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N-Functionalised carbodiimides

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ABSTRACT. A systematic review is presented on the synthesis and the physical and chemical properties of *N*-acyl, *N*-sulphonyl-, *N*-phosphoryl- and *N*-alkenyl-carbodiimides.

The bibliography contains 90 references.

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I. Introduction

Organic carbodiimides are important members of the heterocumulene class of compound. Being highly reactive, they are key starting materials in organic synthesis and, in addition to this, possess of a whole range of properties which have been usefully applied. Since the discovery of the first carbodiimides by Weit in 1874,[1] the chemistry of this class of compound has developed extensively, and data primarily on alkyl and aryl carbodiimides has been surveyed systematically in a number of reviews.[2–5] It is also possible to isolate carbodiimides with functional groups on nitrogen (e.g. RC(O), RSO_2, $R_2P(O)$, $R_2C{=}CR$, R_3Si, etc.), which possess unusual properties quite distinct from unfunctionalised carbodiimides. Most of the work relating to such *N*-functionalised derivatives has been reported during the last 20–25 years and, with the exception of the data relating to *N*-silylcarbodiimides,[6] the information contained therein has not been reviewed.

Up to now, most of the research in this field has been devoted to *N*-acyl-, *N*-sulphonyl-, *N*-phosphoryl- and *N*-alkenyl-carbodiimides. Their syntheses and properties have been examined systematically in the present review.

II. Synthesis of *N*-functionalised carbodiimides

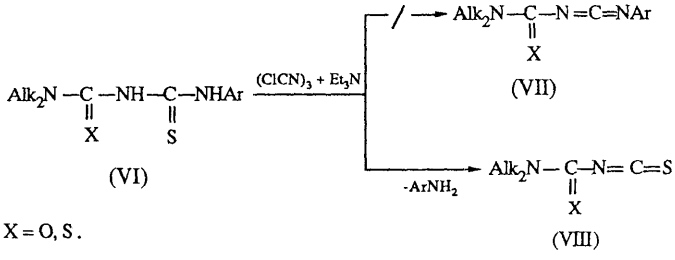
1. *N*-acyl(thioacyl, imidoyl) carbodiimides

Most of the carbodiimides in this category have been prepared by the same methods as used for the synthesis of unsubstituted alkyl and aryl carbodiimides.[4] The commonest route involves dehydrosulphuration of the corresponding thiourea:[7–13]

$$\mathrm{AcylNH{-}C(=S){-}NHR} \xrightarrow[-H_2S]{} \mathrm{AcylN{=}C{=}NR}\ ,\qquad \text{(I)–(V)}$$

R = Alk, Ar.

As seen in Table 1, the yield of carbodiimides (I–V) varies significantly, depending on the nature of the thiourea, the dehydrosulphurating agent, and the reaction conditions. The reaction can be conducted on heating in benzene, acetone or methylene chloride if HgO, PbO or NaOCl is used as the reagent. However, such conditions are unsuitable for preparing *N*-carbamoyl-, *N*-thiocarbamoyl- and *N*-imidoyl-carbodiimides (III–V) which tend to dimerise at elevated temperature. For these carbodiimides, the preferred dehydrosulphurating reagent is cyanuric chloride in the presence of triethylamine, with which reaction can be carried out conveniently at 0 °C; the formation of by-product is minimal and does not complicate the isolation procedure. However, it is not possible to apply this method to the preparation of *N*-(thio)carbamoyl-*N'*-arylcarbodiimides (VII) since the starting (thio)biurets react by cleavage of amine to give the corresponding isothiocyanate (VIII).[9]



X = O, S.

Table 1. *N*-Acyl-, *N*-thioacyl-, and *N*-imidoyl-carbodiimides, AcylN=C=NR (I–V).

Compound	Acyl	Dehydrosulphurating agent	Yield, %	Refs.
(I)	AlkC(O)	HgO	60—90	[7]
		NaClO	см*	[7]
(II)	AlkOC(O)	HgO	37—45	[8]
		$COCl_2 + Et_3N$	см*	[8]
(III)	$Alk_2NC(O)$	$(ClCN)_3 + Et_3N$	53—91	[9]
(IV)	$Ar_2NC(S)$	$(ClCN)_3 + Et_3N$	72—88	[10]
(V)	ArC(=NAr)	$(ClCN)_3 + Et_3N$	72—82	[11, 12]
		$Ph_3P + Et_3N + I_2$	86—95	[13]

*There are no data on the yield.

Mercuric benzamide, diethyl azodicarboxylate–triphenylphosphine and azodibenzoyl–triphenylphosphine[14] have also been used as mild dehydrosulphurating agents for the preparation of *N*-acylcarbodiimides.

A simple route has been devised for the preparation of *N*-ethoxycarbonyl-*N'*-alkylcarbodiimides (IX) as hetero-analogues of *N*-ethoxycarbonylisothiocyanates,[15] which are widely used in the synthesis of heterocyclic compounds. The method is based on the reaction of ethoxycarbonyliminophosgene (X) with sterically hindered primary amines.[16]

$$\underset{\text{(X)}}{EtOC(O)N{=}CCl_2} + AlkNH_2 \xrightarrow[-2HCl]{} \underset{\text{(IX)}}{EtOC(O)N{=}C{=}NAlk},$$

Alk = Pr^i, Bu^i, Bu^t, cyclo-C_6H_{11}.

