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1,1-DIHALOALKYL HETEROCUMULENES: SYNTHESIS AND REACTIONS

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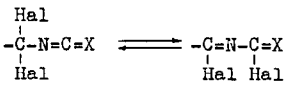
CONTENTS

1. INTRODUCTION

Progress in the chemistry of isocyanates, isothiocyanates, carbodiimides and ketene imines is reflected in numerous reviews and books. During recent years polyfunctional compounds containing heterocumulene and other reactive groups have become valuable reagents in organic synthesis. Among them, 1,1-dihaloalkyl heterocumulenes, $RCHal_2N{=}C{=}X$ (X = O, S, NR, CR_2), are in the first

rank In these compounds the reactivity of the heterocumulene and the halogen atoms in the α-position is enhanced due to their mutual interaction The synthetic possibilities of these compounds are extremely wide The ability of some 1,1-dihaloalkyl heterocumulenes to participate in anionotropic rearrangements involving halogen migration in the azaallylic triad is of particular interest



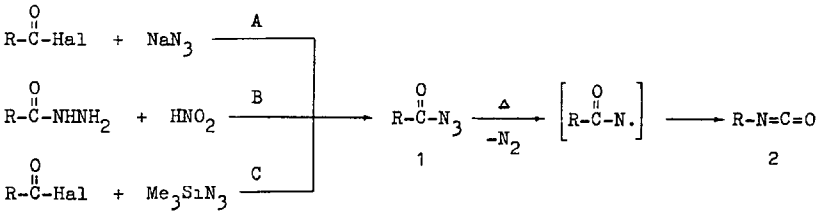
Hal = Cl, Br

The purpose of this Report is a presentation of available information on synthetic methods and chemical conversions of the compounds mentioned above Some reactions discussed here were considered in part, in the review[1] on the chemistry of 1-haloalkyl isocyanates published in 1980

2 METHODS OF SYNTHESIS

2 1 1,1-*Dihaloalkyl isocyanates*

2 1 1 *Curtius, Lossen and Hofmann reactions* The Curtius rearrangement is one of the most general methods for the synthesis of alkyl and aryl isocyanates including alkyl isocyanates with halogen atoms in the α-position [2] This reaction involves the thermal transformation of acyl azides **1** into isocyanates **2** via intermediate acyl nitrenes Acyl azides **1** may be obtained using two methods (i) the reaction of acyl halides with sodium azide (method A) or (ii) the reaction of acyl hydrazides with nitrous acid (method B) [3–13] The Curtius reaction may be also applied to the synthesis of diisocyanates including perfluoroalkylidene diisocyanates O=C=N(CF$_2$)$_n$N=C=O **3** [8] The disadvantage of the classical Curtius reaction is the necessity of working with highly dilute solutions because acyl azides are thermally unstable and explosive This disadvantage is avoided in the modification of the Curtius reaction in which the thermally stable trimethylsilyl azide is used instead of sodium azide (method C) [14,15] In this case the acyl azide is decomposed *in situ* during the mixing of the reagents This increases the safety of the process and allows the use of minimal amounts of solvents



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Recently, a method for the synthesis of perfluoroalkyl mono- and di-isocyanates was proposed which is a modification of the Lossen rearrangement [16] It involves the thermal transformation of bis-silyl derivatives of hydroxamic acids **4** at 250–300°C The derivatives **4** are obtained by the reaction of hydroxamic acids with hexamethyldisilazane (HMDSA)

Table 1. Isocyanates 2 obtained by the Curtius reaction

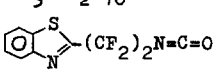
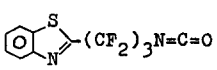
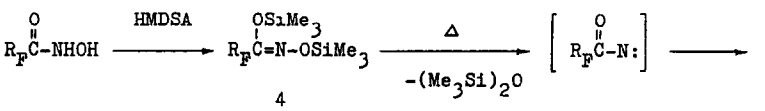
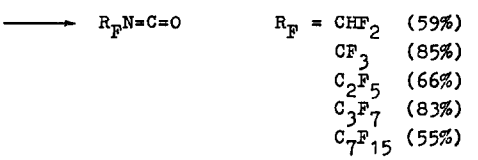
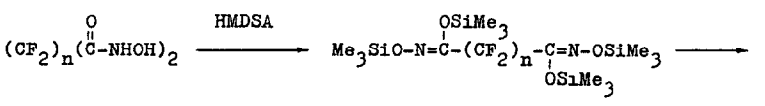
Compound	Method	B.p./torr	Yield[%]	Reference
$CCl_3N{=}C{=}O$	A	119-120°C/760	72	12
$CF_3N{=}C{=}O$	A	-35°C/760	44	6
	A	-36°C/760	26	5
	C	-32°C/760	75	14
$CBr_3N{=}C{=}O$	A	73-75°C/20	45	13
$BrCF_2CClFN{=}C{=}O$	A	89-91°C/760	12	10
$BrCF_2CBrFN{=}C{=}O$	A	107-110°C/760	26	10
$BrCF_2CF_2N{=}C{=}O$	A	50°C/760	43	10
$ClCF_2CF_2N{=}C{=}O$	A	31-31.5°C/760	29	10
$ClCF_2CClFN{=}C{=}O$	A	68-69°C/760	62	10
$CF_3CF_2N{=}C{=}O$	A	-10+ -5°C/760	20	10
$O{=}N(CF_2)_2N{=}C{=}O$	A	23°C/746	32	11
$CF_3(CF_2)_2N{=}C{=}O$	A	24-26°C/739	76	3, 4
	A	24.5°C/760	82	5
	A	27-29°C/760	84	7
$Cl{-}\overset{O}{\overset{\|}{C}}{-}(CF_2)_3N{=}C{=}O$	C	80-83°C/760	17	15
$CF_3(CF_2)_3N{=}C{=}O$	A	52-53°C/753	55	3
$CF_3(CF_2)_4N{=}C{=}O$	A	75-78°C/735	50	3
	C	77-79°C/760	79	15
$CF_3(CF_2)_6N{=}C{=}O$	A	119°C/740	82	3
	A	122-123°C/760	75	7
	C	118-120°C/760	82	15
$CF_3(CF_2)_7N{=}C{=}O$	A	140°C/740	-	3
$CF_3(CF_2)_8N{=}C{=}O$	A	160-161°C/743	-	3
$CF_3(CF_2)_9N{=}C{=}O$	A	180°C/740	-	3
$CF_3(CF_2)_{10}N{=}C{=}O$	A	200°C/740	-	3
	A	114-115°C/8	75	9
	A	128-130°C/15	68	9

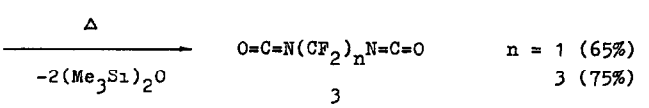
Table 2. Diisocyanates 3 obtained by the Curtius reaction

Compound	Method	B.p./torr	Yield[%]	Reference
$O{=}C{=}N(CF_2)_3N{=}C{=}O$	A	84-85°C/760	72	8
	B		37	8
	C	64-65°C/760	78	15
$O{=}C{=}N(CF_2)_4N{=}C{=}O$	A	105-106°C/760	78	8
	B		34	8
$O{=}C{=}N(CF_2)_8N{=}C{=}O$	A	105°C/220	32	8

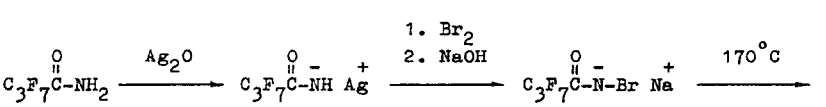


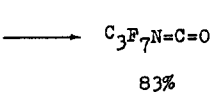




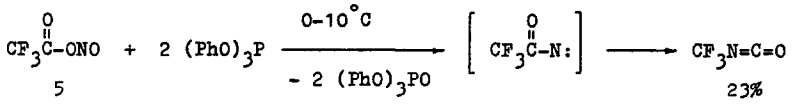


Perfluoroalkyl isocyanates have also been obtained by the Hofmann reaction from anhydrous salts of N-haloalkanamides [17-19]

