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CHEMISTRY OF CHLOROCARBONYL ISOCYANATE

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CONTENTS

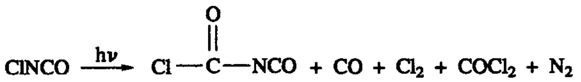
1. INTRODUCTION

Organic isocyanates are highly reactive. They are therefore used to obtain various products of organic synthesis, as well as polymeric materials. In the chemistry of isocyanates, those compounds which contain both an isocyanate group and other reactive functional groups are especially valuable. Such reagents include chlorosulfonyl isocyanate, $ClSO_2NCO$,[1–4] 1-chloroalkyl isocyanates, $R_2CClNCO$[5] and $RCCl_2NCO$,[6] isocyanato silanes, $R_nSi(NCO)_{4-n}$,[7–9] isocyanatophosphoryl dichloride, $Cl_2P(O)NCO$, and other phosphorus-containing isocyanates.[10,11] Recently, chlorocarbonyl isocyanate, ClC(O)NCO, a bifunctional compound with a pronounced electrophilic character, has become important as a new reagent in isocyanate chemistry. The first information about this compound appeared in 1969.[12] Two years later, a simple preparation was discovered by Bayer AG[13,14] and this is now carried out on a commercial scale.[15–17] Several companies now produce chlorocarbonyl isocyanate as a reagent.

The chemistry of chlorocarbonyl isocyanate was considered in a review[18] which was published in 1977. Recently, a short review[19] appeared where some aspects of the use of chlorocarbonyl isocyanate for the synthesis of heterocyclic compounds were discussed. In the present Report the methods of preparation and chemical conversions of chlorocarbonyl isocyanate have been systematized.

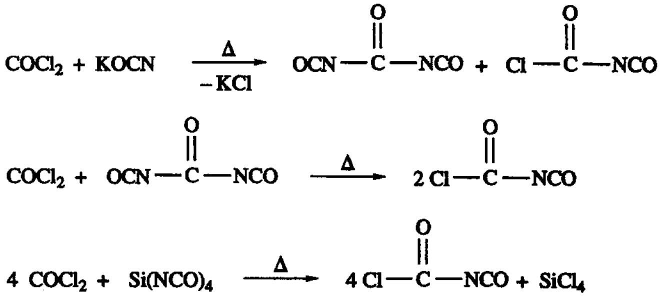
2. PREPARATION OF CHLOROCARBONYL ISOCYANATE

Chlorocarbonyl isocyanate (CCI) was first obtained by the photolysis ($\lambda > 280$ nm) of chloroisocyanate.[12,20] Besides CCI (yield 15%), other gaseous products were formed. The reaction may be considered as a sequence of radical interconversions with the intermediate formation of a hypothetical hydrazine derivative. Later, another route for the synthesis of CCI is described.



$$\mathrm{ClNCO} \xrightarrow{h\nu} \mathrm{Cl{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}NCO} + \mathrm{CO} + \mathrm{Cl_2} + \mathrm{COCl_2} + \mathrm{N_2}$$

This process involves an exchange reaction of phosgene with alkali metal cyanates or silicon tetracyanate.[21] By passing excess phosgene at 400°C through the molten eutectic of potassium and sodium chlorides containing potassium cyanate, carbonyl diisocyanate (75%) and CCI (2%) are obtained. To obtain CCI in higher yields, a redistributive reaction of phosgene with carbonyl diisocyanate is performed. For this purpose, the reaction mixture is heated in a steel autoclave at 180°C for 70 hours yielding CCI (56%). An exchange reaction of phosgene with silicon tetracyanate is performed in an autoclave at 250°C for 60 hours at a reagent ratio of 6 : 1[21] yielding CCI (54%).

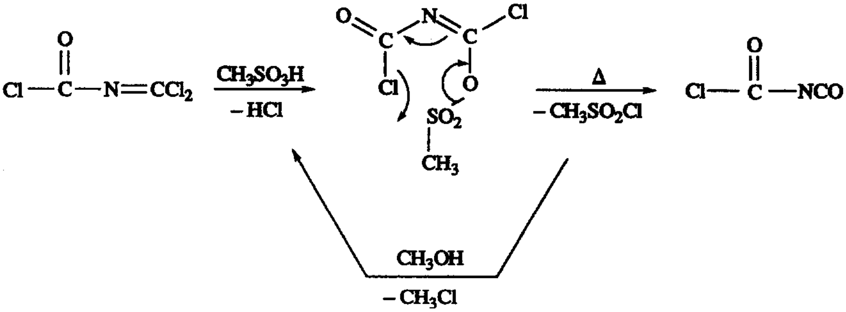


$$\mathrm{COCl_2} + \mathrm{KOCN} \xrightarrow[-\mathrm{KCl}]{\Delta} \mathrm{OCN{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}NCO} + \mathrm{Cl{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}NCO}$$

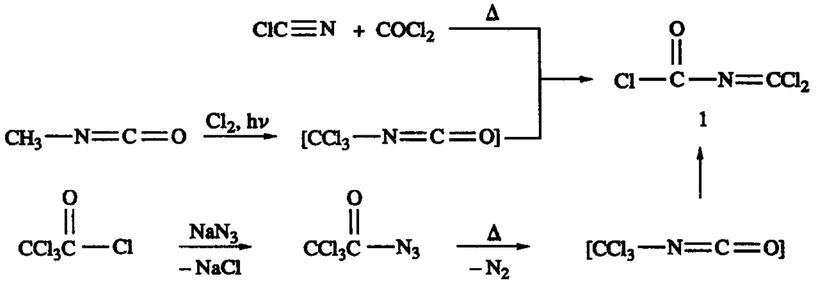
$$\mathrm{COCl_2} + \mathrm{OCN{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}NCO} \xrightarrow{\Delta} 2\,\mathrm{Cl{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}NCO}$$

$$4\,\mathrm{COCl_2} + \mathrm{Si(NCO)_4} \xrightarrow{\Delta} 4\,\mathrm{Cl{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{{-}NCO} + \mathrm{SiCl_4}$$

The most convenient method for preparation of CCI is a partial saponification of N-chlorocarbonyl isocyanide dichloride 1 using methanesulfonic acid or some other strong acid with pK <2.[14-16] Despite the fast and irreversible reaction of CCI with methanesulfonic acid, the process may be divided into two stages by selecting appropriate reaction conditions to yield the final product (90%).[14] The first stage proceeds at 20°C with an evolution of hydrogen chloride. The proposed intermediate then yields methanesulfonyl chloride (90%) at a slightly elevated temperature which is then recycled after its conversion into methanesulfonic acid.



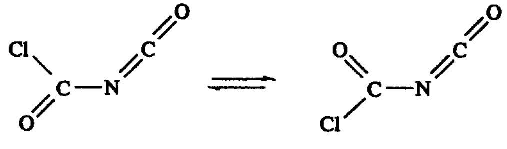
Several methods exist for the preparation of N-chlorocarbonyl isocyanide dichloride **1**. Two of them are used on an industrial scale. By passing the phosgene–cyanogen chloride mixture through a column with activated charcoal, compound **1** is formed under severe conditions (150°C, 55 atm) (89%).[22,29] The process is carried out in a semi-continuously-working apparatus with excess phosgene. This reduces trimerization of cyanogen chloride and decreases the formation of the condensation product of **1** with the second mole of cyanogen chloride. Another method for the synthesis of N-chlorocarbonyl isocyanide dichloride **1** is the chlorination of methyl isocyanate in CCl_4 at 70°C with u.v.-irradiation. This yields the required product (90%).[24,25] On a laboratory scale, the Curtius reaction of the intermediate azide of trichloroacetic acid is used for the preparation of compound **1** (90%).



3. PHYSICAL PROPERTIES AND THE STRUCTURE OF CHLOROCARBONYL ISOCYANATE (CCI)

Chlorocarbonyl isocyanate (CCI) is a colourless liquid, b.p. 64°C,[11] 63.6°C,[16] and m.p. −63°C.[16] The compound may be stored for an infinitely long time in the absence of moisture. Its i.r. spectrum shows intensive absorption bands at 2260 (NCO_{as}), 1818 (C=O) and 1420 (NCO_s) cm^{-1}.

Gas electronography showed that CCI exists as a mixture of *trans-anti-* and *cis-syn*-diastereoisomers in a 3 : 1 ratio ($\Delta G = 0.7(3)$ kcal/mol).[27] Geometrical parameters of the *trans*-conformer are as follows: C=O (isocyanate), C=O (carbonyl), N=C, N–C and C–Cl with bond lengths of 1,139(16), 1,201(16), 1,218(23), 1,384(6) and 1,757(5) Å, respectively; C–N=C, N–C=O, N–C–Cl and N=C=O valence bond angles are 127.1(16)°, 124.8(15)°, 115.8(8)° and 173.4(23)° respectively. *Ab initio* calculations of a moderate level (SCF 6-31GF*) predicts the geometry of the *trans*-conformer satisfactorily. The calculated relative stability of the diastereoisomers differs from the experimental results. The calculations predict the *cis*-form to be more stable than the *trans*-form by 0.40–1.58 kcal/mol. Experimental data demonstrates a larger stability of the *trans*-form. The i.r. and Raman spectral data also give evidence for the existence of at least two CCI conformers, due to the rotation of molecular fragments around the C–N bond.[28]



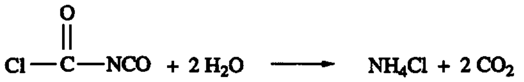
trans *cis*

4. CHEMICAL PROPERTIES OF CHLOROCARBONYL ISOCYANATE

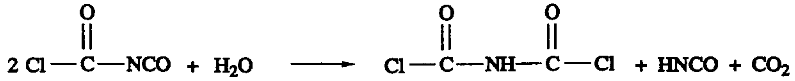
Chlorocarbonyl isocyanate (CCI) is a simple and highly reactive derivative of iminodicarboxylic acid. The chloro and the isocyanato groups selectively participate in chemical reactions. This gives a simple way for the synthesis of isocyanates and their derivatives from alcohols, phenols, thiols and other nucleophilic reagents. The combination of both functional groups allows the use of CCI on a large scale for cyclizations proceeding under mild conditions.