A similar method has been used for the synthesis of *N,N'*-carbonyldicarbodiimides (XI) as hetero-analogues of *N,N'*-carbonyldiisocyanate.[17]

$$Cl_2C{=}N{-}\underset{\underset{O}{\|}}{C}{-}N{=}CCl_2 + 4AlkNH_2 \xrightarrow[-4HCl]{} AlkN{=}C{=}N{-}\underset{\underset{O}{\|}}{C}{-}N{=}C{=}NAlk.$$

(XI)

Recently, it has been shown that *N*-acylcarbodiimides (XII) and *N*-imidoylcarbodiimides (XIII) can be conveniently prepared by the reaction of trichloromethyl dichlorodiazadienes (XIV) or the isomeric pentachloroethylcarbodiimides (XV) with alcohols and amines, respectively.[18]

$$\underset{\text{(XIV)}}{CCl_3CCl{=}N{-}CCl{=}NR} \xrightarrow[-HCl,\ -MeCl]{MeOH} \underset{\text{(XII)}}{CCl_3\overset{\overset{O}{\|}}{C}{-}N{=}C{=}NR}$$

or

$$\underset{\text{(XV)}}{CCl_3CCl_2N{=}C{=}NR} \xrightarrow[-2HCl]{ArNH_2} \underset{\text{(XIII)}}{CCl_3\overset{\overset{NAr}{\|}}{C}{-}N{=}C{=}NR}$$

R = Pr^i, Ph, 2,4,6-$Me_3C_6H_2$.

A number of *N*-acylcarbodiimides have been obtained by the acylation of monosubstituted cyanamides—the method used by Fromm et al. in 1922 for the preparation of the first member of this class to be characterised, namely (XVII).[19] This was obtained by treatment of the cyanamide (XVI) with benzoyl chloride.

$$\underset{\text{(XVI)}}{N{\equiv}C{-}NHCH_2CH_2OH} \xrightarrow{2PhC(O)Cl} \underset{\text{(XVII)}}{PhC(O)N{=}C{=}NCH_2CH_2OC(O)Ph}.$$

In a subsequent development of the method,[20,21] it was proposed that reaction involves initial formation of an acylcyanamide, isomerisation of which yields the desired carbodiimide. This is not unlike the synthesis of *N*-silylcarbodiimides (XIX), which proceeds via *N*-silylation of the corresponding *N*-acylcyanamide (XVIII).[22,23]

$$\underset{\text{(XVIII)}}{RC(O)NH{-}C{\equiv}N} + Me_3SiCl \longrightarrow [RC(O)N(SiMe_3){-}C{\equiv}N] \longrightarrow \underset{\text{(XIX)}}{RC(O)N{=}C{=}NSiMe_3}$$

R = MeO, EtO.

N-Acyl-*N'*-silyl(stannyl)carbodiimides (XX) are obtained in high yield by acylation of the corresponding silyl(stannyl)carbodiimides (XXI) with carboxylic acid anhydrides or halides,[24,25] or with phenyl isocyanate:[26]

$$\underset{\text{(XXI)}}{R_3MN{=}C{=}NMR_3} + R'COX \xrightarrow{20\ ^\circ C} \underset{\text{(XX)}}{R'C(O)N{=}C{=}NMR_3},$$

R_3M = Me_3Si, Bu_3Sn; R' = Me, CF_3, Ph; X = Cl, MeC(O)O.

Catalytic decarboxylation of isocyanates,[27] which has been widely applied to the synthesis of diarylcarbodiimides, cannot be used for the synthesis of *N*-acylcarbodiimides because of their low thermal stability. However, there is a reference to the *in situ* formation of bis(trichloroacetyl)carbodiimides (XXII) by this route.[28]

$$2CCl_3C(O)N{=}C{=}O \xrightarrow[-CO_2]{} \underset{\text{(XXII)}}{CCl_3C(O)N{=}C{=}NC(O)CCl_3}$$

N-Carbamoylcarbodiimides (XXV) have been prepared by the interaction of isothioureas (XXIII) or chloroformamidines (XXIV) with Ag(I)-cyanate.[9] The isomerisation of the intermediate isocyanatoformamidines (XXVI), takes place by a four-centred mechanism. A similar process was identified earlier during the reversible isomerisation of acylisothiocyanates to thioacylisocyanates.[29]

$$\underset{\text{(XXIII)}}{RN{=}C(SCH_2Ph){-}NMe_2} \xrightarrow{AgOCN} \left[RN{=}C(NMe_2){-}N{=}C{=}O\right] \longrightarrow$$

$$\underset{\text{(XXIV)}}{RN{=}C(Cl){-}NMe_2} \xrightarrow{AgOCN} \left[RN{=}C(NMe_2){-}N{=}C{=}O\right] \longrightarrow$$

(XXVI)

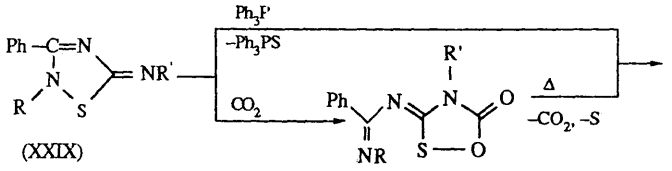
$$\longrightarrow \left[Me_2\overset{+}{N}{=}C(NR){-}\underset{\underset{O}{\|}}{C}{-}N^-\right] \longrightarrow \underset{\text{(XXV)}}{Me_2NC(O){-}N{=}C{=}NR},$$

R = Bu^t.