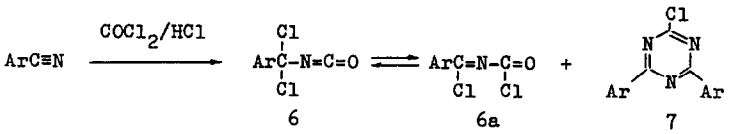


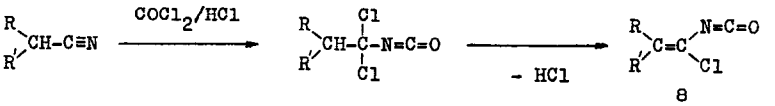


The reaction of trifluoroacetyl nitrite **5** with two moles of triphenyl phosphite may also proceed via a nitrene intermediate leading to trifluoromethyl isocyanate [20]

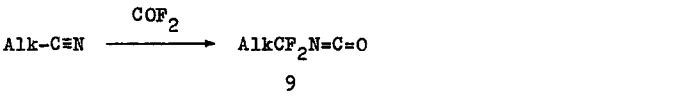


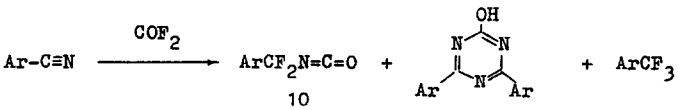
2 1 2 *Addition of phosgene and analogues to the* C≡N *bond* Aromatic nitriles react with phosgene in the presence of hydrogen chloride under forcing conditions (heating in autoclave at 100°C for 200 hours) giving substituted 1,3,5-triazines **7** Using the ratio ArC≡N $COCl_2$ HCl = 4 2 1 (Ar = Ph) phenyl dichloromethyl isocyanate **6** may be isolated in 15% yield it exists predominantly in the N-chlorocarbonylimine form **6a** [21,22] Phosgenation of aliphatic nitriles under similar conditions does not lead to 1,1-dichloroalkyl isocyanates because they eliminate hydrogen chloride giving 1-chloroalkenyl isocyanates **8** [22-24]





Fluorophosgene reacts with nitriles only in the presence of catalysts (HF, NaF, CsF, HgF_2) giving 1,1-difluoroalkyl isocyanates **9**, **10** In the case of aliphatic nitriles, prolonged heating up to 200–300°C in an autoclave is required [25-29] Aromatic nitriles react with fluorophosgene under milder conditions (50°C)[30] but the yields of isocyanates are low because substituted 1,3,5-triazines and aryl fluoromethanes are also produced





The simplest method for the synthesis of trichloromethyl isocyanate, which is used commercially, is the condensation of chlorocyanogen with phosgene [31,32] This reaction is performed under forcing conditions (300°C, autoclave) in the presence of activated charcoal as a catalyst Trichloromethyl isocyanate **11** which exists predominantly in the isomeric form N-chlorocarbonyliminophosgene **11a** is obtained in 71% yield, bis(dichloromethylidene)urea **12** is the second product of the reaction

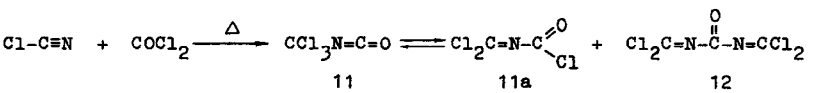
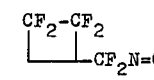
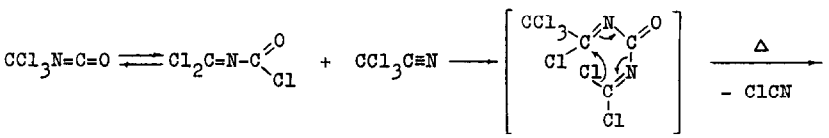


Table 3. 1,1-Difluoroalkyl isocyanates 9, 10

Compound	B.p./760 torr	Yield [%]	Reference
$MeCF_2N{=}C{=}O$	20-21 °C	25	25
	29 °C	45	26
$EtCF_2N{=}C{=}O$	73-77 °C	65	25
	58 °C	96	26
$n\text{-}PrCF_2N{=}C{=}O$	85-91 °C	55	25
$i\text{-}PrCF_2N{=}C{=}O$	69-74 °C	60	25
$ClCH_2CF_2N{=}C{=}O$	68-78 °C	50	25
$CCl_3CF_2N{=}C{=}O$	97-98 °C	80	25
$CF_3CF_2N{=}C{=}O$		18	29
	-8-0 °C	75	25
	136 °C	60	25
$PhCF_2N{=}C{=}O$	-	18	30
$m\text{-}MeC_6H_4CF_2N{=}C{=}O$	-	13	30
$p\text{-}MeC_6H_4CF_2N{=}C{=}O$	-	11	30
$p\text{-}CF_3C_6H_4CF_2N{=}C{=}O$	-	16	30

A preparatively convenient way for obtaining perchloroethyl isocyanate **14** is the interaction of trichloromethyl isocyanate with trichloroacetonitrile at 120°C in the presence of catalytic amount of iron(III) chloride [33] This reaction could be considered as an electrophilic addition of N-chlorocarbonyliminophosgene to the C≡N bond of trichloroacetonitrile The bis(alkylidene)urea **13** formed initially eliminates chlorocyanogen giving the final product



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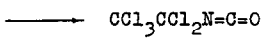
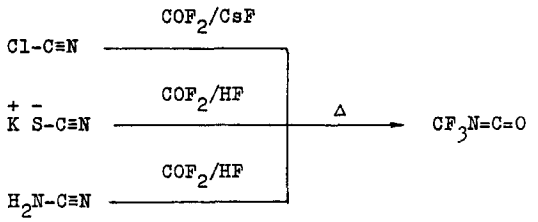
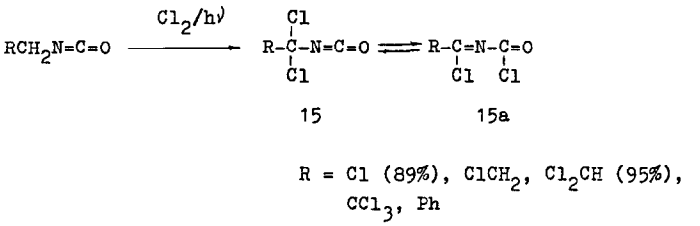


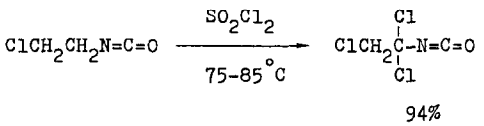
14 (82%)

Synthesis of trifluoromethyl isocyanate by the condensation of fluorophosgene with fluorocyanogen [34] chlorocyanogen, potassium thiocyanate[27] or cyanamide[26] under forcing conditions (100–300°C) in the presence of catalysts has been described

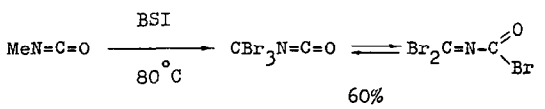


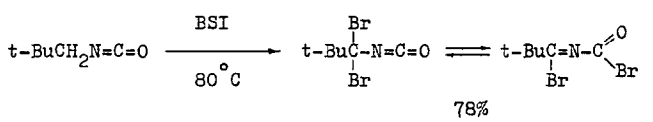
2 1 3 *Halogenation of alkyl, alkenyl, acyl isocyanates and carbamates* The chlorination of alkyl isocyanates is achieved by heating (80–120°C) and UV irradiation [32 35,36] Depending on the nature of a substituent in the starting isocyanates, products of the reaction may have one of two isomeric structures **15** or **15a**, or be present as a mixture of both isomers Sulfuryl chloride may be used as a chlorinating agent, instead of chlorine [37]





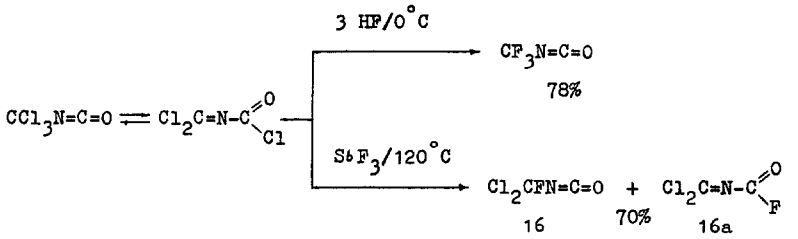
N-Bromosuccinimide (BSI) is applied for the bromination of alkyl isocyanates [38] Products of the reaction, 1,1-dibromoalkyl isocyanates, in contrast to their fluorine and chlorine analogues, are not stable and decompose gradually under storage Bromotropic conversions are characteristic of these compounds