4.1. *Reactions with protic nucleophiles*

4.1.1. *Hydrolysis.* The products of the CCI hydrolysis are ammonium chloride and carbon dioxide. One cannot tell with certainty whether CCI reacts with water (and other nucleophiles) primarily as an isocyanate or as a chloride. It is believed, however, that the reaction with water proceeds via the chlorocarbonyl group because with excess CCI, cyanuric acid and iminodicarbonyl dichloride are isolated.[20]



$$\mathrm{Cl{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NCO + 2\,H_2O \longrightarrow NH_4Cl + 2\,CO_2}$$



$$\mathrm{2\,Cl{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NCO + H_2O \longrightarrow Cl{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl + HNCO + CO_2}$$

4.1.2. *Reaction wih alcohols, phenols, thiols, diols, and polyols.* Chlorocarbonyl isocyanate reacts with these monofunctional nucleophiles under mild conditions (0–20°C, inert solvents) to give adducts **2** which eliminate hydrogen chloride at 70–125°C and are converted into the corresponding isocyanates 3.[29,30] Symmetrical derivatives of the iminodicarboxylic acid **4** are formed with two moles of the nucleophile.[12,20] Unsymmetrical esters of the iminodicarboxylic acid **5** may be obtained by interaction of CCI with two moles of two different alcohols in the presence of one mole of triethylamine which is the scavenger of hydrogen chloride.[31] Among the compounds **4** and **5**, effective insecticides are found.[31] Alkoxycarbonyl isocyanates **3** are used as polyurethane stabilizers.[32] Diaryl esters of the iminodicarboxylic acid **4** (RX = ArO) may be used for synthesis of various heterocyclic compounds instead of CCI.[33]

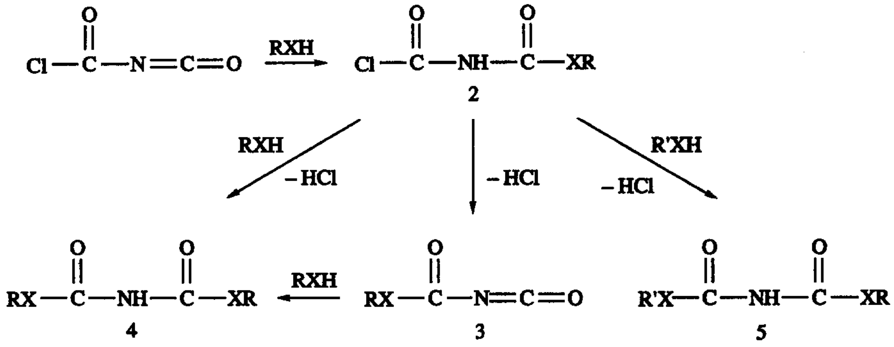
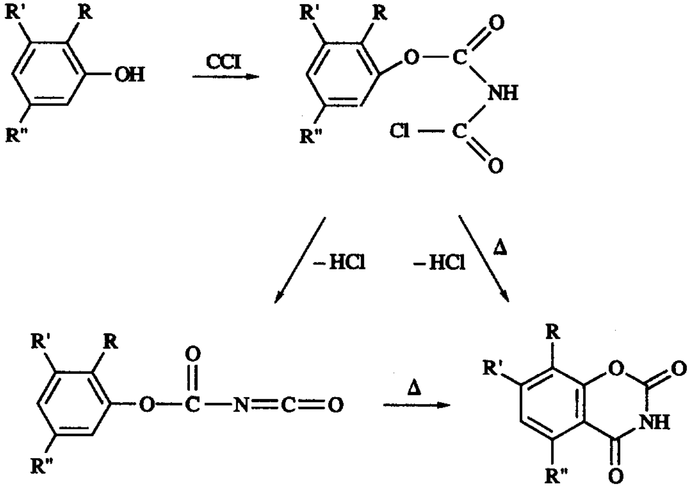


Table 1. Isocyanates 3

RX	B.p./ torr	Yield [%]	Reference
MeO	97°C/760	70	18,29
EtO	114°C/760	76	18,29
$ClCH_2CH_2O$	70°C/11	-	30
CCl_3CH_2O	87°C/15	-	29
$CH_2=CHCH_2O$	50°C/15	70	29
n-$C_8H_{17}O$	113°C/11	85	18,29
n-$C_{14}H_{29}O$	122°C/0.04	-	29
PhO	100°C/15	90	18,29
MeS	125°C/760	66	18
n-BuS	88°C/15	88	18
n-$C_{12}H_{25}S$	111°C/0.04	77	18,29
PhS	115°C/11	73	18,29

Aryloxycarbonyl isocyanates **6** may give products of an intramolecular Friedel–Crafts reaction (benzoxazindiones **7**) in boiling chlorobenzene with catalytic amounts of $FeCl_3$. The presence of electron-donating substituents on the benzene ring facilitates cyclization.[34] The reaction of CCI with phenols may be used as a method for synthesis of these heterocycles **7** (Table 2).

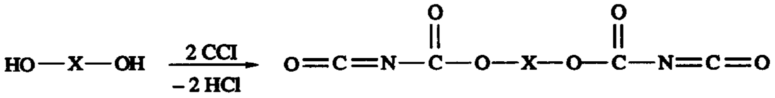


6 **7**

Table 2. Benzoxazindiones **7**[34]

R	R'	R"	Yield [%]
H	H	H	89
H	H	MeO	86
Me	Me	Me	84
—CH=CH—		H	76
Br	H	H	22

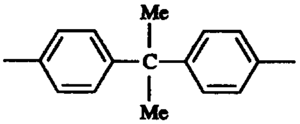
Diols and polyols give di- (**8**) and poly-isocyanates with CCI[29,30] which may be used as monomers for obtaining elastic polyiminoesters,[35] and as additives to commercial di- and polyisocyanates, to make them water and light resistive.[36]



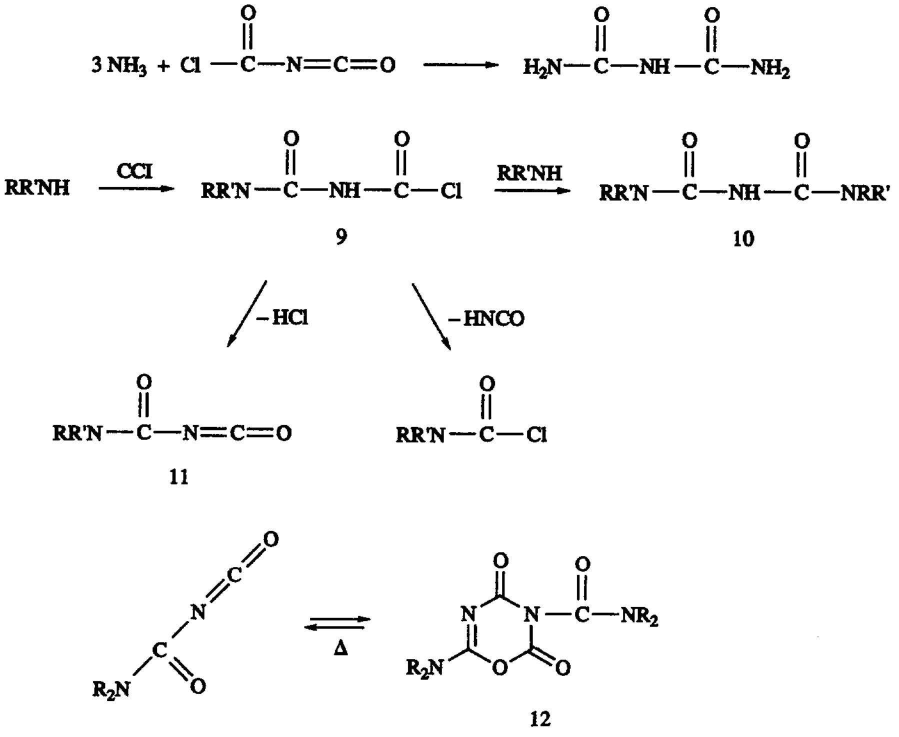
$$HO{-}X{-}OH \xrightarrow[-2\,HCl]{2\,CCI} O{=}C{=}N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}X{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N{=}C{=}O$$

8

Table 3. Diisocyanates **8**

X	B.p./torr	Yield [%]	Reference
—$(CH_2)_4$—	100°C/0.1	59	29
—$(CH_2)_6$—	123°C/0.09	90	18
—$(CH_2CH_2O)_2CH_2CH_2$—	170°C/0.1	85	18
	200–210°C/0.1	90	18

4.1.3. *Reactions with amino compounds.* By treating CCI with excess ammonia in acetonitrile at 20°C, biuret is formed (91%).[20] In reactions of CCI with secondary amines the primary products are allophanoyl chlorides **9** which give biurets **10** with the second mole of the amine.[18] Compounds **9** eliminate hydrogen chloride at 70–125°C and are converted into carbamoyl isocyanates **11**. These are obtained in good yields only in the case of aliphatic-aromatic secondary amines. With dialkylamines, the yields of isocyanates **11** are lower, due to a side reaction producing carbamoyl chlorides.[18] A characteristic reaction of carbamoyl isocyanates **11** is their dimerization of a [4+2] cycloaddition type under mild conditions. The dimers are substituted 1,3,5-oxazinediones **12** which are cleaved into initial isocyanates on heating above 100°C.



$$3\,NH_3 + Cl-\overset{O}{\overset{\|}{C}}-N{=}C{=}O \longrightarrow H_2N-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-NH_2$$

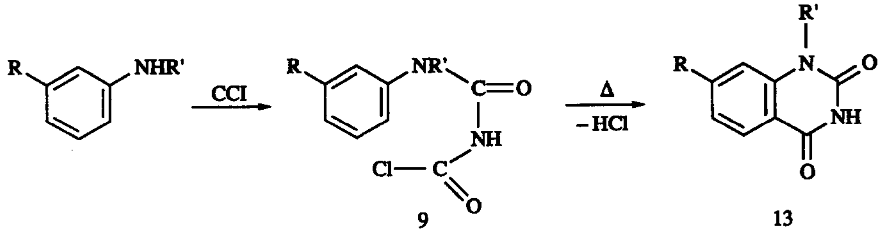
$$RR'NH \xrightarrow{CCI} RR'N-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{RR'NH} RR'N-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-NRR'$$

$$RR'N-\overset{O}{\overset{\|}{C}}-N{=}C{=}O \qquad RR'N-\overset{O}{\overset{\|}{C}}-Cl$$

Table 4. Carbamoyl isocyanates 11[18]

R	R'	B.p./torr	Yield [%]
Me	Me	62°C/17	43
Et	4-ClC$_6$H$_4$	98°C/0.03	86
n-Bu	Ph	118°C/0.4	72

Aliphatic-aromatic allophanoyl chlorides **9** undergo an intramolecular cyclization (220°C, in an autoclave, in the presence of Friedel–Crafts catalyst) giving quinazolidinediones **13**.[18,34] A compound with a quinazoline structure is also formed by interaction of CCI with N,N-dimethyl-*p*-toluidine in similar conditions.



9

13

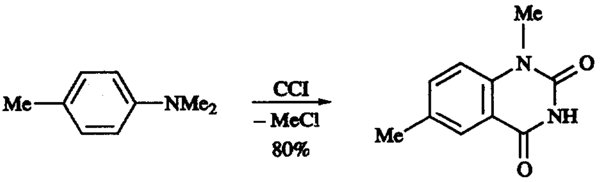
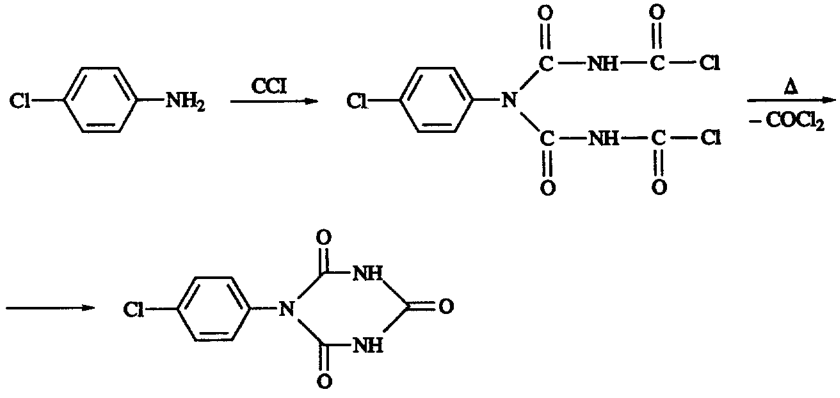


Table 5. Quinazolidinediones 13[34]

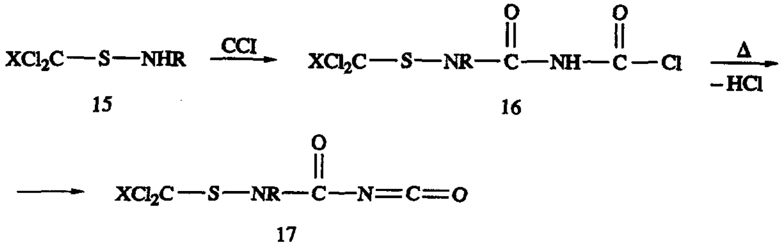
R	R'	Yield [%]
H	Me	34
H	Et	62
H	n-Bu	62
H	i-Bu	45
Me	n-Bu	60

Reaction of primary aromatic amines with CCI does not lead to quinazolidinediones. In this case the reaction proceeds via a 1 : 2 adduct which converts into a monosubstituted isocyanurate, **14**, after elimination of phosgene.[18] Similar products were obtained also with aliphatic primary amines, but in this reaction hydrochlorides rather than free amines should be used.