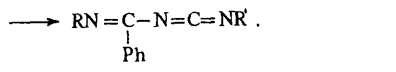
Zimmerman and Olofson devised a novel route to carbodiimides (XXVII) based on the ring opening of 1,2,4-oxadiazolium salts (XXVIII) on treatment with triethylamine.[30]

$$\underset{\text{(XXVIII)}}{Ph{-}C(=N{-}O{-}){=}N{-}CH{=}CH{-}NAlk^+\ BF_4^-} \xrightarrow{Et_3N} \underset{\text{(XXVII)}}{PhC(O){-}N{=}C{=}NAlk}.$$

Other five-membered heterocyclic compounds, e.g. 1,2,4-thiadiazolines, may be converted to *N*-imidoylcarbodiimides, e.g. (XXX), by reaction with triphenylphosphine[13] or carbon dioxide.[31]

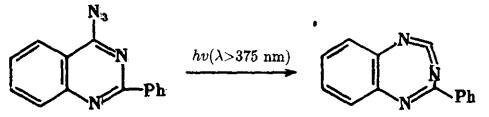


(XXIX)



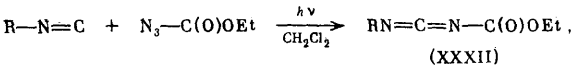
(XXX)

The cyclic imidoylcarbodiimide (XXXI) has been detected spectroscopically as a product derived by photochemical decomposition of 4-azido-2-phenylquinazoline in an argon matrix at 10 K.[32]

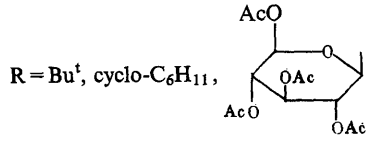


(XXXI)

However, photochemical decomposition of ethyl azidoformate in the presence of isonitriles leads to the corresponding *N*-carbalkoxycarbodiimides (XXXII) in high yield.[33]

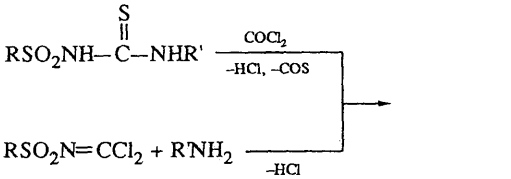


(XXXII)



2. *N*-Sulphonylcarbodiimides

The first representative of this class of compound were prepared by heating the corresponding *N*-sulphonylthiourea with phosgene in toluene or chlorobenzene.[34–39] Reaction proceeds by the initial formation of the corresponding *N*-sulphonylchloroformamidine (XXXIII), dehydrochlorination of which yields the desired carbodiimides (XXXIV).[40–42] The chloroformamidines are also formed as intermediates in the preparation of (XXXIV) from *N*-sulphonyliminophosgenes and primary amines.[43–47]

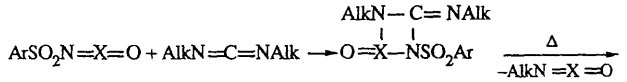


(XXXIII)

(XXXIV)

R, R' = Alk, Ar.

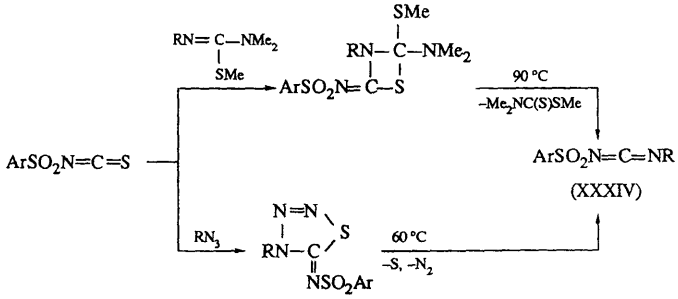
The synthesis of *N*-sulphonylcarbodiimides by metathesis with other types *N*-sulphonylheterocumulene is also worthy of note. Normally, reactions of this type involve initial formation of a [2+2]-cycloadduct, which subsequently decomposes on increasing the temperature. Thus, *N*-sulphonylcarbodiimides (XXXIV) are obtained in high yield by the interaction of *N*-arylsulphonylisocyanates[48–50] or *N*-sulphonylthionylimines[51] with *N,N'*-dialkylcarbodiimides.



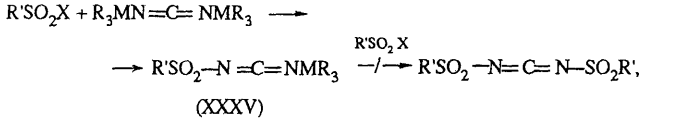
(XXXIV)

X = C, S.

In a similar way, *N*-sulphonylcarbodiimides can be obtained by reaction of *N*-sulphonylisothiocyanates with isothioureas[52] or azides.[53,54]



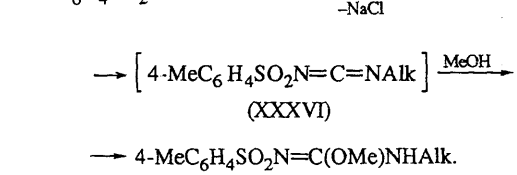
N-Sulphonylcarbodiimides of type (XXXV) have been prepared by sulphonylation of elementoorganic [Group 4] carbodiimides with sulphonyl chlorides.[55,56] However, it is not possible to obtain symmetrical *N,N'*-disulphonylcarbodiimides by reaction of (XXXV) with a second molecule of RSO_2X, presumably because the electron-accepting *N*-sulphonyl group in (XXXV) deactivates the M–N bond.