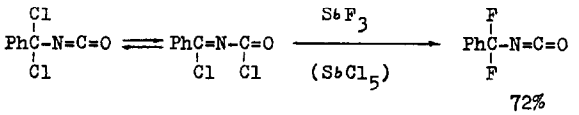




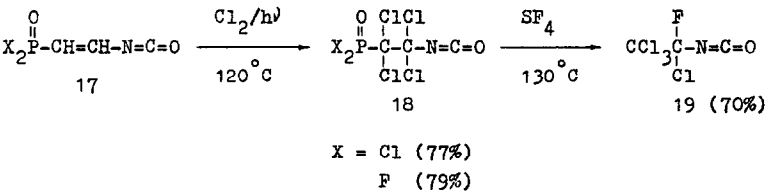
A convenient method for the preparation of 1,1-difluoroalkyl isocyanates is fluorination of the corresponding chloro- compounds with hydrogen fluoride[39,40] or antimony(III) fluoride [41 42] After fluorination of trichloromethyl isocyanate with antimony(III) fluoride, a mixture of the isomers—

dichloro(fluoro)methyl isocyanate **16** and N-(dichloromethylidene)carbamoyl fluoride **16a**—was isolated in the ratio (1 14) [41]

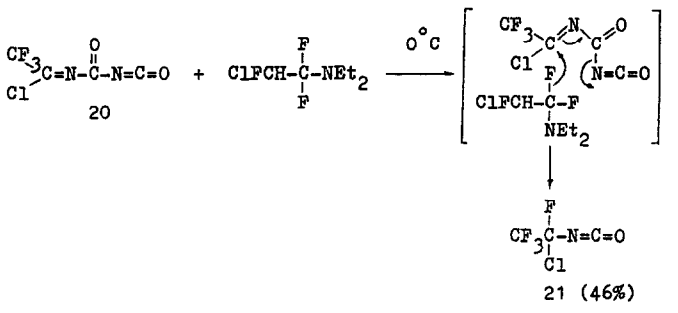




2-Phosphonyl vinyl isocyanates **17** are chlorinated by heating and UV irradiation giving isocyanates **18** Fluorination of the compounds **18** with sulfur tetrafluoride is accompanied by the cleavage of the C–P bond yielding the isocyanate **19** [43]

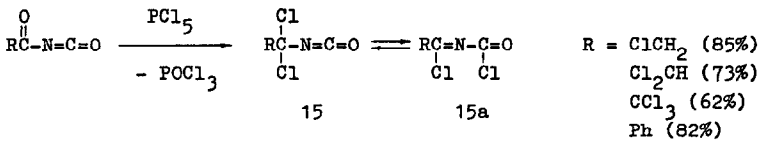


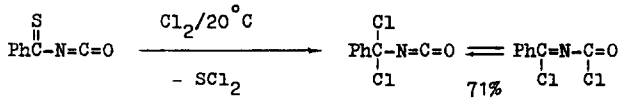
N-(Alkylidene)carbamoyl isocyanates **20** are very easily fluorinated with an α-fluorinated tertiary amine giving the isocyanate **21** An interaction probably begins from a nucleophilic attack of an amine α-fluorine atom on the electrophilic carbon in the azomethine group of the compound **20** when the N=C=O moiety shows pseudo-halogenic properties [44]



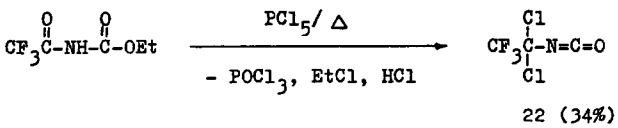
A preparative method for the synthesis of 1,1-dichloroalkyl isocyanates **15** is the reaction of acyl isocyanates with phosphorus pentachloride in boiling chlorobenzene [45,46] Phenyldichloromethyl

isocyanate may be obtained under mild conditions by the chlorination of thiobenzoyl isocyanate with elementary chlorine [47]

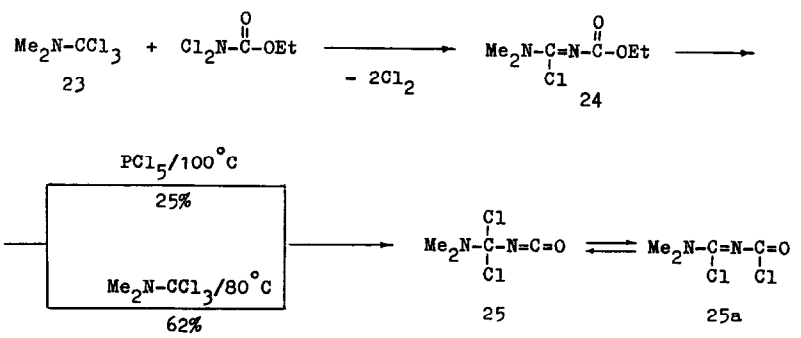


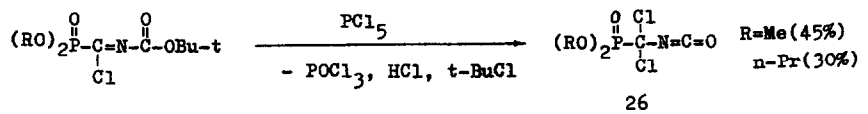


One method for the generation of isocyanates is the reaction of N-substituted carbamates with phosphorus pentachloride [2] In several cases this method may be used for the synthesis of 1,1-dichloroalkyl isocyanates For example, interaction of N-trifluoroacetylethyl carbamate with phosphorus pentachloride at 175°C gave the isocyanate **22** [48]

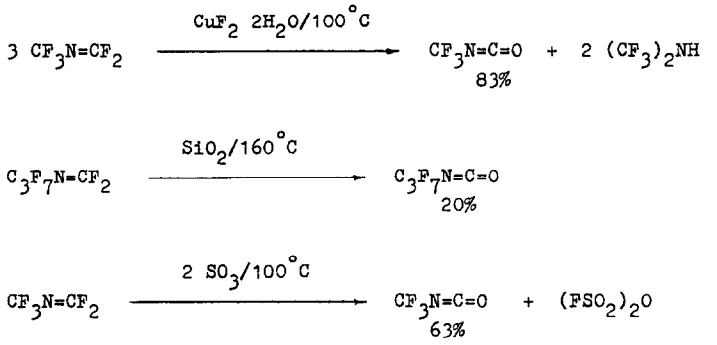


N-(Alkylidene)carbamate **24**—the condensation product from trichloromethylamine **23** and N,N-dichlorocarbamate—treated with PCl_5 or **23**, gives dialkylaminodichloromethyl isocyanate **25** which exists in equilibrium with the iminocarbonyl chloride form **25a** [49] Similarly, phosphorylated dichloromethyl isocyanate **26** may be obtained [50]

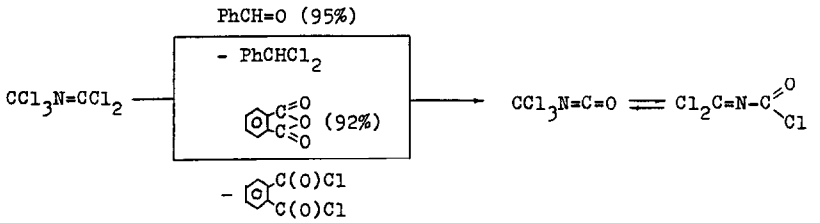




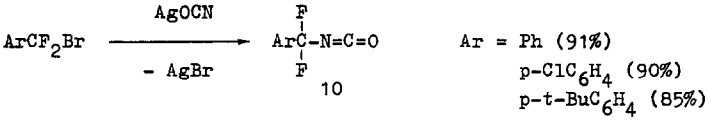
2 1 4 *Hydrolysis of perhalo-2-azaalkenes* By careful hydrolysis of perfluoro-2-azapropene with copper(II) fluoride hydrate, trifluoromethyl isocyanate may be obtained in high yield [51,52] The disadvantage of this method is the use of a large amount of azapropene as an acceptor for hydrogen fluoride Perfluoroalkyl isocyanates are also obtained by treatment of perfluoro-2-azaalkenes with silicon dioxide[51] or sulfur trioxide[53] under forcing conditions