14 (77%)

By interaction of CCI with trihalomethanesulfenamides **15** at 10°C in chlorobenzene, adducts **16** are formed which undergo smooth dehydrochlorination yielding carbamoyl isocyanates **17**.[37,38] In the case of the compound **15a** (X = F, R = Ph), together with the formation of an isocyanate **17**, a cleavage of the S–N bond occurs in the adduct, and 2,4,6-trioxo-1-phenylhexahydro-1,3,5-triazine is formed (24%). The isocyanates **17** react with amines, alcohols and phenols yielding the corresponding biurets and allophanates which show a high fungicidal activity.[39,40]



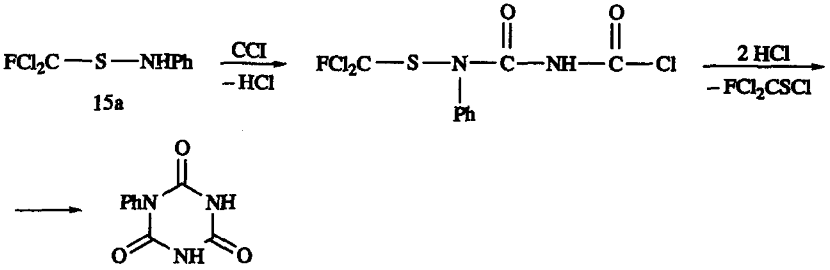
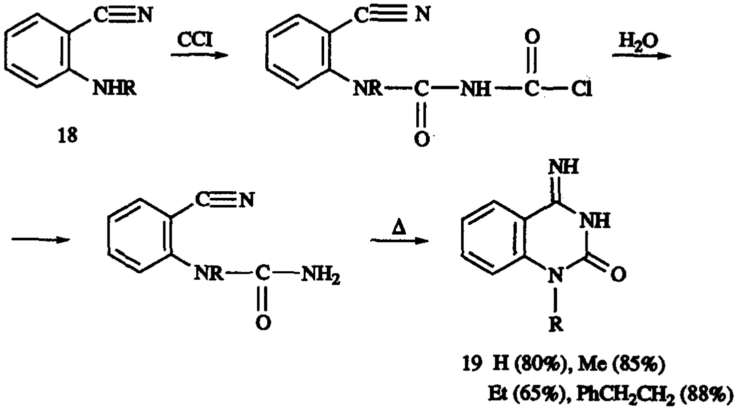


Table 6. Carbamoyl isocyanates 17[37]

X	R	B.p./torr	Yield [%]
F	Ph	122-125°C/0.2	8.5
F	Me	93-96°C/14	17
F	$MeOCH_2CH_2$	78-80°C/0.1	21
F	c-C_6H_{11}	158-160°C/11	76
Cl	n-Bu	90-92°C/0.1	58

ortho-Cyanosubstituted arylaliphatic amines **18** react with CCI yielding 3,4-dihydro-2(1H)-quinazolinones **19**.[41,42] With CCI, enehydrazines **20** yield substituted N-aminouracils **21**.[43]



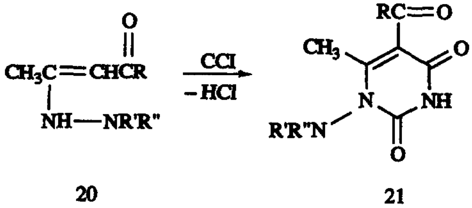
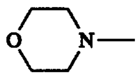
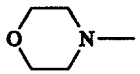
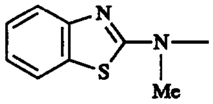
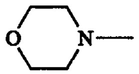
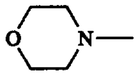
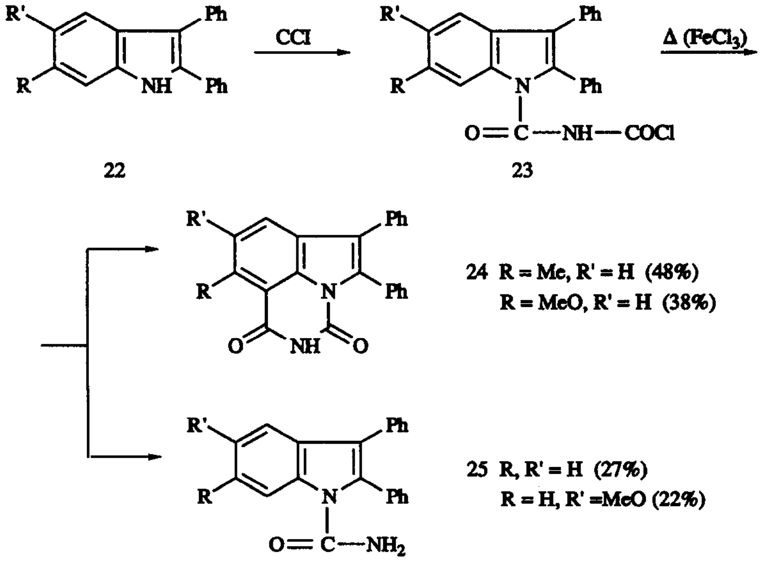


Table 7. N-Aminouracils 21[43]

R	R'R''N	Yield [%]
EtO		76
c-$C_6H_{11}O$		60
EtO		67
$PhCH_2NH$		55
Me		50

Chlorocarbonyl isocyanate reacts with heterocycles containing the NH groups. Thus, treatment of CCI with indoles **22** at 5–10°C in nitromethane leads to the products **23**. Boiling the reaction mixture with catalytic amounts of $FeCl_3$ promotes further reactions.[44] If R is an electron-donating substituent, products of intramolecular cyclization, which are substituted pyrroloquinazolines **24**, are formed. In other cases N-carbamoylindoles **25** are obtained. Similarly, reaction with carbazole leads to N-carbamoylcarbazole **26** (33%).

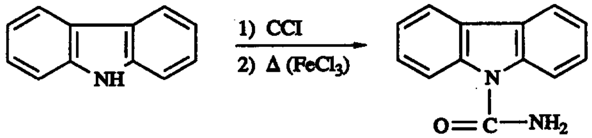


22

23

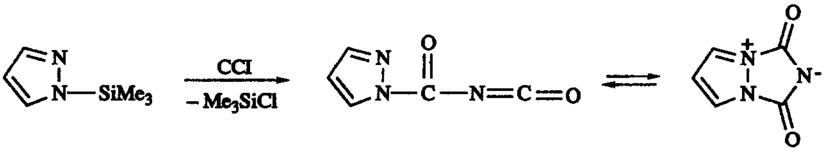
24 R = Me, R' = H (48%)
R = MeO, R' = H (38%)

25 R, R' = H (27%)
R = H, R' = MeO (22%)

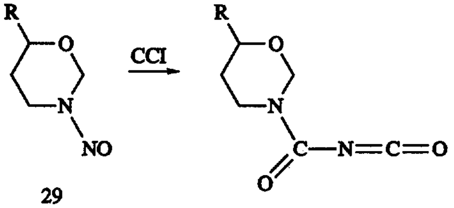


26

N-(Trimethylsilyl)pyrazole reacts with CCI (0°C, in benzene) to give the carbamoyl isocyanate **27** which converts reversibly into the cross-conjugated heterocyclic mesomeric betaine **28**.[45] N-Nitrososubstituted heterocycles, for example N-nitrosotetrahydro-1,3-oxazines **29**, may also be used in this type of reaction.[46]



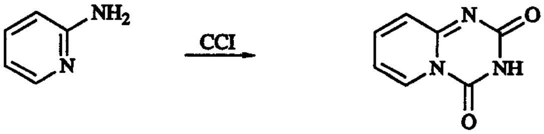
27 (60%) 28



29

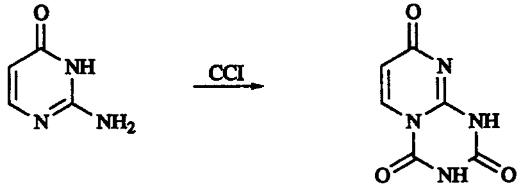
Reaction of CCI with heterocyclic amines yields condensed heterocyclic compounds. Cyclocondensation of 5-aminopyrazole **30**, 2-aminopyridine **32**, 2-aminopyrimidines **34**, **36** and 2-aminoquinazoline **38** with CCI gives the corresponding derivatives of pyrazolo[3,4-*d*]pyrimidine **31**, pyrido[1,2-*a*]-1,3,5-triazine **33**, pyrimido[1,2-*a*]-1,3,5-triazines **35**, **37** and triazino[1,2-*a*]quinazoline **39**. These reactions proceed under mild conditions in the presence of an organic amine (hydrogen chloride scavenger) or by heating in an inert solvent.[47–49] Similar cyclocondensations are also used for the synthesis of nucleosides containing condensed heterocycles.[50,51] Among the products of these reactions, biologically active compounds were found which included some herbicides[52,53] and antitumour agents.[54]

30 31 (53%)[47]



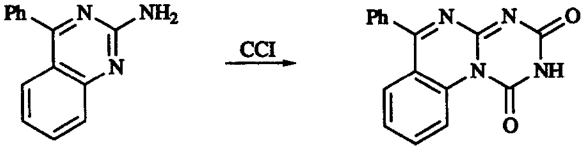
32 33 (88%)[48]

34 35 (83%)[48]



36

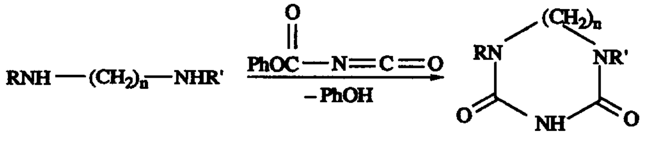
37[49]



38

39 (86%)[48]

For cyclizations of strongly basic derivatives of hydrazine, aminales or ethylenediamine, like **40**, a derivative of CCI, phenoxycarbonyl isocyanate, should be used rather than CCI.[18] Products of these reactions (five-, six- and seven-membered heterocyclic compounds **41**) are listed (Table 8).



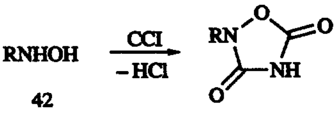
40

41

Table 8. Heterocyclic compounds 41[18]

R	R'	n	Yield [%]
Me	H	0	30
Ph	H	0	96
4-ClC_6H_4	H	0	75
4-MeC_6H_4	H	0	65
Ph	MeC(O)	0	87
2-$MeOC(O)C_6H_4$	4-$MeOC(O)C_6H_4$	1	50
Me	Me	2	83
$PhCH_2$	$PhCH_2$	2	79
α-Pyridylmethyl	α-Pyridylmethyl	2	77
c-C_6H_{11}	c-C_6H_{11}	2	67
n-Bu	n-Bu	2	80

N-Alkylhydroxylamines, e.g. **42**, are smoothly converted into 2-alkyl-1,2,4-oxadiazolidine-3,5-diones, e.g. **43**, by treatment with CCI in the presence of triethylamine.[55]

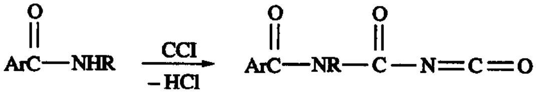


42

43 

$\mathrm{R} = \mathrm{Me}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{NHCH_2CH_2}$ (98%)

4.1.4. *Reactions with amides of carboxylic, sulfonic and phosphorus acids, and amidines.* Chlorocarbonyl isocyanate reacts with monosubstituted amides of various acids. Heating at 80–100°C in an inert solvent is necessary. For N-alkylamides of aromatic carboxylic acids, the reaction proceeds in boiling benzene and may be a convenient method for the synthesis of N-aroylcarbamoyl isocyanates **44**.[56] N-Alkylamides of aliphatic carboxylic acids also react with CCI under similar conditions but the reaction products undergo polymerization. N-Alkylamides of trichloro- and trifluoroacetic acids do not react with CCI under these conditions. For reactions of CCI with some disubstituted amides of carboxylic acids, see Section 4.3.2.