(XXXV)

X = Cl, NCO; R_3M = Me_3Si, Bu_3Sn, Et_3Ge.

There is also the possibility of preparing *N*-sulphonylcarbodiimides (XXXVI) by the scheme: N + CN→NCN, e.g. from Chloroamine T and alkyl isonitriles.[58] However, the desired carbodiimides have only been identified by subsequent adduct formation, e.g. with methanol.



(XXXVI)

3. *N*-Phosphorylcarbodiimides

By comparison with *N*-acyl- and *N*-sulphonyl-carbodiimides, *N*-phosphoryl analogues are less stable because of their tendency to disproportionate and polymerise spontaneously.

It has been reported that a number of *N*-phosphorylcarbodiimides (XXXVII) may be prepared by elimination of H_2S from the corresponding thiourea with HgO or $COCl_2$ in the presence of molecular sieves.[59]

$$R_2P(O)NH-\overset{\overset{S}{\|}}{C}-NHR' \xrightarrow{HgO \text{ or } COCl_2} R_2P(O)N=C=NR'.$$

(XXXVII)

The same reaction with the thiophosphorylated thiourea (XXXVIII) is more complex, being associated with the formation of an *N*-thiophosphorylisothiocyanate and an *N*-thiophosphoryl-guanidine.[60]

$$(EtO)_2\overset{\overset{S}{\|}}{P}NH-\overset{\overset{S}{\|}}{C}-NHPh \xrightarrow{HgO}$$

(XXXVIII)

$$\longrightarrow (EtO)_2\overset{\overset{S}{\|}}{P}N=C=S + (EtO)_2\overset{\overset{S}{\|}}{P}N=C(NHPh)_2.$$

Dehydrochlorination of *N*-phosphorylated chloroformamidines (XXXIX), obtained either from the corresponding *N*-phosphorylated urea or by treatment of *N*-phosphorylated iminophosgenes with primary amines, affords the corresponding *N*-phosphoryl-*N'*-arylcarbodiimides (XL) in high yield.[61]

$$ArNH-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{N}HP(OAlk)_2 \xrightarrow{PCl_5} ArNH-\overset{\overset{Cl}{|}}{\underset{|}{C}}=\overset{\overset{O}{\|}}{N}P(OAlk)_2 \xleftarrow{ArNH_2} Cl_2C=\overset{\overset{O}{\|}}{N}P(OAlk)_2$$

(XXXIX)

$$\downarrow Et_3N$$

$$ArN=C=\overset{\overset{O}{\|}}{N}P(OAlk)_2.$$

(XL)

The *N*-phosphorylcarbodiimides (XLI) and (XLII) may be prepared conveniently from metalated *N*-phosphorylcyanamides[62] or by treatment of Ag(I)-cyanamide with phosphorus(V) acid chlorides.[63–65]

$$M[Ph_2P(X)NCN] + R_3M'Cl \xrightarrow[-MCl]{} Ph_2P(X)N=C=NM'R_3,$$

(XLI)

$$Ag_2CN_2 + 2Ph_2P(X)Cl \xrightarrow[-2AgCl]{} Ph_2P(X)N=C=NP(X)Ph_2$$

(XLII)

M = Na, Ag; X = O,S; R_3M' = Ph_3Si, Ph_3Sn, Ph_3Pb, Me_3Sn.

By using diphenylhalogenophosphines in the latter reaction, the desired carbodiimide was isolated in the form of a 1:1:1 adduct, $Ph_2P-N=C=N-PPh_2 \cdot AgHal \cdot solvent$.[63]

Replacement of a trimethylsilyl group in the carbodiimides (XLIII) by a phosphoryl, thiophosphoryl or iminophosphoryl group can only be achieved under forcing conditions.[66–68] Thus, *N*-difluorothiophosphoryl-*N'*-trimethylsilylcarbodiimide (XLIV) is obtained in 35% yield by prolonged heating (50 h) of the reactants at 140–150 °C.[66]

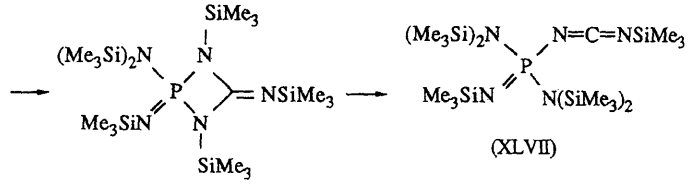
$$Me_3SiN=C=NSiMe_3 + P(S)F_3 \longrightarrow Me_3SiN=C=NP(S)F_2 + Me_3SiF.$$

(XLIII) (XLIV)

On the other hand, reaction of carbodiimides (XLIII) with the aminodiiminophosphorane (XLV) readily affords a [2+2]-cycloadduct (XLVI), which is converted to (XLVII) on standing over a long period.[69]

$$Me_3SiN=C=NSiMe_3 + \underset{Me_3SiN}{\overset{(Me_3Si)_2N}{}}P=NSiMe_3 \longrightarrow$$

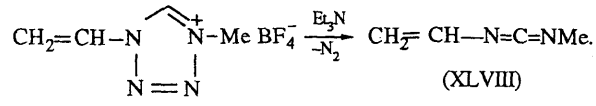
(XLIII) (XLV)