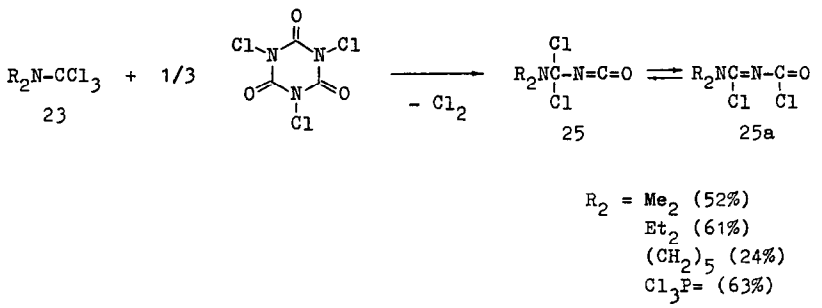
Trichloromethyl isocyanate is obtained in high yield by treatment of perchloro-2-azapropene with benzaldehyde or phthalic anhydride at 120–150°C in the presence of Lewis acid catalysts [54]



2 1 5 *Exchange reactions* A number of methods exist for introducing the isocyanate group by exchange reactions Thus treatment of aryl bromodifluoromethanes with silver cyanate gave aryl difluoromethyl isocyanates **10** [55] The reaction proceeds in methylene chloride at 20°C

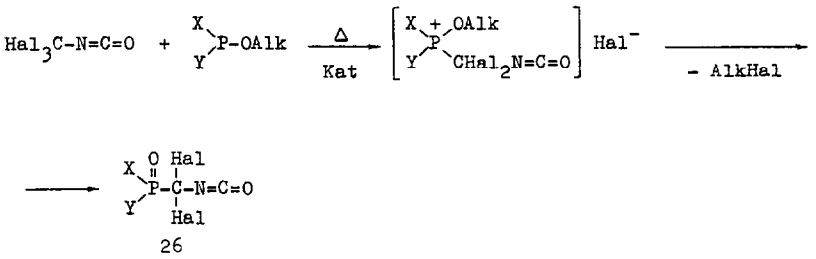


One of the mobile chlorine atoms in trichloromethylamines **23** can be replaced by the isocyanate group upon treatment with N,N′,N″-trichloroisocyanurate [56–58] The reaction proceeds in dichloromethane at 40–80°C Instead of trichloroisocyanurate, silver cyanate may be used [59]



$R_2 = Me_2$ (52%)
Et_2 (61%)
$(CH_2)_5$ (24%)
$Cl_3P=$ (63%)

2 1 6 *Arbuzov reaction* To obtain phosphonyl dihalomethyl isocyanates **26**, treatment of trichloromethyl and tribromomethyl isocyanates with phosphites or halophosphite is convenient, this reaction proceeds via an Arbuzov rearrangement [12,13,50,60] The reaction is performed at 80–120°C in the presence of catalytic amount of iron(III) chloride

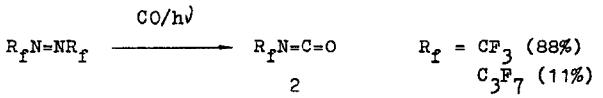


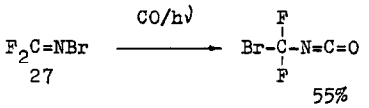
2 1 7 *Special methods of synthesis of* 1,1-*difluoroalkyl isocyanates* Carbonylation of some nitrogen-containing compounds is used to obtain 1,1-difluoroalkyl isocyanates Perfluoroazoalkanes react with carbon monoxide under forcing conditions (325°C, 650 atm) giving perfluoroalkyl isocyanates **2** [61] N-Bromodifluoromethaneimine **27** reacts with carbon monoxide under mild conditions

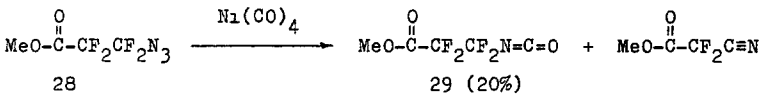
Table 4. Phosphonyl dihalomethyl isocyanates 26

Hal	X	Y	B.p./torr	Yield[%]	Reference
Cl	Cl	Cl	80-82°C/13	71	50
Cl	F	F	117-119°C/760	50	50
Cl	Cl	OEt	53-66°C/0.06	20	50
Cl	OEt	OEt	61-63°C/0.05	20	12
Br	Cl	Cl	125-127°C/20	58	13
Br	F	F	62-68°C/20	27	13
Cl	Cl	OCH_2CH_2Cl	70-72°C/0.05	37	60

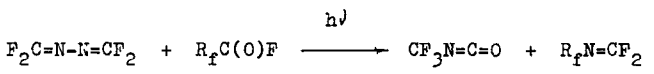
(20°C, UV-irradiation) yielding bromodifluoromethyl isocyanate [62] Treatment of the azide **28** with nickel tetracarbonyl at 25°C in acetonitrile yields the isocyanate **29** [63]

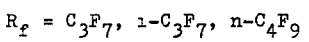




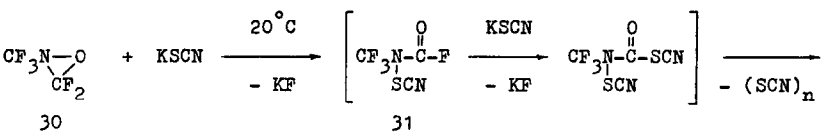


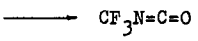
Photolysis of a mixture of perfluoro-2,3-diazabuta-1,3-diene and perfluoroacyl fluorides gives trifluoromethyl isocyanate (yield 20–36%) and N-perfluoroalkyl iminoyl difluorides [64]



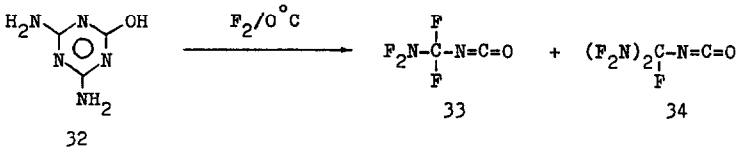


An original method for synthesis of trifluoromethyl isocyanate involves the treatment of oxaziridine **30** with mercaptans or alkali metal thiocyanate [65,66] In the case of the reaction with potassium thiocyanate, the nucleophile is supposed to attack the oxaziridine nitrogen initially The resulting adduct **31** is then attacked with the excess of nucleophile giving trifluoromethyl isocyanate (90%)



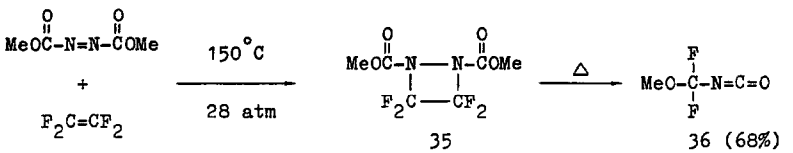


According to patent data,[67] the isocyanates **33** and **34** were prepared by fluorination of ammeline **32** in the presence of sodium fluoride as HF acceptor Isocyanates **33**, **34** may explode under percussion

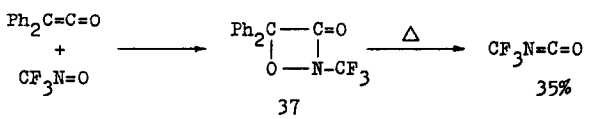


32 33 34

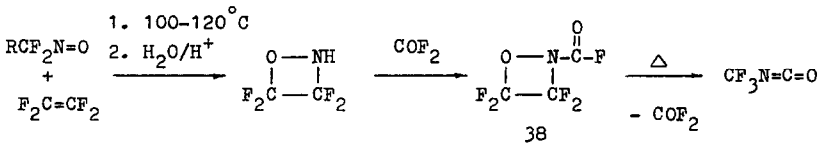
1,1-Difluoroalkyl isocyanates are obtained at the thermolysis of some nitrogen heterocycles Thus, diazetidine **35**—product of cycloaddition of tetrafluoroethylene to dimethyl azodicarboxylate—is cleaved at 600°C *in vacuo* giving methoxydifluoromethyl isocyanate **36** [68,69] Oxazetidine **37** obtained from diphenyl ketene and trifluoronitrosomethane yields trifluoromethyl isocyanate after heating to 300°C [70] Trifluoromethyl isocyanate may also be obtained by pyrolysis of oxazetidine **38** at 400°C [71]