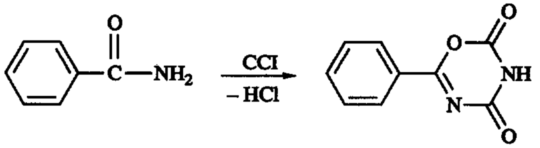
$$\mathrm{ArC(=O){-}NHR} \xrightarrow[-\mathrm{HCl}]{\mathrm{CCI}} \mathrm{ArC(=O){-}NR{-}C(=O){-}N{=}C{=}O}$$

44

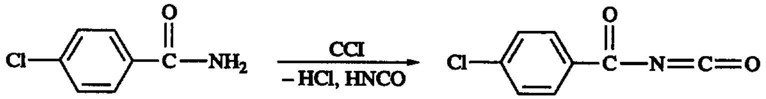
Table 9. N-Alkyl-N-aroylcarbamoyl isocyanates 44[56]

R	Ar	B.p./torr	Yield [%]
Me	Ph	86°C/0.2	65
i-Pr	Ph	96°C/0.2	55
Me	4-MeC_6H_4	95°C/0.2	70
i-Pr	4-MeC_6H_4	86°C/0.08	48
Me	4-ClC_6H_4	106°C/0.2	60
i-Pr	4-ClC_6H_4	100°C/0.1	65

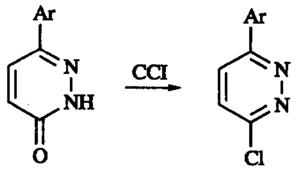
Benzamide reacts with CCI giving the oxadiazine **45**.[18] Slight changes in the nucleophilicity of the centers responsible for cyclisation may entirely change the direction of a process. Thus, 4-chlorobenzoyl isocyanate is primarily formed in a similar reaction with 4-chlorobenzamide.[18]



45 (90%)



In one case, the role of CCI as a chlorinating agent, in a reaction with compounds containing an amide moiety, was noted. Substituted 3-(2H)pyridazinones **46** are converted into 3-chloropyridazines **47** by treatment with CCI in boiling acetonitrile.[57]



46

47 Ar = Ph (71%), 4-MeC_6H_4 (70%)
4-$MeOC_6H_4$ (73%)
4-ClC_6H_4 (71%)
3,4-$Me_2C_6H_3$ (70%)

Monosubstituted amides of alkane- and arenesulfonic acids **48** react with CCI in boiling chlorobenzene giving N-sulfonylcarbamoyl isocyanates **49**.[58] N-Alkylsulfamoyl chlorides and fluorides **50** react with CCI at 0°C in dichloroethane in the presence of HCl scavenger giving N-halosulfonylcarbamoyl isocyanates **51**.[59] Isocyanates **49** have been proposed as water scavengers in polyurethanes.[58]

$$R'SO_2NHR \xrightarrow[-HCl]{CCI} R'SO_2NR{-}\overset{O}{\overset{\|}{C}}{-}N{=}C{=}O$$

48 **49**

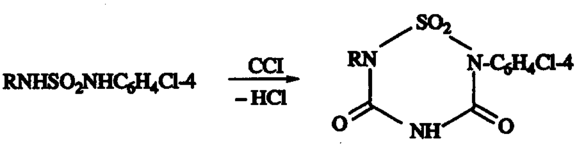
$$XSO_2NHR \xrightarrow[-HCl]{CCI} XSO_2NR{-}\overset{O}{\overset{\|}{C}}{-}N{=}C{=}O$$

50 **51**

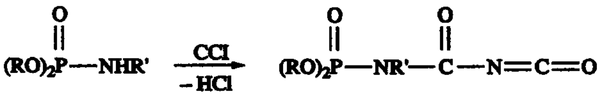
Table 10. N-Sulfonylcarbamoyl isocyanates 49, 51

R	R' or X	B.p./torr	Yield [%]	Reference
Me	Me	150°C/15	90	58
Et	Me	120°C/0.1	78	58
Me	Ph	145°C/0.1	93	58
i-Pr	4-MeC$_6$H$_4$	148-150°C/0.1	91	58
CH$_2$=CHCH$_2$	Me	124°C/0.1	72	58
Ph	Ph	M.p. 98-100°C	93	58
Me	Cl	56-60°C/0.15	71	59
Me	F	39-42°C/0.15	55	59
Et	Cl	68-70°C/0.2	66	59
Pr	Cl	66-70°C/0.2	71	59
Bu	Cl	70-75°C/0.2	67	59

N,N′-Disubstituted sulfonediamides **52** treated with CCI in boiling toluene giving substituted S,S-dioxidethiatriazinediones **53** have been recommended as herbicides.[60] N-Alkylamides of dialkylphosphoric acid **54** react with CCI in boiling CCl$_4$ to give N-alkyl-N-phosphonylcarbamoyl isocyanates **55**.[61]



52 **53** R = Me (70%), i-Pr (98%)



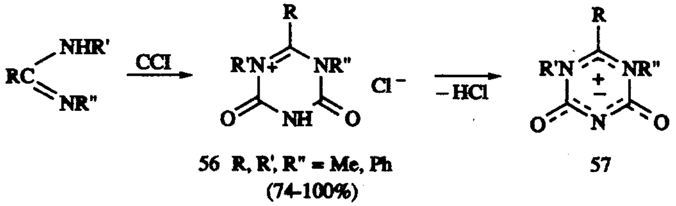
$$(RO)_2\overset{O}{\overset{\|}{P}}{-}NHR' \xrightarrow[-HCl]{CCI} (RO)_2\overset{O}{\overset{\|}{P}}{-}NR'{-}\overset{O}{\overset{\|}{C}}{-}N{=}C{=}O$$

54 **55**

Table 11. N-Alkyl-N-phosphonylcarbamoyl isocyanates 55[61]

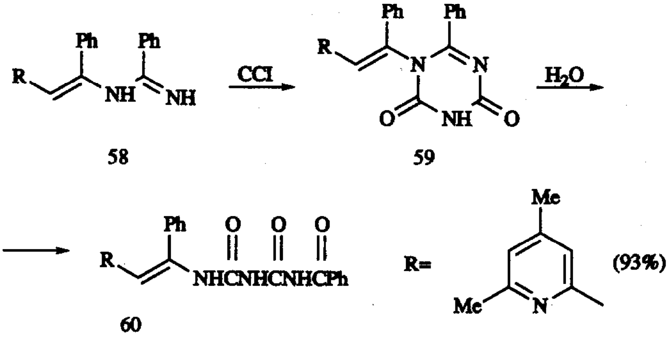
R	R'	B.p./torr	Yield [%]
Et	Me	69°C/0.1	85
Et	Et	67°C/0.05	75
i-Pr	Et	70°C/0.05	80

Treatment of N,N′-disubstituted amidines with CCI leads to triazinium cations **56** which are converted into heterocyclic mesomeric betaines (4-oxo-4,5-dihydro-*s*-triazin-1-ium-2-olates **57**).[18,45,62] Compounds of type **57** may also be obtained from ethoxycarbonyl isocyanate, instead of CCI.[62] By interaction of CCI with the monosubstituted amidine **58** in boiling tetrahydrofuran, the triazine **59** is formed which is converted into the biuret **60**.[63]



56 R, R', R" = Me, Ph (74-100%)

57



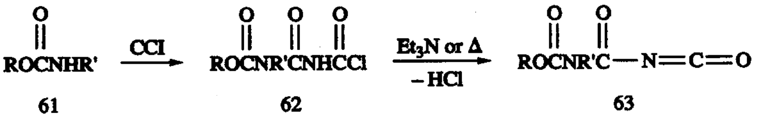
58

59

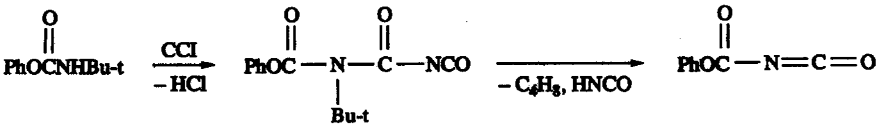
60

(93%)

4.1.5. *Reactions with carbamates, ureas and their thio-analogues.* N-Monosubstituted carbamates **61** give the adducts **62** with CCI under mild conditions (20°C). Treatment with organic bases or boiling in inert solvents (toluene, chlorobenzene) gives carbamoyl isocyanates **63**.[64–69] Isocyanates **63** undergo gradual dimerization on prolonged standing, like dialkylcarbamoyl isocyanates (see Section 4.1.3.). In the case of phenyl N-*tert*-butyl carbamate, isobutylene and cyanic acid are formed, and phenoxycarbonyl isocyanate is formed as a stable product.[66] Derivatives of isocyanates **63** with amines, alcohols and phenols are recommended as effective fungicides, insecticides and herbicides.[67–69]



$$\underset{\mathbf{61}}{\mathrm{RO\overset{O}{\overset{\|}{C}}NHR'}} \xrightarrow{\mathrm{CCI}} \underset{\mathbf{62}}{\mathrm{RO\overset{O}{\overset{\|}{C}}NR'\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}Cl}} \xrightarrow[\mathrm{-HCl}]{\mathrm{Et_3N\ or\ \Delta}} \underset{\mathbf{63}}{\mathrm{RO\overset{O}{\overset{\|}{C}}NR'\overset{O}{\overset{\|}{C}}{-}N{=}C{=}O}}$$

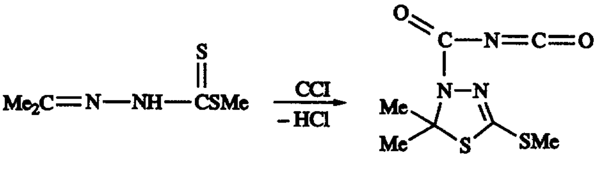


$$\mathrm{PhO\overset{O}{\overset{\|}{C}}NHBu\text{-}t} \xrightarrow[\mathrm{-HCl}]{\mathrm{CCI}} \mathrm{PhO\overset{O}{\overset{\|}{C}}{-}\underset{\underset{Bu\text{-}t}{|}}{N}{-}\overset{O}{\overset{\|}{C}}{-}NCO} \xrightarrow[\mathrm{-C_4H_8,\ HNCO}]{} \mathrm{PhO\overset{O}{\overset{\|}{C}}{-}N{=}C{=}O}$$

Table 12. Carbamoyl isocyanates 63

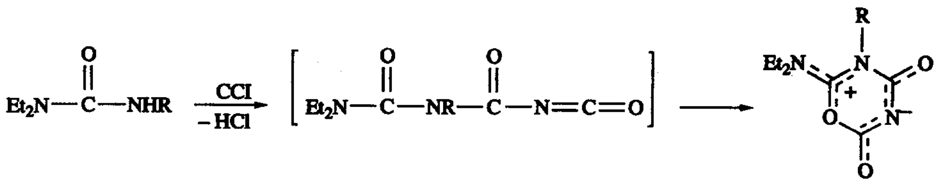
R	R'	B.p./torr	Yield [%]	Reference
Me	i-Pr	94-95°C/10	72	64
Me	s-Bu	45-46°C/0.08	70	64
Et	i-Pr	108°C/10	60	65
Et	s-Bu	40-41°C/0.07	75	64
—CH_2CH_2—		110°C/0.1	40	65
Ph	Me	97°C/0.08	76	66
Ph	i-Pr	125°C/0.1	53	66
Ph	i-Bu	125-128°C/0.3	86	66
Ph	c-C_5H_9	128-130°C/0.08	57	66
Ph	c-C_6H_{11}	145-160°C/0.1	33	66
Ph	c-C_6H_{11}CHMe	151°C/0.1	55	66
Ph	Ph	162°C/0.1	86	66
Et	Ph	130-135°C/0.8	-	67
Et	neo-C_5H_{11}	70-74°C/0.2	-	67
Ph	neo-C_5H_{11}	111-112°C/0.1	88	66
4-MeC_6H_4	3-$CF_3C_6H_4$	260°C/0.075	96	69