(XLVI) (XLVII)

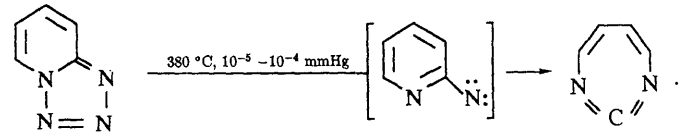
4. *N*-Alkenylcarbodiimides

The highly reactive vinylcarbodiimides were unknown before 1970. The first member of this class of compound—the unstable *N*-methyl-*N'*-vinylcarbodiimides (XLVIII)—was obtained by fragmentation of a tetrazolium salt with triethylamine in sulfolane.[30]



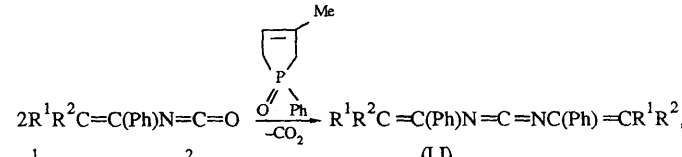
(XLVIII)

According to spectroscopic data, the relatively stable cyclic divinylcarbodiimide (XLIX) is formed by thermal rearrangement of the nitrene (L), obtainable by thermolysis of tetrazolo[1,5-*a*]pyridine at high temperature.[70]



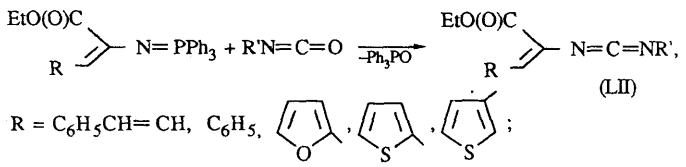
(L) (XLIX)

The stability of *N*-alkenylcarbodiimides increases significantly with substitution in the alkenyl residue. Thus, the stable *N,N'*-bis-(1-alkenyl)carbodiimides (LI) are obtained by catalytic decarboxylation of the corresponding *N*-alkenylisocyanate.[71]



(LI)

The most general and convenient route to *N*-alkenylcarbodiimides (LII) involves aza-Wittig conversion of the corresponding *N*-alkenyliminophosphorane,[72–77] e. g.

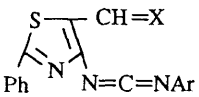


(LII)

R = $C_6H_5CH{=}CH$, C_6H_5, ;

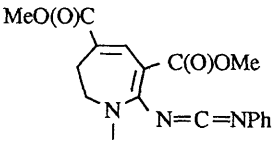
R' = Alk, Ar.

If the carbon–carbon double bond of the *N*-alkenyliminophosphorane is in the form of a pyrrole,[78] pyrazole,[79,80] or pyrimidine[81,82] ring, the corresponding carbodiimides are only formed as intermediates. However, thiazole[79] and azepine[83] derivatives afford stable carbodiimides (LIII) and (LIV).



(LIII)

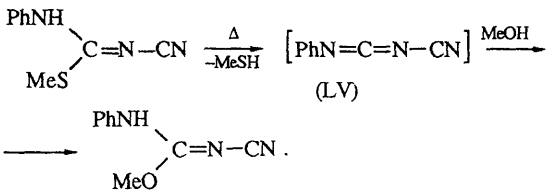
X = O, NAr.



(LIV)

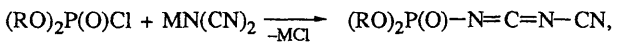
5. Other types of *N*-functionalised carbodiimide

In this category are *N*-cyano- and *N*-amino-carbodiimides which are relatively unstable and, as a rule, are only isolable by derivatisation. Thus, *N*-phenyl-*N'*-cyanocarbodiimide (LV) is formed by thermal elimination of methanethiol from *N*-phenyl-*N'*-cyano-*S*-methylisothiourea.[84]



(LV)

The stability of *N*-cyanocarbodiimides is significantly increased if an *N*-phosphoryl residue is present. Thus, *N*-cyano-*N'*-phosphorylcarbodiimides (LVI) are quite stable.[64,65]



(LVI)

M = Na, K, Ag.

N-Dialkylaminocarbodiimides, $Alk_2N{-}N{=}C{=}NR$, are very unstable, readily dimerising immediately they are formed. A few of these compounds have been mentioned in an earlier review.[85]

III. Physical and chemical properties

1. Physical properties

The majority of *N*-functionalised carbodiimides are crystalline compounds or liquids which may be distilled under a high vacuum. Like unfunctionalised carbodiimides, they are readily soluble in organic solvents, but are less stable on prolonged storage even with the exclusion of atmospheric moisture.

The IR spectra of these carbodiimides are characterised by intense absorption in the region 2130–2170 cm^{-1}, corresponding to the N=C=N function. The nature of the *N*-substituent does not have a significant effect on the position of this absorption band. However, with certain *N*-acylcarbodiimides[17,21] and *N*-sulphonylcarbodiimides,[35] the absorption is shifted into the region 2185–2200 cm^{-1}.