35 36 (68%)

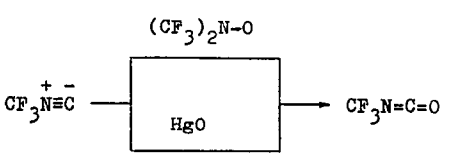


37 35%



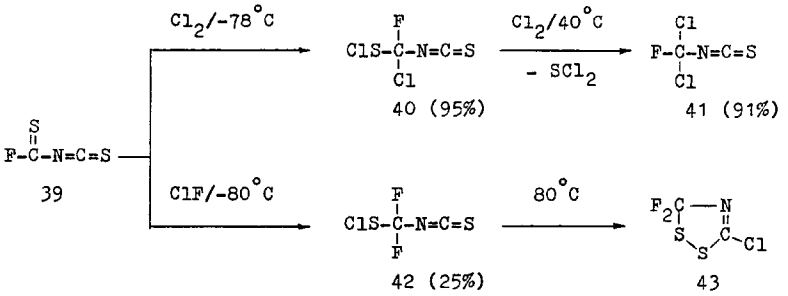
38

Trifluoromethyl isocyanate is obtained in low yield by treatment of trifluoromethyl isocyanide with bis(trifluoromethyl)aminoxide[72] or mercury(II) oxide[73] under mild conditions (20°C)

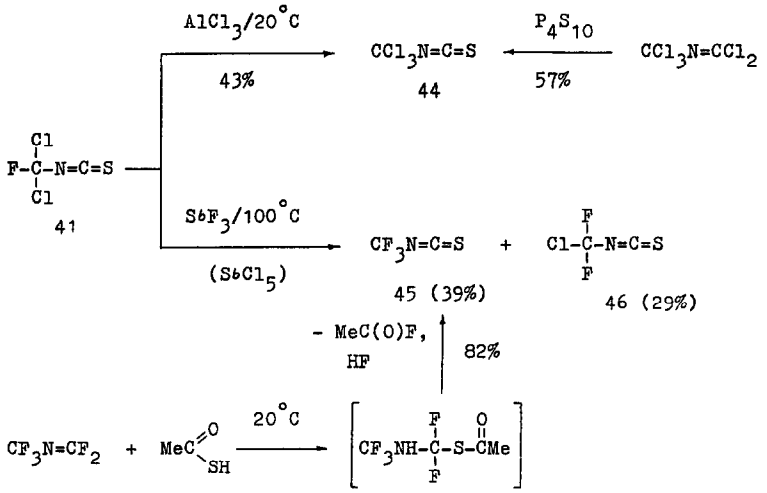


2 2 1,1-*Dihaloalkyl isothiocyanates*

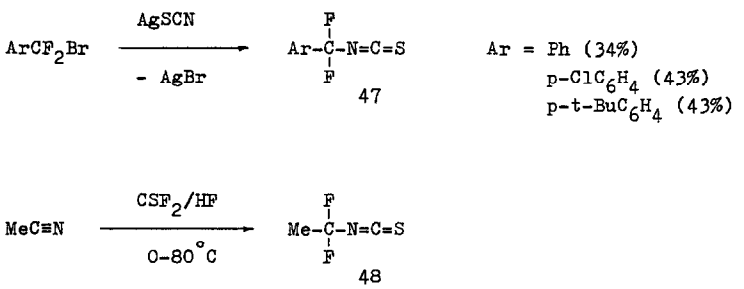
1,1-Dihaloalkyl isothiocyanates **40, 41** are prepared in high yields by chlorination of fluorothiocarbonyl isothiocyanate **39** under mild conditions [74,75] Isothiocyanate **39** adds chlorofluoride giving the isothiocyanate **42** which then yields the 1,2,4-dithiazole **43** at heating [76,77]



The isothiocyanate **41** may be converted into other 1,1-dihaloalkyl isothiocyanates **44–46** by treatment with aluminium chloride or antimonium(III) fluoride [74] The synthesis of the isothiocyanate **44** involves the reaction of perchloro-2-azapropene with phosphorus(V) sulfide at 150°C [78] To obtain trifluoromethyl isothiocyanate **45**, the reaction of perfluoro-2-azapropene with thioacetic acid may be used [79] The interaction is supposed to proceed via an unstable addition product which eliminates acetyl fluoride and hydrogen fluoride giving the final product **45**



Aryl difluoromethyl isothiocyanates **47** are obtained by an exchange reaction of aryl difluorobromomethanes with silver thiocyanate at 20°C [55] According to patent data,[28] 1,1-difluoroethyl isothiocyanate **48** may be obtained by treatment of acetonitrile with fluorothiophosgene catalysed with hydrogen fluoride



Alkyl thiocyanates RS—C≡N are known to isomerize into more thermodynamically stable isothiocyanates RN=C=S For 1,1-dichloroalkyl thiocyanates $RCCl_2SCN$, similar conversions are not observed [80]

2 3 1,1-*Dihaloalkyl carbodiimides*

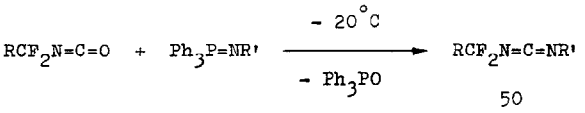
A general method for the synthesis of carbodiimides **49** containing a trifluoromethyl substituent is a reaction of perfluoro-2-azapropene with primary amines [81,82] The reaction is performed under mild conditions (−10°C) in the presence of potassium fluoride as the HF acceptor If in this reaction organic bases, like trimethylamine, are used, instead of potassium fluoride, then the carbodiimides **49** cannot be prepared because they give di- or tri-meric products [83]

$$CF_3N{=}CF_2 + RNH_2 \xrightarrow[-\ KHF_2]{KF} CF_3N{=}C{=}NR \quad \mathbf{49}$$

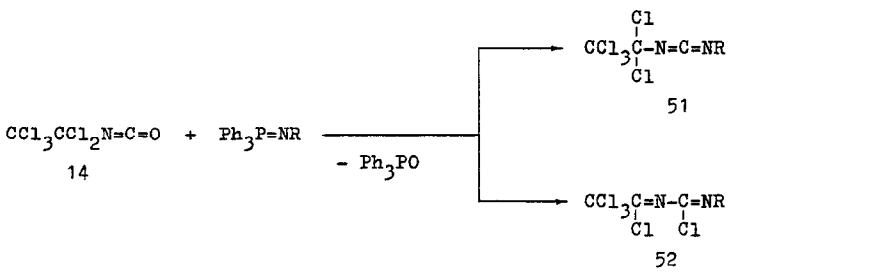
Table 5. N-Alkyl(aryl)-N′-trifluoromethyl carbodiimides 49

R	B.p./torr	Yield[%]	Reference
Et	75°C/90	46	81
$H_2C{=}CHCH_2$	111°C/760	72	81
t-Bu	46°C/70	58	81
n-C_6H_{11}	61°C/9	69	81
Ph	45-47°C/4	80	81
p-$MeOC_6H_4$	81°C/2	69	81
$(MeO)_2P(O)C(Me)Et$	89°C/2	58	82
$(EtO)_2P(O)C(Me)Et$	92-94°C/2	60	82
$(EtO)_2P(O)C(Me)n\text{-}Pr$	103-104°C/2	40	82
$(EtO)_2P(O)C(Me)n\text{-}Bu$	111-113°C/2	50	82
$(i\text{-}BuO)_2P(O)C(Me)Et$	130-132°C/2	72	82

To obtain 1,1-difluoroalkyl carbodiimides **50** the Staudinger reaction between 1,1-difluroalkyl isocyanates and phosphine imines may be used [42,84,85]



When perchloroethyl isocyanate **14** is used in the Staudinger reaction, 1,1-dichloroalkyl carbodiimides **51** or their isomers—dichlorodiazadienes **52** are formed [85,86] Carbodiimides **51** are obtained only with sterically hindered substituents R at the nitrogen atom, for example, when R = *t*–Bu With less steric hindrance (R = i–Pr, Ph) the reaction products are diazadienes **52**, when R = 2,4,6–$Me_3C_6H_2$, a mixture of the isomers **51** and **52** is obtained (1 7)