Reaction of CCI with the N-alkylideneaminosubstituted dithiocarbamate **64** at 20°C in benzene proceeds very specifically. The more nucleophilic nitrogen atom of compound **64** is subjected to the electrophilic attack; the reaction is accompanied by cyclization without any participation of the isocyanate group, and the final product is carbamoyl isocyanate **65**.[70]



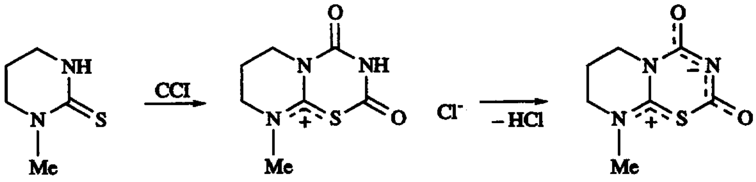
64 **65** (98%)

Trisubstituted ureas **66**, like N-monosubstituted carbamates **61**, give products with CCI easily. However, after loss of hydrogen chloride by treatment with an organic base or heating, the expected carbamoyl isocyanates **67** are not formed. Due to the intramolecular attack of the isocyanate group at the nucleophilic oxygen atom of the urea fragment, the reaction products are cross-conjugated heterocyclic mesomeric betaines, 3-alkyl-2-diethylamino-6-oxo-1,6-dihydro-1,3,5-oxadiazin-3-ium-4-olates **68**.[45,64,65]



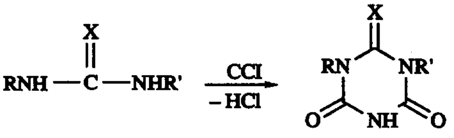
66 **67** **68** R = i-Pr (80%)
n-Bu (85%)

The behavior of trisubstituted thioureas such as the cyclic thiourea **69**, towards CCI is similar. If the reaction shown below is performed in mild conditions and in the absence of the hydrogen chloride scavenger, a stable salt-like product **70** is formed which gives the heterocyclic mesomeric betaine **71** after cleavage of hydrogen chloride with an organic base.[45,71]



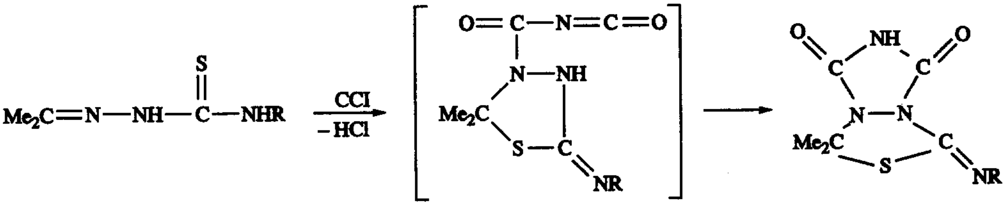
69 70 71 (70%)

N,N′-Disubstituted ureas and thioureas **72** give isocyanurates or thioisocyanurates **73** with CCI in boiling toluene or methylene dichloride.[72–80] The compounds **73** include effective herbicides,[72,77] drugs against coccidosis and toxoplasmosis of birds and animals,[73–76,78–80] and animal growth stimulators.[76]



72 73

N-Alkylideneaminosubstituted thioureas **74** give bicyclic compounds **75** with CCI at 20°C in chloroform.[70] The electrophile attacks the more nucleophilic nitrogen atom of the compound **74** primarily, then intramolecular cyclization can occur.

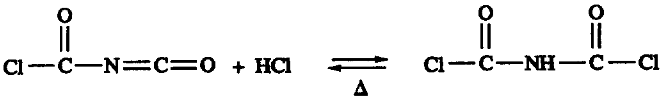


74

75 R = Me (87%)
Ph (83%)
$CH_2{=}CHCH_2$(89%)

4.2. *Reactions with acids*

4.2.1. *Reaction with hydrogen chloride.* Dry hydrogen chloride adds to CCI easily at 20°C giving imidodicarboxyl dichloride **76** which melts at 88–89°C yielding the starting materials.[18]

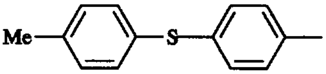
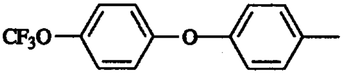
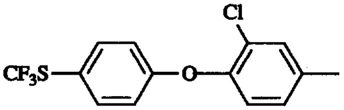
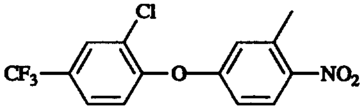
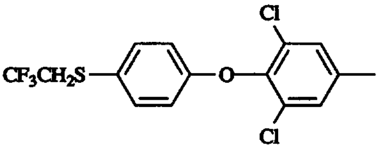
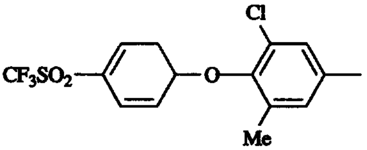


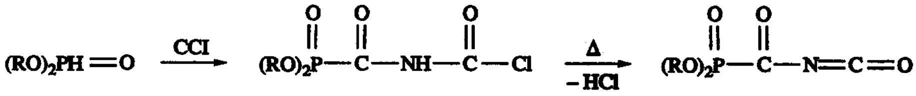
$$\mathrm{Cl{-}\overset{\overset{O}{\|}}{C}{-}N{=}C{=}O + HCl \underset{\Delta}{\rightleftharpoons} Cl{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}Cl}$$

76

4.2.2. *Reactions with phosphorus acids.* Chlorocarbonyl isocyanate reacts vigorously with dialkyl phosphites and dialkyl dithiophosphates giving products which lose hydrogen chloride on heating (boiling in benzene) and convert into isocyanates of dialkylphosphonoformic acid **77** and isocyanates of O,O-dialkyldithiophosphatecarbonic acid **78**, respectively.[65,81]

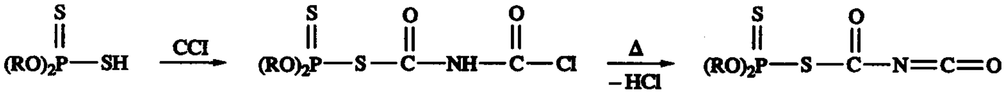
Table 13. Isocyanurates and thioisocyanurates 73

R	R'	X	Yield [%]	Reference
Me	Me	O	85	18, 72
Me	Me	S	95	18, 72
i-Pr	i-Pr	O	98	18, 72
$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	O	86	18, 72
t-Bu	t-Bu	O	75	18, 72
c-C_6H_{11}	Me	O	98	18, 72
c-C_6H_{11}	$CH_2{=}CHCH_2$	S	36	18, 72
Ph	Me	O	84	18, 72
Ph	Me	S	42	18, 72
Ph	n-Bu	S	72	18, 72
3,4-$Cl_2C_6H_3$	Me	O	94	18, 72
4-$PhOC_6H_4$	Me	O	80	73
	Me	O	87	74
	Et	O	67	75
	Me	O	89	76
	Me	O	83	77
	Me	O	80	78
	Me	S	97	79



$$(RO)_2PH{=}O \xrightarrow{CCI} (RO)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{\Delta} (RO)_2\overset{O}{\overset{\|}{P}}-\overset{O}{\overset{\|}{C}}-N{=}C{=}O$$

77



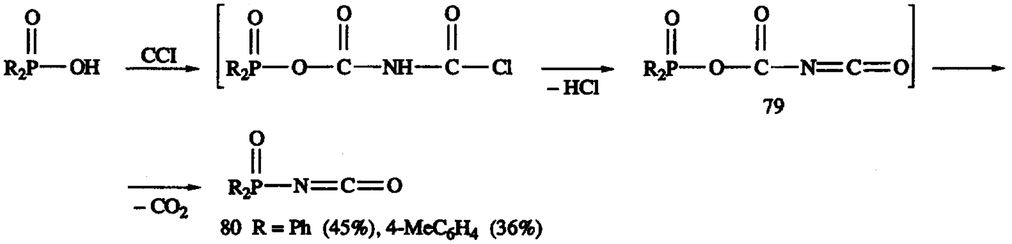
$$(RO)_2\overset{S}{\overset{\|}{P}}-SH \xrightarrow{CCI} (RO)_2\overset{S}{\overset{\|}{P}}-S-\overset{O}{\overset{\|}{C}}-NH-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[-HCl]{\Delta} (RO)_2\overset{S}{\overset{\|}{P}}-S-\overset{O}{\overset{\|}{C}}-N{=}C{=}O$$

78

Table 14. Phosphorylated isocyanates 77, 78, $X{-}\overset{\overset{O}{\|}}{C}{-}N{=}C{=}O$ [81]

X	B.p./torr	Yield [%]
$(MeO)_2P(O)$	51°C/0.08	62
$(EtO)_2P(O)$	60°C/0.1	65
$(i\text{-}PrO)_2P(O)$	58°C/0.05	52
$(EtO)_2P(S)S$	65°C/0.05	65
$(i\text{-}PrO)_2P(S)S$	68°C/0.08	60

Phosphinic acids react with CCI in similar conditions but the primarily formed isocyanates **79** are unstable and lose carbon dioxide under the reaction conditions yielding isocyanates of phosphinic acids **80**.[65,81] The reaction is better performed in the presence of the hydrogen chloride scavenger (triethylamine), otherwise the yield of the products **80** decreases. This reaction demonstrates a rare case of the direct conversion of an acid into its isocyanate.

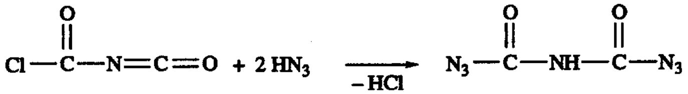


$$R_2\overset{\overset{O}{\|}}{P}{-}OH \xrightarrow{CCI} \left[R_2\overset{\overset{O}{\|}}{P}{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow[-HCl]{} R_2\overset{\overset{O}{\|}}{P}{-}O{-}\overset{\overset{O}{\|}}{C}{-}N{=}C{=}O\right] \longrightarrow \xrightarrow[-CO_2]{} R_2\overset{\overset{O}{\|}}{P}{-}N{=}C{=}O$$

79

80 R = Ph (45%), 4-MeC_6H_4 (36%)

4.2.3. *Reaction with hydrazoic acid.* Treatment of CCI with hydrazoic acid in ether at 20°C gives di(azidocarbonyl)amine **81**, a crystalline compound which detonates percussively.[82]

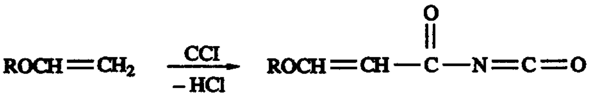


$$Cl{-}\overset{\overset{O}{\|}}{C}{-}N{=}C{=}O + 2\,HN_3 \xrightarrow[-HCl]{} N_3{-}\overset{\overset{O}{\|}}{C}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}N_3$$

81

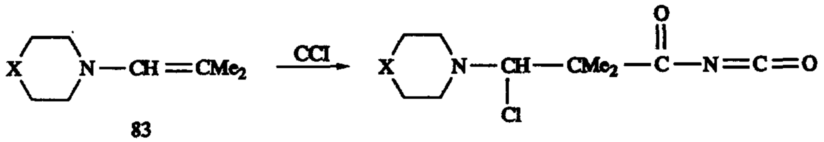
4.3. *Addition to polar multiple bonds*

4.3.1. *Reactions with vinyl ethers and enamines.* In contrast with chlorosulfonyl isocyanate, $ClSO_2NCO$,[3] chlorocarbonyl isocyanate does not add to the C═C bond of common olefines. However, compounds containing electron-rich C═C bonds react with CCI easily under mild conditions. Thus, interaction of CCI with vinyl ethers in the presence of the hydrogen chloride scavenger (triethylamine) in ether at 20°C gives rise to isocyanates of β-alkoxyacrylic acid **82**.[83] CCI also adds easily to the enamine **83** C═C bond yielding acyl isocyanates **84**, possibly with the salt-like structure **84a**.[84] CCI undergoes cycloaddition with some enamines (see Section 4.6.)