^1H NMR and ^{13}C NMR spectroscopic data are available for *N*-acylcarbodiimides;[17,18,30] ^{31}P NMR data for *N*-phosphorylcarbodiimides,[62,64] and ^1H NMR data for *N*-alkenylcarbodiimides.[35,71,74,75,83]

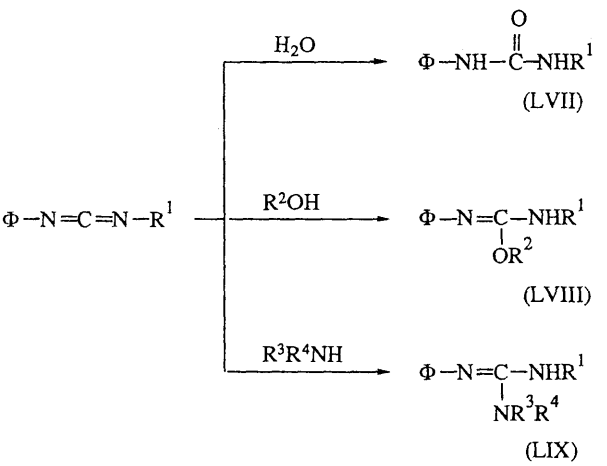
Theoretical calculations have been made on the hypothetical difluorocarbodiimide, F–N=C=N–F, in order to study the geometry of the molecule and its isomerisation.[86]

2. Chemical properties

a) Reactions with nucleophiles

The chemistry of *N*-functionalised carbodiimides is determined to a large extent by the presence of both the heterocumulene bond and the functional group. The electron-accepting acyl, sulphonyl and phosphoryl groups significantly increases the electrophilicity of the heterocumulene bond and facilitate the reactions of these compounds with nucleophiles.

Substituted ureas (LVII),[9,18,40,45,46,52,53,60,62] isoureas (LVIII)[10,12,40,58] and guanidines (LIX)[12,40,42,58] are formed by the reaction of the corresponding *N*-functionalised carbodiimide with water, alcohols (or phenols) and amines, respectively, at room temperature in the absence of a catalyst.



(LVII)

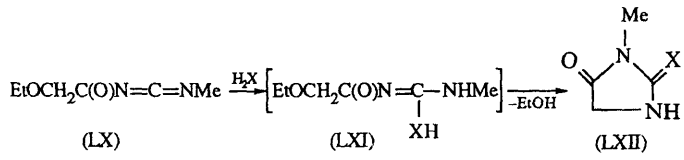
(LVIII)

(LIX)

Φ = $Alk_2NC(S)$, $ArN(=CAr)$, $ArSO_2$, $AlkSO_2$, Alk_2P, $(AlkO)_2P(O)$;

R^1, R^2 = Alk, Ar; R^3 = H, Alk; R^4 = Alk, Ar.

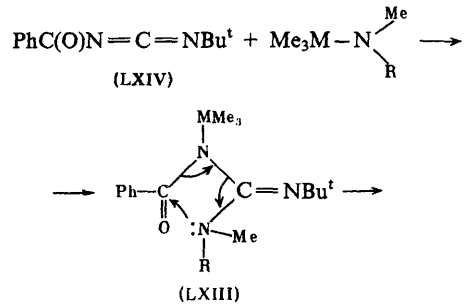
The reaction of carbodiimide (LX) with amines and hydrazines, however, does not stop at adduct formation (LXI); instead, the latter cyclises to give the corresponding hydantoin derivative (LXII) [30] by elimination of ethanol.



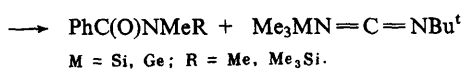
(LX) (LXI) (LXII)

X = NAlk, N —NHAlk .

Similarly, the guanidine derivative (LXIII), obtained from carbodiimide (LXIV), fragments with participation of the benzoyl group.[87]



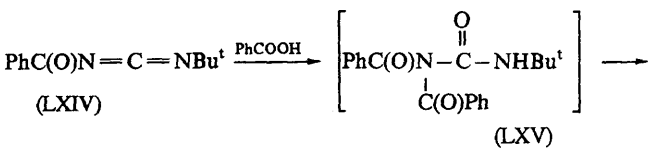
(LXIV) (LXIII)



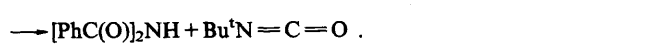
M = Si, Ge; R = Me, Me_3Si.

b) Reactions with electrophiles

The *N*-benzoylcarbodiimide (LXIV) reacts with benzoic acid in conventional manner[4] to give the *N,N*-dibenzoylurea (LXV), which undergoes subsequent cleavage to give the imide (LXVI) and tert-butyl isocyanate.[14]

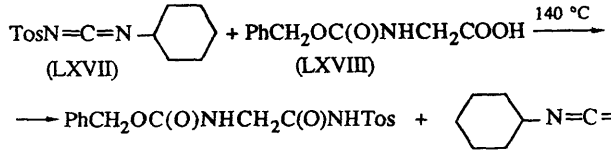


(LXIV) (LXV)



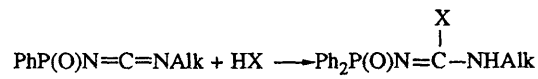
(LXVI)

The *N*-tosylcarbodiimide (LXVII) reacts similarly with *N*-carbobenzoxyglycine (LXVIII).[38]



(LXVII) (LXVIII)

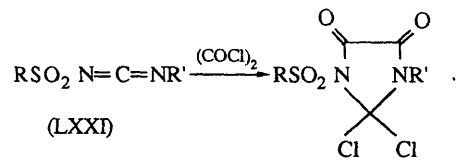
N-Phosphorylated carbodiimides (LXIX) react with inorganic acids by adduct formation across the C=N bond.[88]



(LXIX) (LXX)

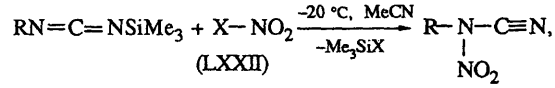
X = Cl, CN .