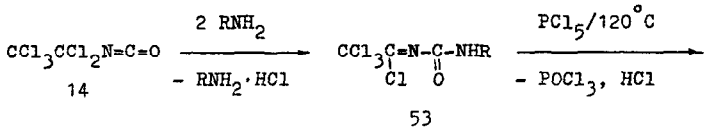


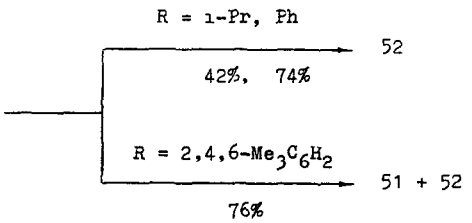
A more preparatively convenient method for the synthesis of dichlorodiazadienes **52** involves treatment of N-(alkylidene)ureas **53** with phosphorus pentachloride Treatment of N-mesityl (alkylidene)urea (**53**, R = 2,4,6–$Me_3C_6H_2$) with phosphorus pentachloride gives rise to a mixture

Table 6. Carbodiimides 50 obtained by Staudinger reaction

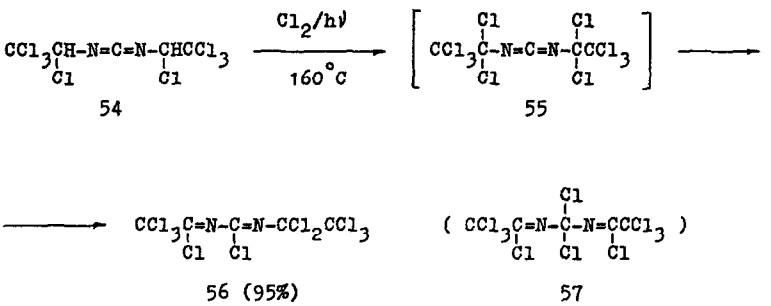
R	R'	B.p./torr	Yield[%]	Reference
CF_3CF_2	Ph	72°C/7	37	84
CCl_3	i-Pr	87°C/10	42	85
CCl_3	Ph	65°C/0.04	43	85
CCl_3	2,4,6-$Me_3C_6H_2$	98°C/0.07	63	85
Ph	i-Pr	74-76°C/1	36	42
Ph	2,4,6-$Me_3C_6H_2$	126-128°C/0.02	75	42

of isomers **51**+**52** The ureas **53** are obtained by the reaction of perchloroethyl isocyanate **14** with two moles of a primary amine at −20°C in ether [85,86]

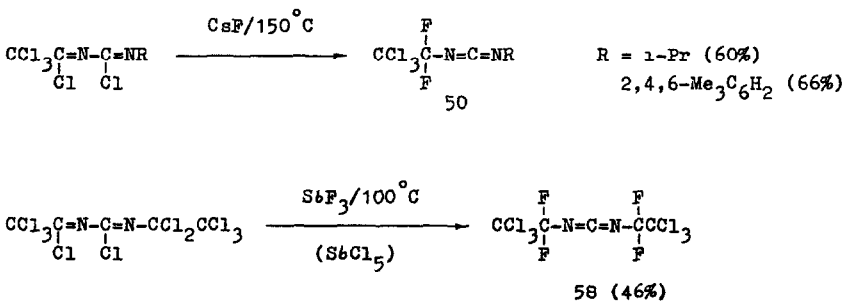




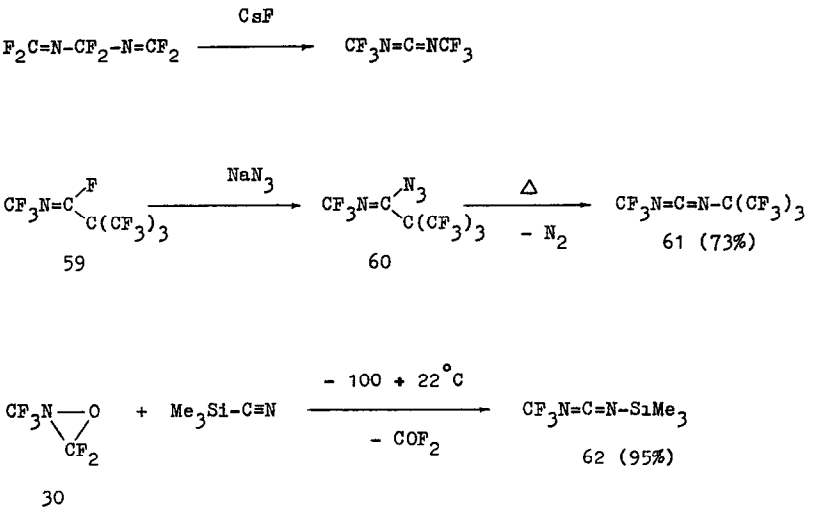
The chlorination of bis(tetrachloroethyl) carbodiimide **54** gives rise to perchlorodiazadiene **56**, instead of expected bis(perchloroethyl) carbodiimide **55** [86,87] Evidently, formation of diazadiene **56** is a result of a chlorotropic shift in the C—N=C triad of the intermediate carbodiimide **55** Of the two possible chlorotropic isomers **56** and **57**, clear evidence (^{35}Cl NQR and ^{13}C NMR) is given in support of the structure **56**



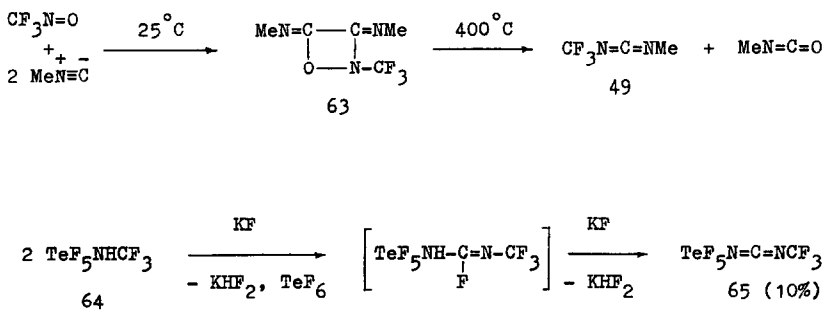
1,1-Difluoroalkyl carbodiimides **50** and **58** are obtained by fluorination of respective chlorine compounds with caesium fluoride or antimony(III) fluoride in the presence of catalytic amount of antimony(V) chloride [85-87]



Several special methods for the synthesis of perfluoroalkyl carbodiimides are noted In the presence of caesium fluoride, perfluoro-2,4-diazapenta-1,4-diene isomerizes rapidly at room temperature giving bis(trifluoromethyl) carbodiimide [88] Imidoyl azide **60** prepared from perfluoroazomethine **59** on heating to 300°C undergoes a Curtius-like rearrangement giving the perfluorocarbodiimide **61** [89] By treatment of perfluorooxaziridine **30** with trimethylsilyl cyanide the N-silyl carbodiimide **62** is obtained [90]

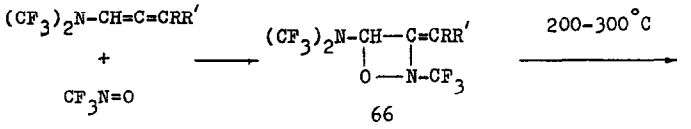


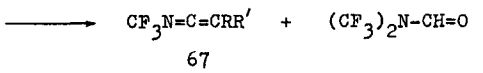
Trifluoronitrosomethane with methyl isocyanide gives the cyclic adduct **63** which is cleaved by heating *in vacuo* giving N-trifluoromethyl carbodiimide **49** and methyl isocyanate [70] The carbodiimide **65** with a tellurium–nitrogen bond is obtained by condensation of the amine **64** at −80°C in the presence of potassium fluoride as HF acceptor [91]



2 4 *Other* 1,1-*dihaloalkyl heterocumulenes*

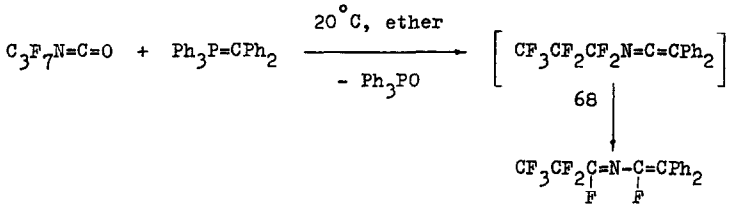
N-Trifluoromethyl keteneimines **67** are obtained in high yield by pyrolysis of oxazetidines **66** which are produced by condensation of trifluoronitrosomethane with allenes [92]