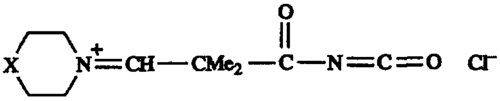
$$ROCH{=}CH_2 \xrightarrow[-HCl]{CCI} ROCH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}N{=}C{=}O$$

82



83

84 X = O (68%)
CH$_2$ (100%)

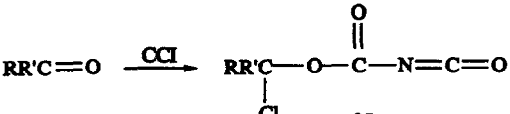


84a

Table 15. β-Alkoxyacryloyl isocyanates 82[83]

R	B.p./torr	Yield [%]
Et	89°C/10	36
i-Pr	94°C/10	39
n-Bu	43°C/0.5	43

4.3.2 *Reactions with aldehydes and ketones.* CCI is added to the carbonyl group of aldehydes and ketones giving 1-chloroalkoxycarbonyl isocyanates **85** in boiling benzene.[65,85,86] In the case of aldehydes, presence of the base catalyst (pyridine) is needed.

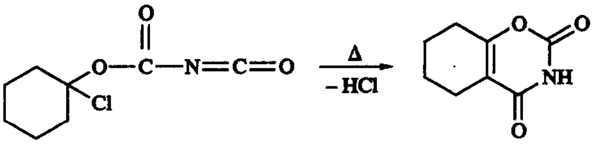


85

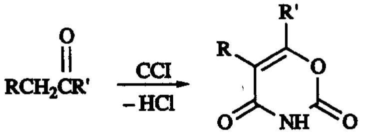
Table 16. 1-Chloroalkoxycarbonyl isocyanates 85[86]

R	R'	B.p./torr	Yield [%]
Me	Me	50°C/12	38
Me	Et	61°C/12	25
— (CH$_2$)$_5$ —		45°C/0.5	45
CCl$_3$	H	89°C/12	69
Ph	H	73°C/0.06	80

Isocyanates **85** are usually thermally stable compounds but those having hydrogen atoms in the α-position of alkyl substituents lose hydrogen chloride above 100°C and undergo cyclization giving 1,3-oxazine-2,4-diones **86**.[65] For the synthesis of compounds **86**, the direct reaction of CCI with carbonyl compounds having two or three hydrogen atoms in the α-position of an alkyl substituent is better.[87] The reaction is performed without solvent at 90–130°C. Oxazinediones **86** may be used in photography for obtaining high quality images.[87] Effective insecticides have been found among derivatives of the isocyanates **85**.[88]



86a (65%)

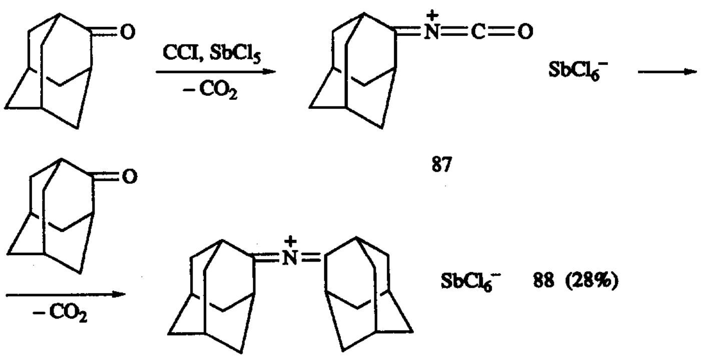


86

Table 17. 1,3-Oxazine-2,4-diones 86[87]

R	R'	Yield [%]
—$(CH_2)_4$—		34.5
—$(CH_2)_3$—		49
H	t-Bu	50
H	$Me_2C{=}CH$	10
H	Ph	55
H	$4\text{-}ClC_6H_4$	50
H	$4\text{-}MeOC_6H_4$	48
H	$PhCH{=}CH$	55.8
Me	Et	51
Me	Ph	46.5
Et	Pr	20
Et	Ph	35
Pr	Ph	53.5
MeC(O)	Me	68
MeOC(O)	Ph	65
EtOC(O)	Me	77

In the presence of a Lewis acid, the reaction of CCI with some carbonyl compounds which are unable to enolise proceeds according to another scheme. Treatment of 2-adamantanone with CCI in a 2 : 1 ratio in the presence of an equimolar quantity of $SbCl_5$ (reagents are mixed at −50°C in chloroform, and then the reaction mixture is boiled) yielded 2-azaallenium hexachloroantimonate **88** via the intermediate 1-oxa-3-azabutatrienium hexachloroantimonate **87**.[89] In this reaction CCI is a '=C=' synthon. Some N,N-disubstituted amides of carboxylic acids react with CCI in methylene dichloride at −20°C in the presence of an equimolar quantity of $SbCl_5$ giving stable salts, 4-dimethylamino-1-oxa-3-azabutatrienium hexachloroantimonates **90**, in high yield.[90] A similar reaction does not occur with N,N-disubstituted carbamates.



87

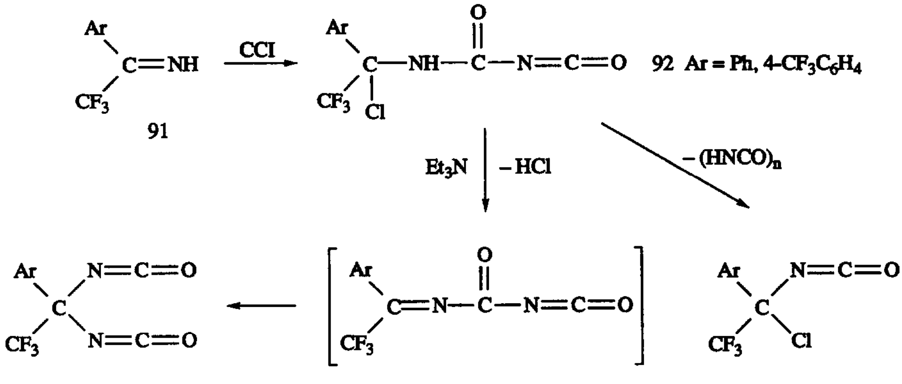
88 (28%)

$$\mathrm{Me_2N{-}CR{=}O} \xrightarrow[-\mathrm{CO_2}]{\mathrm{CCI,\ SbCl_5}} \mathrm{Me_2N{-}CR{=}\overset{+}{N}{=}C{=}O} \quad \mathrm{SbCl_6^-}$$

89

90 R = H (90%)
t-Bu (81%)

4.3.3. *Reactions with imino compounds.* N-Unsubstituted imino compounds (ketimines, imino esters) react with CCI very easily (−20°C, in inert solvent). Depending on the nucleophilicity of the imine, the reaction may proceed in two directions.[91–96] Ketimines **91** with decreased nucleophilicity, due to the influence of the electron-withdrawing CF_3 group, give the products **92** with CCI which are produced by CCI addition to the imine C═N bond. The removal of hydrogen chloride by treatment with the organic base triethylamine, yields geminal diisocyanatoalkanes **94**. The formation of the compounds **94** is supposed to be connected with the [1, 3] rearrangement of the intermediate compounds **93**. This is due to the migration of the NCO group in the azaallylic C═N–C triad. Besides dehydrochlorination, treatment of the adduct **92** with triethylamine causes partial loss of isocyanic acid giving rise to the formation of 1-chloroalkyl isocyanates **95**. Therefore, diisocyanates **94** are always obtained with the admixture of minor quantities of isocyanates **95** which may be easily separated from the major product as triethylamine adducts. The yield of pure diisocyanates **94** is *ca.* 40%.[91,92]



Imino-compounds **96** with enhanced nucleophilicity react with CCI differently. In these cases, the reaction proceeds by addition of an imine to the NCO group of CCI. The resulting carbamoyl chlorides **97** split off hydrogen chloride by heating to 80–120°C or cooling by treatment with an organic base giving N-alkylidenecarbamoyl isocyanates **98**.[91,93,95,96] In some cases the carbamoyl chlorides **97** react with the imines as they are forming. This reaction dominates with diphenyl ketimine, and the major product is the biuret **99**.[93]

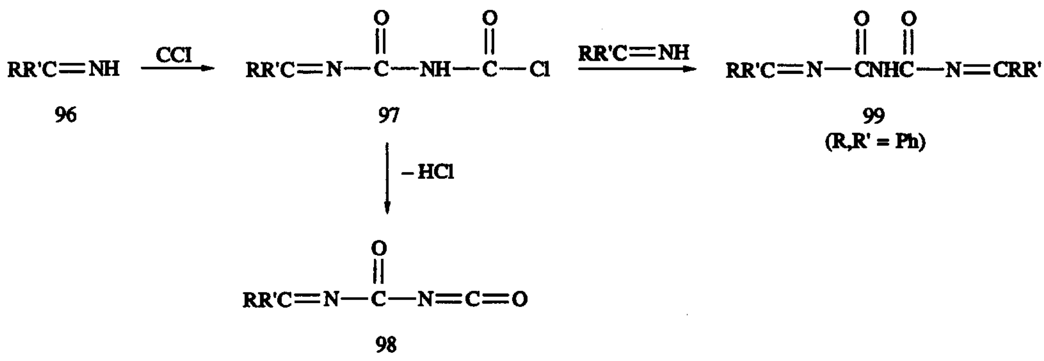


Table 18. N-Alkylidenecarbamoyl isocyanates 98

R	R'	B.p./torr	Yield [%]	Reference
t-Bu	t-Bu	49°C/0.05	65	91
CF_3	MeO	49°C/12	85	91
CCl_3	MeO	62°C/0.03	55	93
CF_3	BuO	41°C/12	60	96
CCl_3	EtS	82°C/0.2	46	96

Chlorocarbonyl isocyanate is added smoothly to N-substituted imines **100** at 25°C in an inert solvent forming the thermally stable carbamoyl isocyanates **101**.[97] Carbamoyl isocyanates **103** obtained by the addition of CCI to imines **102** containing primary or secondary alkyl substituents at the carbon atom of azomethine group are thermally unstable compounds. They cannot be distilled in vacuo because they undergo cyclization above 90°C, giving pyrimidine derivatives. If a secondary alkyl substituent is attached to the azomethine group, the reaction products are substituted 6-chloro-5,6-dihydropyrimidine-2,4-diones **104**.[98] With primary alkyl substituents, hydrogen chloride loss leads to the formation of substituted uracils **105**.[99–101] Among the uracils **105** prepared by this method, substances with hypnotic properties have been found[101] as well as effective plant protecting agents.[99,100]

$$\mathrm{ArCH{=}NR} \xrightarrow{\mathrm{CCI}} \mathrm{ArCH(Cl){-}NR{-}C({=}O){-}N{=}C{=}O}$$

Table 19. Carbamoyl isocyanates 101[97]

R	Ar	B.p./torr	Yield [%]
Me	Ph	112°C/0.05	66
Me	$4\text{-}ClC_6H_4$	115°C/0.1	86
i-Pr	Ph	115°C/0.15	65
$c\text{-}C_6H_{11}$	Ph	142°C/0.07	15
Ph	Ph	152°C/0.1	70

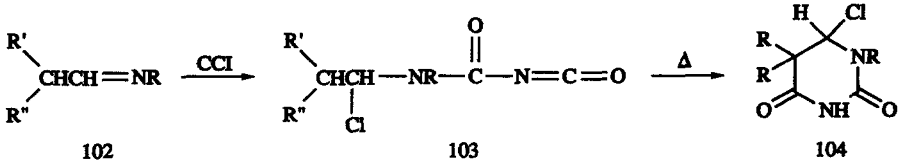
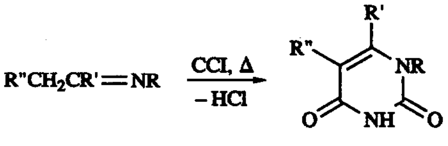