N-Sulphonylcarbodiimides (LXXI) are slowly acylated with oxalyl chloride, but do not react with phosgene because of the decrease in basicity of the nitrogen atoms of the carbodiimide group.[35,53]



(LXXI)

The reaction of *N*-acyl- or *N*-sulphonyl-carbodiimides with neutral nitrating agents (LXXII) proceeds by cleavage of the Si—N bond rather than by addition across the carbodiimide residue.[22]



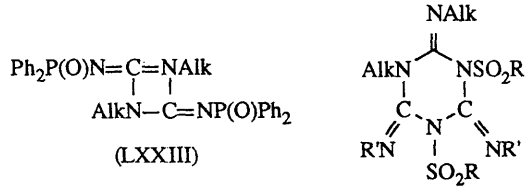
(LXXII)

R = MeOC(O); X—NO_2 = N_2O_5, $(NO_2)_2SiF_6$; R = $MeSO_2$;

X—NO_2 = $(NO_2)_2SiF_6$.

c) Cycloaddition

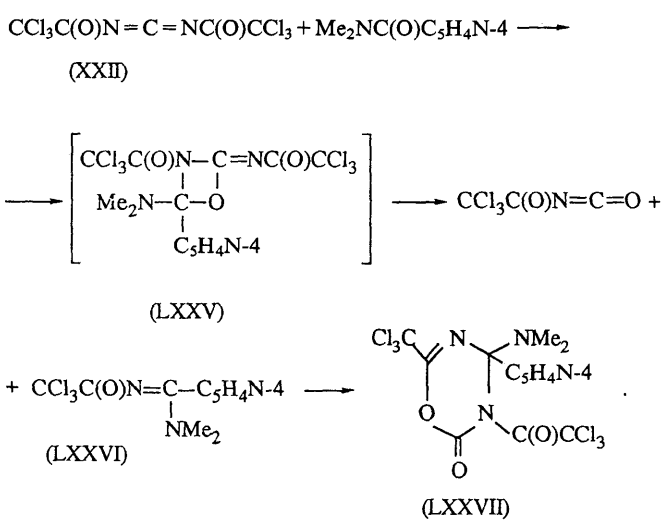
N-Phosphorylated carbodiimides readily dimerise by [2+2]-cycloaddition to give the diazetidines (LXXIII).[88] However, *N*-sulphonylcarbodiimides react with dialkylcarbodiimides to give [2+2+2]-cycloadducts (LXXIV).[49]



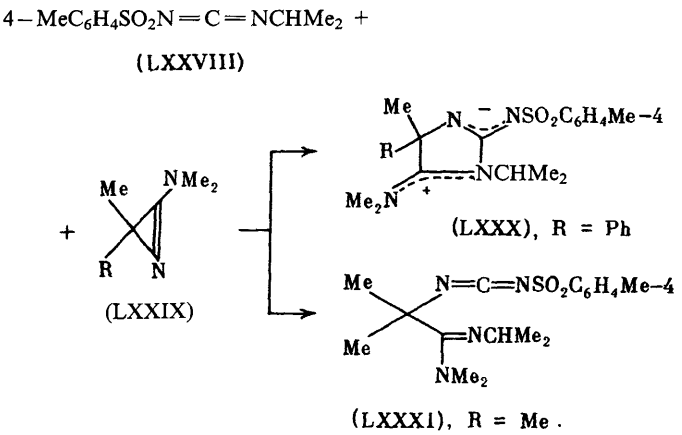
(LXXIII) (LXXIV)

The reaction of bis(trichloroacetyl)carbodiimide (XXII) with *N,N'*-dimethylisonicotinamide leads initially to the adduct (LXXV), which undergoes fragmentation to give trichloroacetyl isocyanate

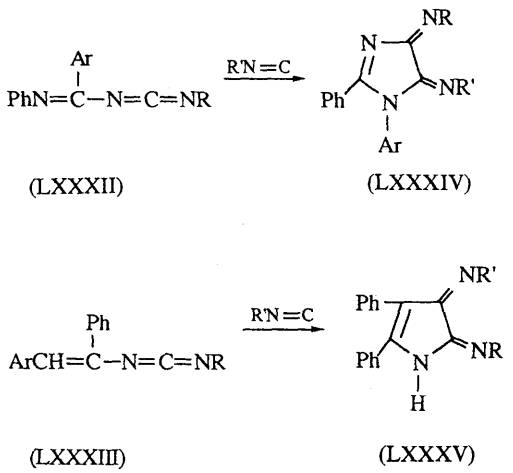
and the amidine (LXXVI). The latter reacts subsequently to give the oxadiazine (LXXVII).[28]



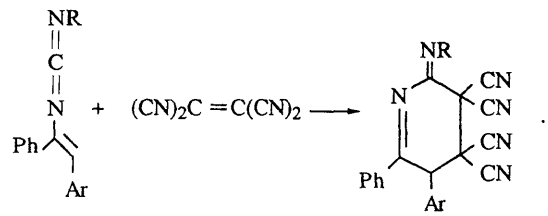
The reaction of the *N*-sulphonylcarbodiimide (LXXVIII) with azirine (LXXIX) proceeds by an initial [2+2]-cycloaddition, after which the resulting[2+2]-adduct is converted either to a zwitterionic imidazoline (LXXX) or to a carbodiimide (LXXXI), depending on the nature of the R group on the azirine ring.[89]