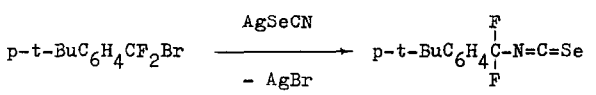
67, R=R′=H (100%)
R = H, R′ = $(CF_3)_2N$ (98%)
R = R′ = $(CF_3)_2N$ (90%)

By treatment of perfluoropropyl isocyanate with diphenylmethylene(triphenyl)phosphorane the keteneimine **68** is formed which isomerizes to the perfluoroazadiene **69** with migration of a mobile α-fluorine atom in the C—N=C triad even at ambient temperature [93]



69 (92%)

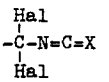
1,1-Difluoroalkyl isoselenocyanate **70** is obtained by the exchange reaction of aryl bromodifluoromethane at 20°C in methylene chloride [55]



70 (39%)

3 PROPERTIES

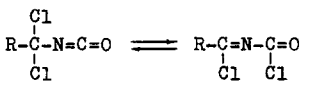
A peculiarity of isocyanates, carbodiimides and other heterocumulenes with two halogen atoms in the α-position of their alkyl substituents, is their highly electrophilic character and higher reactivity compared with usual alkyl(aryl) heterocumulenes In molecules of these compounds two electrophilic centres exist



As a rule, reactions of 1,1-dihaloalkyl heterocumulenes with nucleophilic reagents proceed with participation of both heterocumulene group and α-C-atoms Differences in reactivity of these two groups may be differentiated by a careful choice of nucleophilic reagent and conditions

3 1 *Anionotropic conversions*

An important property of 1,1-dihaloalkyl heterocumulenes is their ability to undergo anionotropic conversions These conversions are most thoroughly investigated for 1-chloroalkyl isocyanates [1] The position of equilibrium A ⇄ B depends on the nature of a substituent R and may be completely shifted towards one of the two forms For example, the heterocumulene structure A exists when R = CCl_3, CF_3 but the equilibrium is completely shifted towards the iminocarbonyl chloride form B when R = Ar

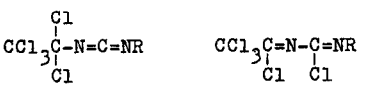


A B

The iminocarbonyl chloride form B is preferred with increasing number of chlorine atoms at the α-carbon atom Thus, chloromethyl isocyanate has the heterocumulene structure $ClCH_2N{=}C{=}O$, dichloromethyl isocyanate is a mixture of isomers $Cl_2CH{-}N{=}C{=}O \rightleftarrows ClCH{=}N{-}C(O)Cl$, and trichloromethyl isocyanate exists predominantly as N-chlorocarbonylimonophosgene $Cl_2C{=}N{-}C(O)Cl$

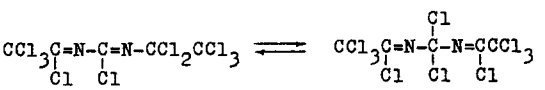
For 1,1-difluoroalkyl isocyanates, no conversion into the corresponding iminocarbonyl fluorides is observed As for the corresponding bromo-compounds, they are unstable and may have either isocyanate or the iminocarbonyl bromide structure [13 38]

As was mentioned above (see 2 3), some 1,1-dichloroalkyl carbodiimides have a heterocumulene structure C only when sterically hindered substituents R are located at the nitrogen atom In other cases an isomeric diazadiene structure D is preferred No conversion between these forms is observed



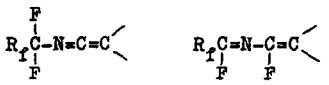
C D

Recently[94] a reversible chlorotropic isomerization of perchloro-3,5-diazahepta-2,4-diene **56** into perchloro-3,5-diazahepta-2,5-diene **57** was observed by rapid cooling of a molten compound **56** with liquid nitrogen and subsequent crystallization of glassy product at ambient temperature The isomer **57** is stable at liquid nitrogen temperature but converts completely into the thermodynamically more stable compound **56** at ambient temperature during several days



56 57

As was mentioned above (see 2 4), N-(1,1-difluoroalkyl) keteneimines described in literature may exist either in heterocumulene E or the azadiene G form

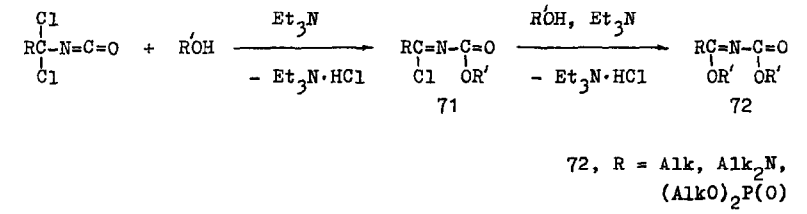


E G

All known 1,1-dihaloalkyl isothiocyanates $RCHal_2N{=}C{=}S$ exist in heterocumulene form exclusively

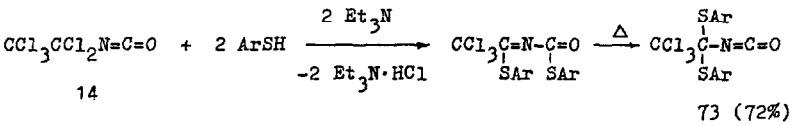
3 2 *Reactions with protic nucleophilic agents*

3 2 1 *Reactions with alcohols, phenols, thiophenols* 1,1-Dichloroalkyl isocyanates react with one mole of alcohol or phenol under mild conditions (0°C) in the presence of an organic base producing N-alkylidenecarbamates **71** which convert into the carbamates **72** under the effect of excess alcohol [12,43,50 56,60,95,96] The reaction of perchloroethyl isocyanate **14** with two moles of *p*-chlorothiophenol proceeds similarly However the thiocarbamate is unstable thermodynamically and rearranges into 1',1-di(arylthio)alkyl isocyanate **73** by heating to 130°C [97] In contrast with 1,1-dichloroalkyl isocyanates, the reaction of perfluoroalkyl isocyanates with alcohols (0–20°C) involves only the N=C=O group leading to the relatively stable carbamates **74** The latter are cleaved by heating with excess alcohol giving perfluorocarboxylates **75** and carbamates **76** [5 8,98] More stable addition products, the thiocarbamates **77**, are formed in reactions of perfluoroalkyl isothiocyanates **45**, with alcohols [79]



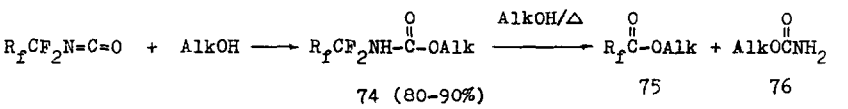
71 72

72, R = Alk, Alk_2N, $(AlkO)_2P(O)$

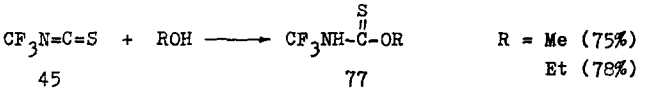


14 73 (72%)

Ar = p-ClC_6H_4



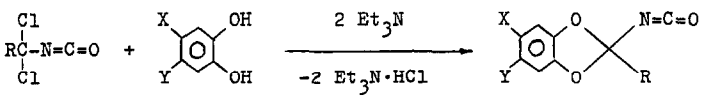
74 (80–90%) 75 76



45 77 R = Me (75%), Et (78%)