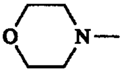
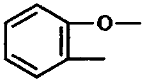
Table 20. 6-Chloro-5,6-dihydropyrimidine-2,4-diones 104[98]

R	R'	R"	Yield [%]
Me	Me	Me	57
i-Pr	Me	Me	78
Me	—$CH_2CH{=}CHCH_2CH_2$—		44
c-C_6H_{11}	Me	Me	92
c-C_6H_{11}	—$CH_2CH{=}CHCH_2CH_2$—		91
$PhCH_2$	Me	Me	70

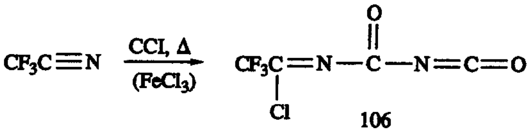


102 105

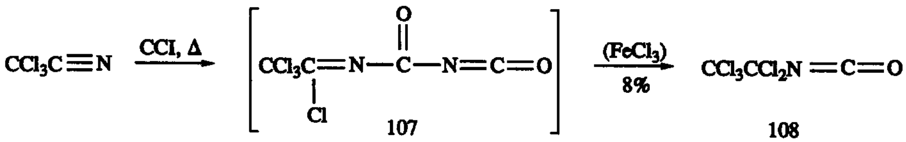
Table 21. Uracils 105

R	R'	R"	Yield [%]	Reference
i-Pr	Me	H	47.5	99
Me	—$(CH_2)_3$—		-	99
Bu	H	Me	-	99
c-C_6H_{11}	H	Me	-	99
c-C_6H_{11}	Et	Me	-	99
c-C_6H_{11}	—$(CH_2)_3$—		-	99
c-C_6H_{11}	—$(CH_2)_4$—		36.3	99
$PhCH_2$	Me	H	78	99
Ph	H	Me	-	99
Ph	Me	H	-	99
Ph	Et	Me	-	99
Ph	—$(CH_2)_4$—		-	99
Ph	Ar	H	50-80	101
4-ClC_6H_4	Ph	H	97.4	101
—OCH_2CH_2—		H	41.6	100
	H	H	73.2	100
		H	93	100
$PhCH_2O$	Ph	H	48	100

4.3.4. *Reactions with nitriles, cyanates, cyanamides, and carbodiimides.* Addition of CCI to the C≡N bond of some nitriles is possible under vigorous conditions. Thus, by a prolonged heating of the CCI–trifluoroacetonitrile mixture at 200°C in an autoclave in the presence of catalytic amounts of $FeCl_3$, the carbamoyl isocyanate **106** is formed (12%).[95] Similar reaction with trichloroacetonitrile proceeds under milder conditions (120°C, normal pressure); however, the reaction mixture undergoes some polymerisation and perchloroethyl isocyanate **108** may be isolated in low yield which seems to be formed due to the exchange of the NCO and chlorine groups in the intermediate isocyanate **107**.[96]

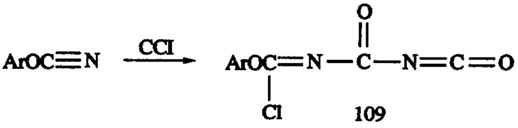


$CF_3C\equiv N \xrightarrow[(FeCl_3)]{CCI,\ \Delta} CF_3C(Cl)=N-C(=O)-N=C=O$ **106**



$CCl_3C\equiv N \xrightarrow{CCI,\ \Delta} [CCl_3C(Cl)=N-C(=O)-N=C=O]$ **107** $\xrightarrow[8\%]{(FeCl_3)} CCl_3CCl_2N=C=O$ **108**

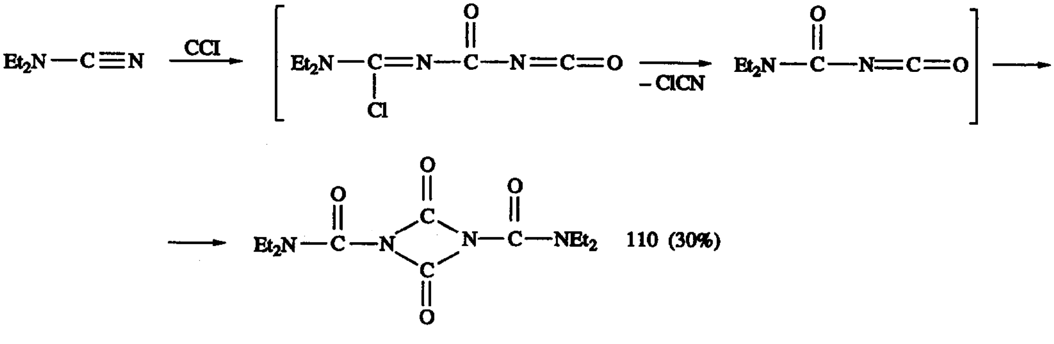
Addition of CCI to the C≡N bond of organic cyanates and cyanamides proceeds easily. Aryl cyanates react with CCI in boiling benzene in the presence of catalytic amounts of pyridine, giving carbamoyl isocyanates **109**.[102,103] Dialkyl cyanamides react with CCI in boiling benzene without any catalyst. The reaction products are carbamoyl isocyanate dimers **110**.[65]



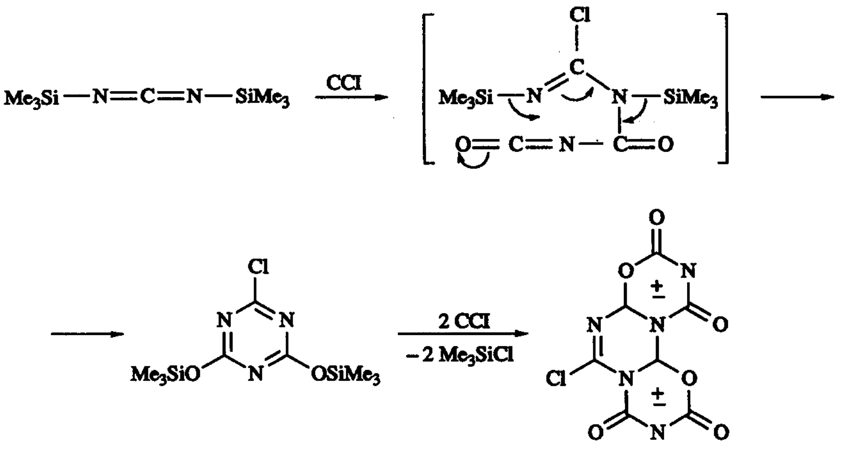
$ArOC\equiv N \xrightarrow{CCI} ArOC(Cl)=N-C(=O)-N=C=O$ **109**

Table 22. Carbamoyl isocyanates 109[103]

Ar	B.p./torr	Yield [%]
Ph	72°C/0.5	58
4-MeC_6H_4	88°C/0.2	55
4-ClC_6H_4	92°C/0.1	54

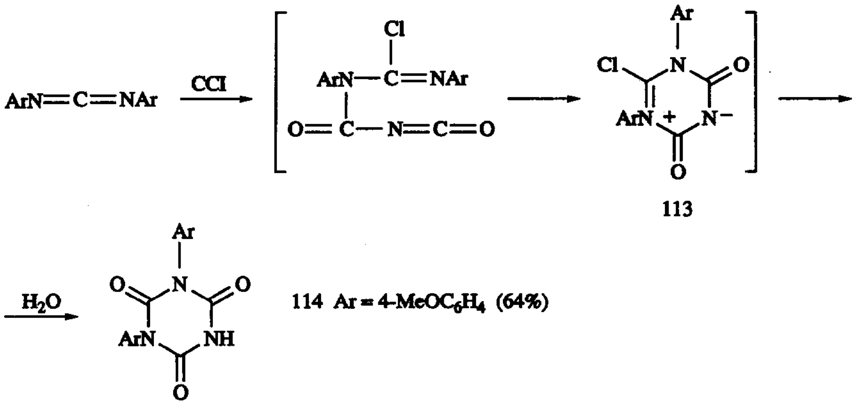


Chlorocarbonyl isocyanate reacts with bis(trimethylsilyl)carbodiimide under mild conditions (20°C, in ether) giving 2,4-bis(trimethylsilyloxy)-6-chloro-1,3,5-triazine **111**.[104] The reaction begins with the addition of CCI to the carbodiimide C═N bond and the resulting adduct then undergoes cyclization with a simultaneous migration of trimethylsilyl groups from the nitrogen to the oxygen atom. The yield of triazine **111** is 64%. If the reaction is performed with excess CCI, the heterocyclic mesomeric betaine **112** is obtained.[45,96] CCI reacts with diarylcarbodiimides in similar conditions giving the betaines **113** which are hydrolysed to the triazinetriones, for example **114**.[105]



111

112



113

114 $Ar = 4\text{-}MeOC_6H_4$ (64%)

4.4. *Cleavage of cyclic and chain nucleophiles*

Chlorocarbonyl isocyanate reacts with oxiranes at 40°C in the presence of $AlCl_3$ catalyst giving 2-chloroalkoxycarbonyl isocyanates **115**.[106] The epoxide containing a hydroxyl group, for example the glycide **116**, reacts with CCI giving the polycycloaddition products **117**.[18]

115

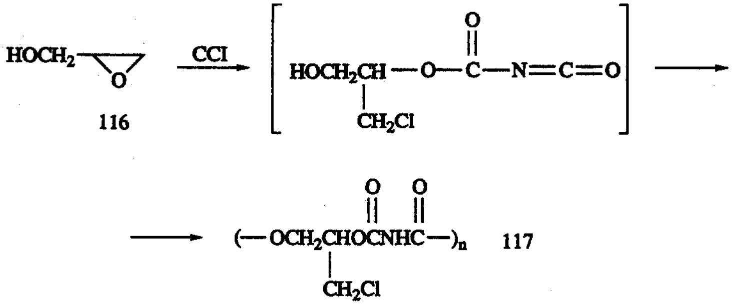
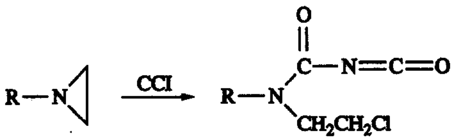


Table 23. 2-Chloroalkoxycarbonyl isocyanates 115[106]

R	B.p./torr	Yield [%]
H	70°C/11	56
Me	80°C/14	-
Et	83°C/13	-
$ClCH_2$	65°C/0.3	-
$CH_2{=}CHCH_2OCH_2$	80-90°C/0.15	-
Ph	100°C/0.1	55

The N-alkyl aziridine ring is easily cleaved by treatment with CCI (20°C, in benzene) yielding carbamoyl isocyanates **118**.[107] N-Phosphorylated aziridines react in a similar way.

