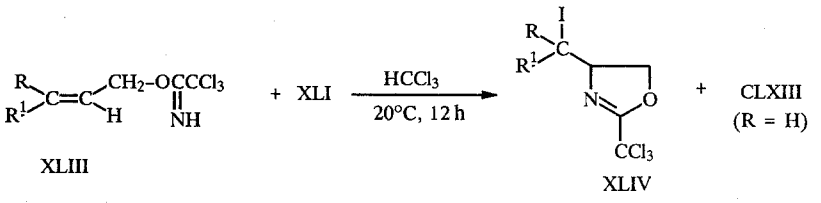
As we noted earlier, either oxazole derivatives XLIV or oxazine derivatives CLXIII may be formed by the action of iodosuccinimide (XLI) on allyl alcohol imidates. The E configuration of the allyl imidates favors the formation of oxazine derivatives; electronic factors have substantial significance [27]; the yields of the cyclization products range from 80% to 95%:



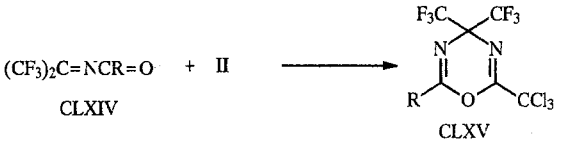
CLXIII

Similarly, CLXIII (without an iodine atom in the 4 position), where R = H, R1 = H, and R2 = $CH(I)CH_2CH_3$, was obtained in 90% yield from E-$MeCH_2CH{=}CHCH_2CH_2OC(CCl_3){=}NH$ [27].

In a number of cases an oxygen atom in the β position relative to the double bond of the E-allyl imidates has a substantial effect, and mixtures of XLIV and CLXIII are formed as a result of the reaction [27]:

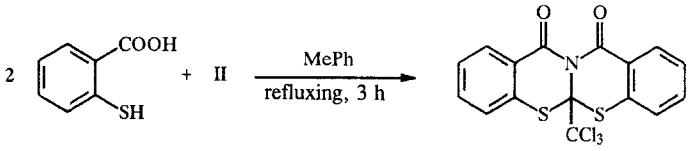


Electron-deficient dienes CLXIV undergo cycloaddition with an electron-deficient dienophile — nitrile II — to give [4+2] adducts CLXV [118]:



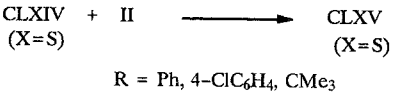
R = Ph, 4-ClC_6H_4, CMe_3

Four-ring system CLXVI is formed in the reaction of nitrile II with 2-mercaptobenzoic acid in refluxing toluene [119]:

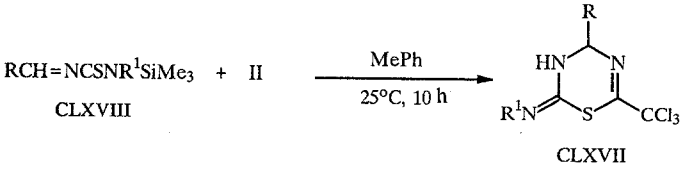


CLXVI (80%)

Heterocyclic six-membered systems CLXV (X = S) and CLXVII, which contain a sulfur atom and two nitrogen atoms in their rings, were synthesized by [4+2] cycloaddition of heterodienes CLXIV (X = S) [118] or CLXVIII [120] with nitrile II:

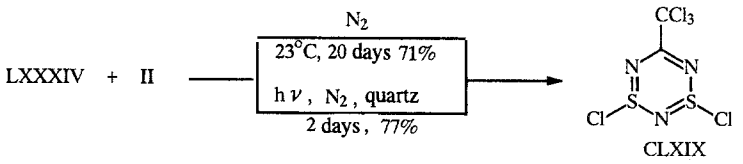


R = Ph, 4-ClC_6H_4, CMe_3



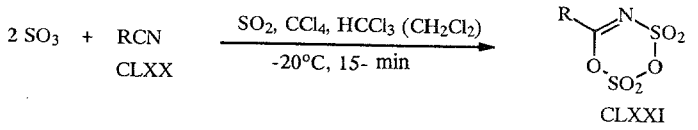
R = Ph, R^1 = Ph (90%); R = 2-thienyl-2, R^1 = Ph (87%); R = Ph, R^1 = 4-ClC_6H_4 (83%); R = 2-thienyl-2, R^1 = 4-ClC_6H_4 (91%)

Two methods for obtaining 1,3-dichloro-5-(trichloromethyl)-1,3,2,4,6-dithiatriazine (CLXIX) from nitrile II and trichlorotriazene LXXXIV have been described (see above) [54, 121]:



CLXIX

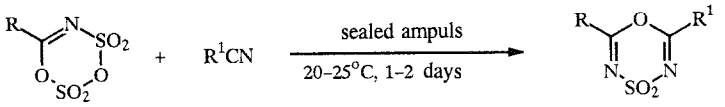
The reaction of nitrile II with sulfur trioxide was studied in a series of papers [122-125]. It was found that nitriles RCN CLXX and SO_3 form 6-substituted 1,3,2,4,5-dioxadithiazine 2,2,4,4-tetroxides CLXXI at −20°C:



CLXXI

R = CCl_3, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$

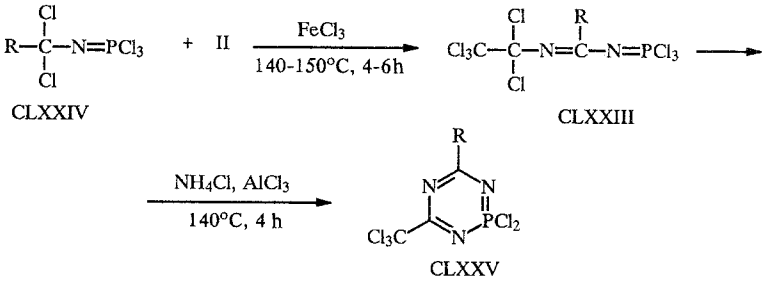
3,5-Disubstituted 4-oxa-1,2,6-thiadiazine 1,1-dioxides CLXXII are formed in the reaction of CLXXI (R = Ph) with nitrile II or CLXXI (R = CCl_3) with 4-$NO_2C_6H_4CN$ [124]:



CLXXI CLXXII

R = Ph, CCl_3; R^1 = CCl_3, 4-$NO_2C_6H_4$

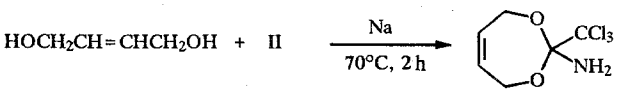
The products of the reaction of CLXXIII, formed from nitrile II and CLXXIV, are converted by treatment with ammonium chloride and aluminum chloride to six-membered heterocyclic systems CLXXV, which contain a phosphorus atom and three nitrogen atoms in their rings [126]:



CLXXIV CLXXIII CLXXV

R = CCl_3 (62%); CF_3 (45%)

5. Seven-Membered Heterocyclic Compounds. There is a single report regarding the synthesis of a seven-membered heterocyclic compound on the basis of nitrile II: 2-amino-2-(trichloromethyl)-4,7-dihydro-1,3-dioxepine (CLXXVI) was obtained in the reaction of nitrile II with 2-butene-1,4-diol [127]:



CLXXVI

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