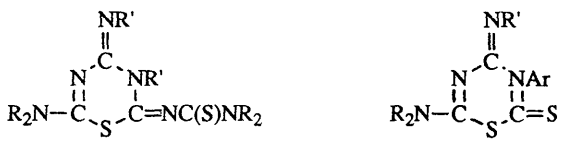
Cycloaddition is particularly favourable with *N*-acyl derivatives, their analogues, and with *N*-alkenyl derivatives which are prone to undergo 1,4-dipole formation. Such compounds are notably of value in the synthesis of various types of heterocycle. Thus, imidoylcarbodiimides (LXXXII) and *N*-alkenylcarbodiimides (LXXXIII) form cycloadducts with isonitriles, namely the respective 4,5-diiminoimidazolines (LXXXIV) and 2,5-diiminopyrrolines (LXXXV).[74]



The interaction of carbodiimides (LXXXIII) with tetracyanoethylene proceeds by [4+2]-cycloaddition to give the tetrahydropyridines (LXXXVI).[72]

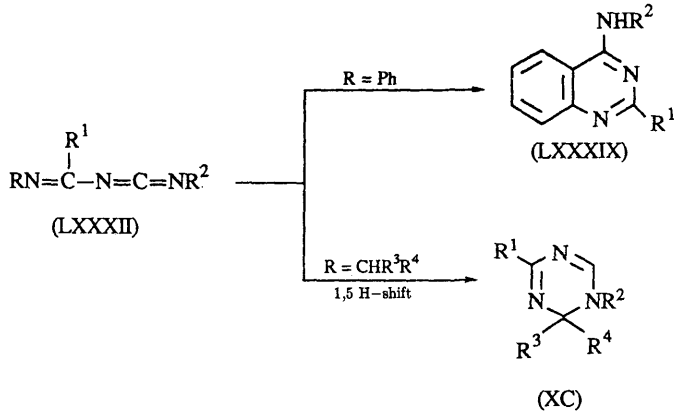


Similarly, dimerisation of *N*-thiocarbamoylcarbodiimides, and reaction of the latter with isothiocyanates, leads to the respective thiadiazines (LXXXVII) and (LXXXVIII).[10]



Recently there has been much interest in the spontaneous intramolecular heterocyclisation of imidoylcarbodiimides (LXXXII).[31] These react with participation of phenyl or alkyl substituent on the

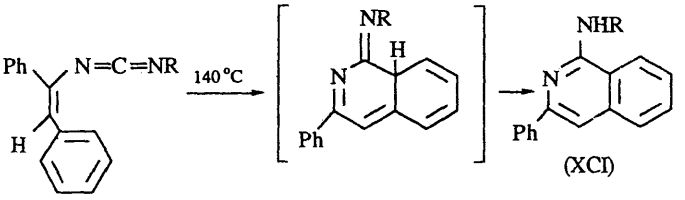
imidoyl nitrogen to give 4-aminoquinazolines (LXXXIX) or dihydro-1,3,5-triazines (XC).



(LXXXII) (LXXXIX) (XC)

R^1 = Ar; R^2, R^3, R^4 = Alk, Ar.

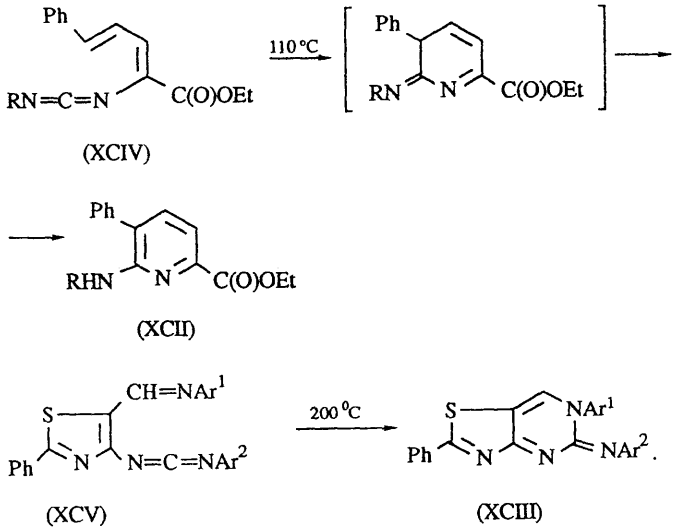
N-Alkenylcarbodiimides (LXXXIII) undergo a similar cyclisation to give substituted quinolines (XCI), but only on heating in xylene.[72]



(LXXXIII) (XCI)

R = Alk, Ar.

The pyridine (XCII) and pyrimidine derivatives (XCIII) have been prepared by a novel route based on the electrocyclisation of carbodiimides (XCIV) and (XCV), respectively.[77,79,82]



(XCIV) (XCII) (XCV) (XCIII)

A recently published review makes reference to a similar type of heterocyclisation based on the intermediate formation of *N*-heteroarylcarbodiimides possessing an alkenyl group on the heterocyclic ring.[90]

From the present review, it is evident that *N*-functionalised carbodiimides possess quite novel properties, as distinct from those of unfunctionalised carbodiimides. The potential for the development of new routes to a variety of acyclic and heterocyclic compounds is clear to see.

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