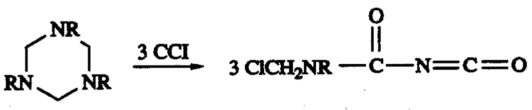


118

Table 24. Carbamoyl isocyanates 118[107]

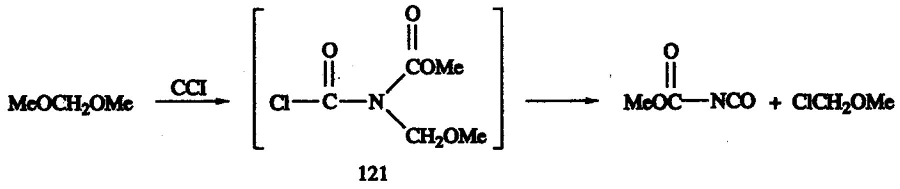
R	B.p./torr	Yield [%]
$N{\equiv}CCH_2CH_2$	130-132°C/0.03	80
$PhCH_2CH_2$	115°C/0.05	60
$(EtO)_2P(O)$	99°C/0.08	69
$(PrO)_2P(O)$	122-123°C/0.06	70

Cleavage of the 1,3,5-trialkylhexahydrotriazine ring **119** with CCI proceeds as easily as that of the aziridine cycle (20°C, in benzene): N-alkyl-N-chloromethyl carbamoyl isocyanates **120** are obtained.[108] Treatment of CCI with dimethoxymethane leads to the cleavage products of the intermediate adduct **121**—methoxycarbonyl isocyanate and chloromethyl ether.[18]



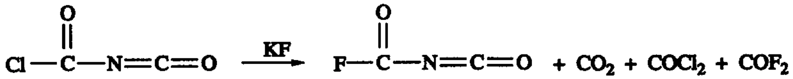
119

120 R = i-Pr (35%)
$PhCH_2$ (45%)



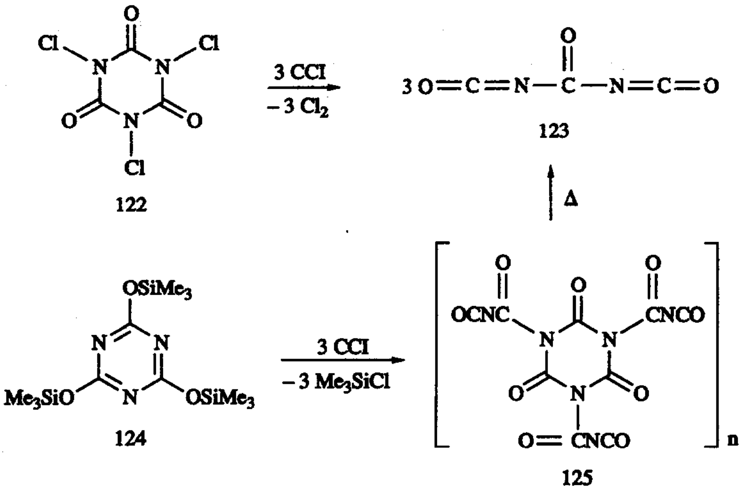
4.5. *Exchange reactions*

CCI as a carbonyl chloride can exchange the chlorine atom with other potential anions. Under harsh conditions (200°C) the chlorine atom is substituted by the fluorine atom using potassium fluoride. However, this reaction cannot be used as a method for the preparation of fluorocarbonyl isocyanate because it leads to a complex mixture of gaseous products.[20] The exchange reaction of fluorophosgene with trimethylsilyl isocyanate or tetraisocyanatosilane (230°C, in autoclave) may be used for the preparation of fluorocarbonyl isocyanate (70%).[109]

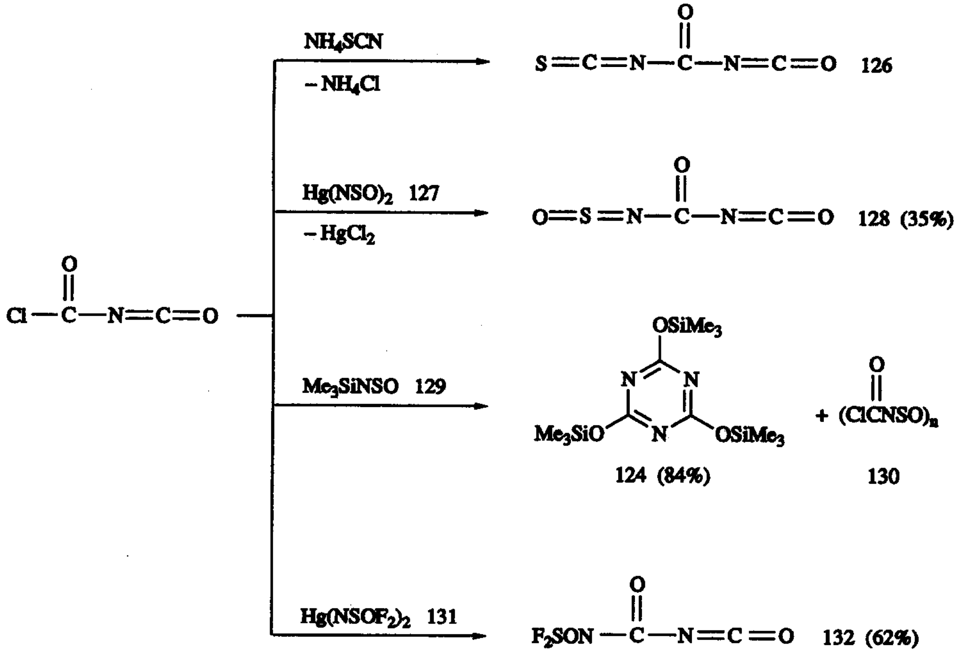


$$Cl-\overset{O}{\overset{\|}{C}}-N=C=O \xrightarrow{KF} F-\overset{O}{\overset{\|}{C}}-N=C=O + CO_2 + COCl_2 + COF_2$$

Several methods exist for the replacement of the chlorine atom in the CCI molecule by the isocyanate group. By heating the mixture of CCI and trichlorocyanuric acid **122** at 150°C in dichlorobenzene, carbonyl diisocyanate **123** is obtained (82%).[110,111] Instead of the compound **122**, the Na or K salt of dichlorocyanuric acid may be used. A simpler preparation of the compound **123** is the exchange reaction of the compound **122** with phosgene at 180°C in trichlorobenzene. The yield of the diisocyanate **123** is 80%.[111] A convenient and preparatively simple way for obtaining compound **123** is the reaction of CCI with 2,4,6-tris(trimethylsilyl)cyanurate **124**.[112] The reaction is performed in ether at 20°C. After the distillation of solvent, an amorphous powder-like residue is obtained which is supposed to be a polymer of the tris-isocyanate **125**; this product depolymerizes smoothly on heating to 150°C to give carbonyl diisocyanate **123** (100%).

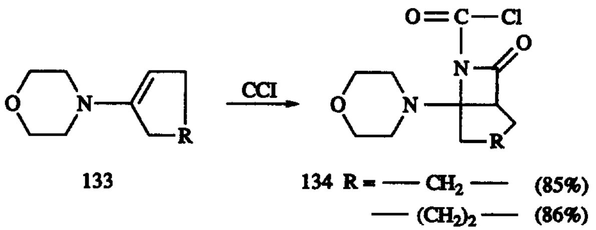


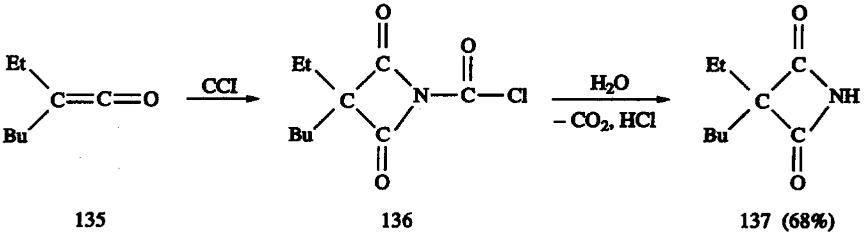
The replacement of the chlorine atom by the isothiocyanate group proceeds smoothly by treatment of CCI with ammonium rhodanide in liquid sulfur dioxide at −22°C yielding isothiocyanatocarbonyl isocyanate **126** (76%).[113] N-Isocyanatocarbonyl sulfinylimine **128** is obtained by treatment of mercury bis(sulfinylimine) **127** with CCI.[114] The reaction starts at −78°C and is finished at 20°C without any solvent. If N-trimethylsilyl sulfinylimine **129** is used instead of the compound **127**, the compound **128** is not obtained. In this case, the NCO group of CCI shows its pseudohalogen character, and as a result, tris(trimethylsilyl)cyanurate **124** and chlorocarbonyl sulfinylimine **130** are formed. The latter is polymerized under the reaction conditions.[115] Treatment of mercury bis(imidosulfuryl difluoride) **131** with CCI at 20°C in methylene dichloride gives rise to the N-isocyanatocarbonyl imidosulfuryl difluoride **132**.[116]



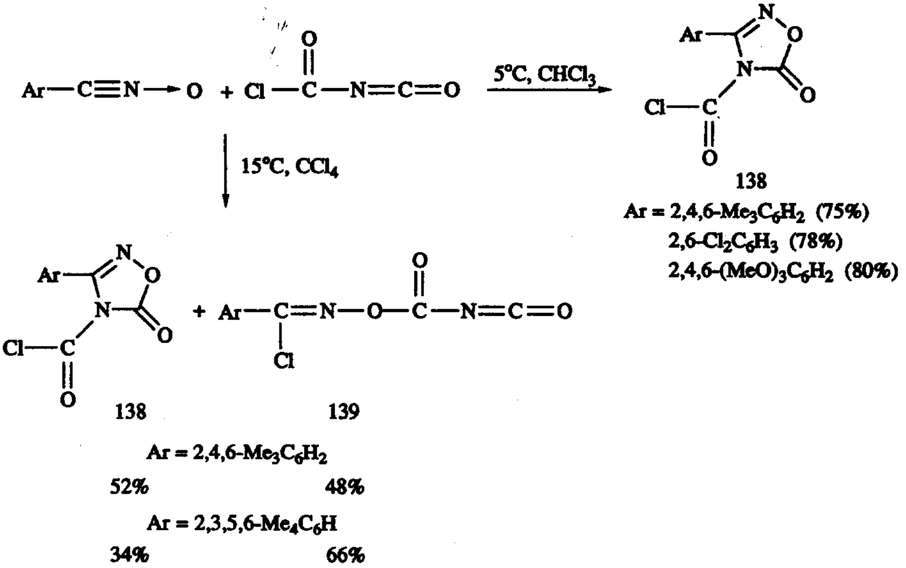
4.6. *Cycloaddition reactions*

In contrast with acyl isocyanates[117] and chlorosulfonyl isocyanate,[3,4] cycloadditions occur less frequently with CCI. Treatment of cyclic enamines **133** with CCI under mild conditions (−20°C, in ether) gives rise to [2+2] cycloaddition products **134**.[84] By interaction of CCI with the substituted ketene **135** at 0°C and the subsequent hydrolysis of the adduct **136**, the malonimide **137** is obtained.[118]





Aromatic nitrile oxides react with CCI in chloroform at 5°C giving the [3+2] cycloaddition products which are substituted Δ^2-1,2,4-oxadiazoline-5-ones **138**.[119] If the reaction is performed in a non-polar solvent (CCl_4), both cycloaddition products **138** and the linear products O-isocyanatocarbonyl hydroxamoyl chlorides **139**, are formed.[120]



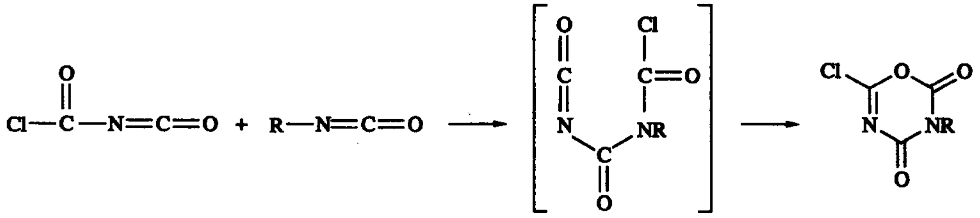
138

Ar = 2,4,6-$Me_3C_6H_2$ (75%)
2,6-$Cl_2C_6H_3$ (78%)
2,4,6-$(MeO)_3C_6H_2$ (80%)

138 **139**

Ar = 2,4,6-$Me_3C_6H_2$
52% 48%
Ar = 2,3,5,6-Me_4C_6H
34% 66%

Finally, CCI may give the [2+4] cycloaddition products **141** with aliphatic isocyanates. The intermediate compound **140** seem to be formed in this reaction.[18]



140 **141**

R = Me, $MeOCH_2$

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