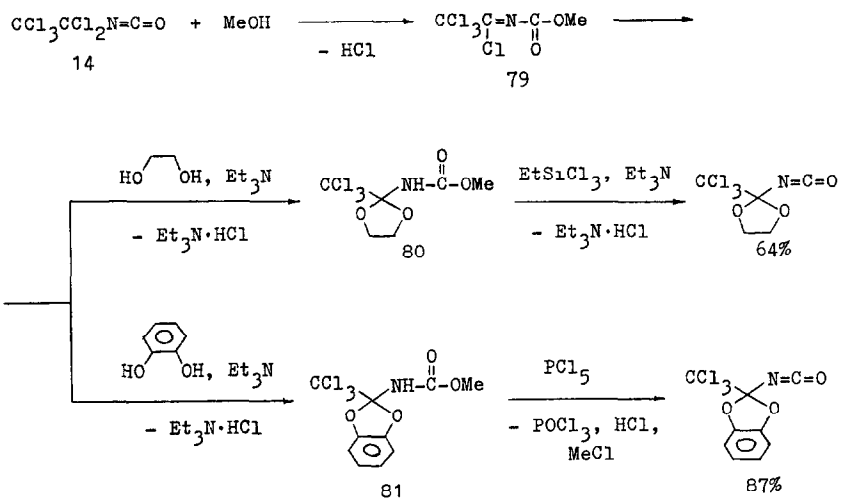
The behaviour of 1,1-dichloroalkyl isocyanates containing an electron withdrawing substituent R (like CCl_3, CF_3) in reactions with catechols is unusual The reaction proceeds under mild

conditions (0–20°C) in the presence of HCl acceptor, the products are the isocyanato-1,3-dioxolanes **78** [99] Application of this reaction is restricted to catechol derivatives because aliphatic 1,2-diols in



78

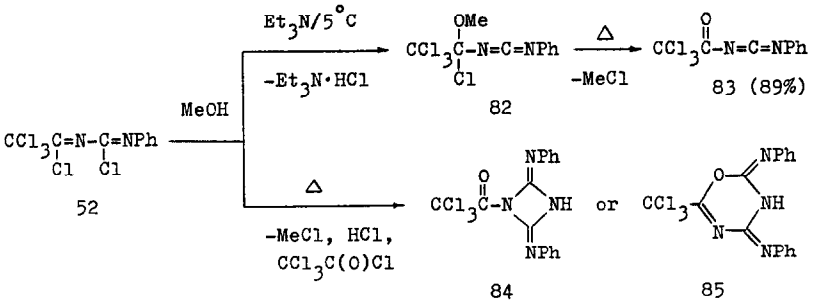
these conditions give polycondensation products Wider scope is possible for a modified method[100] which consists of preliminary addition of a methanol molecule to the isocyanate group of compound **14** The carbamate **79**, with ethylene glycol or catechol in the presence of triethylamine, gives the dioxolanylcarbamates **80** and **81**, respectively, which after heating with ethyl trichlorosilane in benzene or with phosphorus pentachloride in toluene gave isocyanato-1,3-dioxolanes in good yields



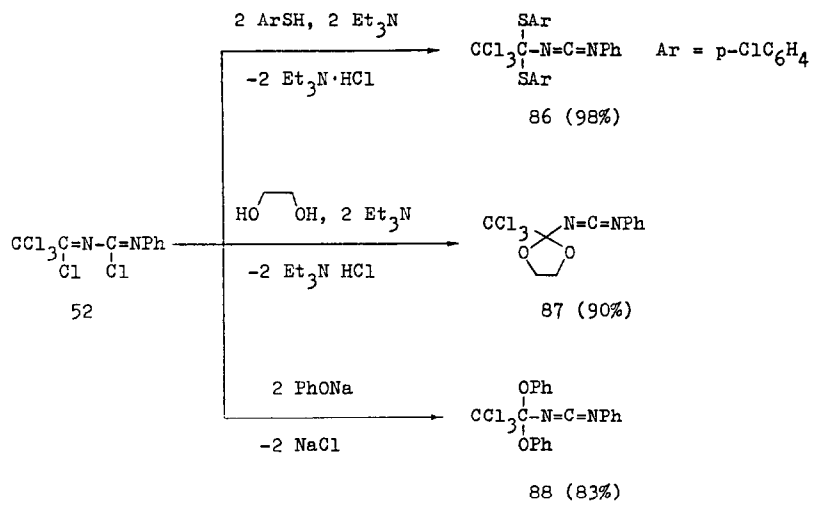
As was already mentioned (see 2 3), for 1,1-dichloroalkyl carbodiimides, the isomeric form of dichlorodiazadienes is preferred Interaction of the latter with some protic nucleophiles gives rise to carbodiimides Thus, dichlorodiazadiene **52** treated with one mole of methanol in the presence of triethylamine gives primarily methoxychlorocarbodiimide **82**, which eliminates methyl chloride at heating to 90°C giving acyl carbodiimide **83** However, if the reaction of diazadiene **52** with methanol is performed in the absence of HCl acceptor then no acyl carbodiimide **83** is obtained and the final product is a cyclic compound **84** or **85** [101]

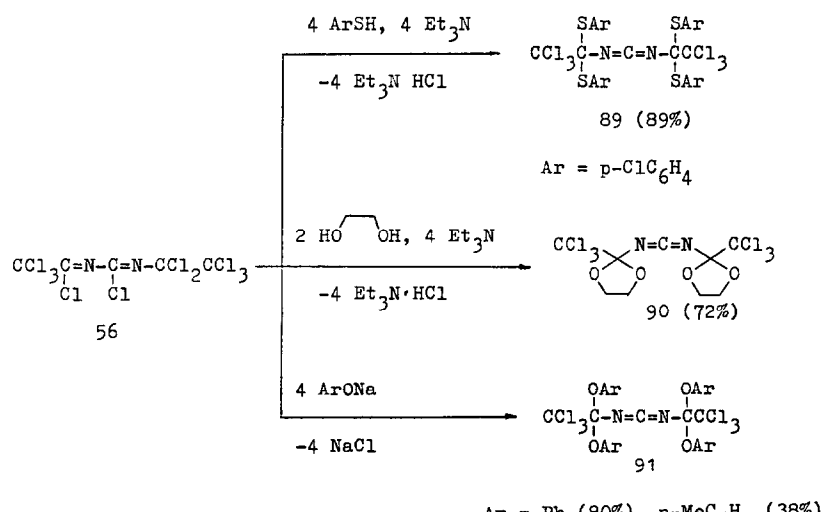
Table 7. Isocyanato-1,3-dioxolanes 78[99]

R	X	Y	Yield[%]
CCl_3	H	H	46
CF_3	H	H	71
CF_3	Cl	H	58
CF_3	Cl	Cl	42

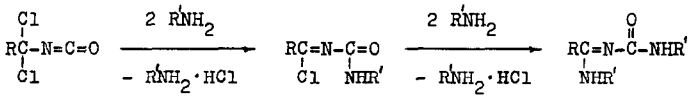


Treatment of diazadienes **52** and **56** with thiophenols or ethylene glycol in the presence of HCl acceptor, as well as with sodium phenolates, yields 1,1-disubstituted carbodiimides **86–88** and **89–91**, respectively [86,87,101]



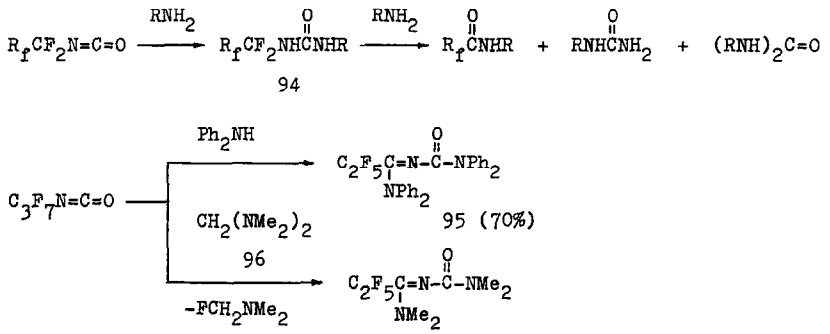


3 2 2 *Reactions with amines* The reaction of 1,1-dichloroalkyl isocyanates with primary amines gave alkylideneureas **92** and **93** [47,68,80,102] Similar products are obtained with N-silyl amines [103]

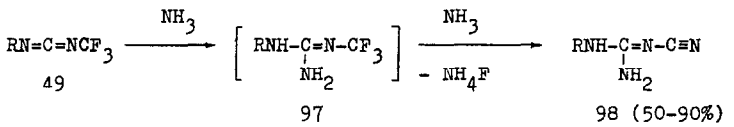


R = Alk, Ar, Alk_2N
R′ = Alk, Ar

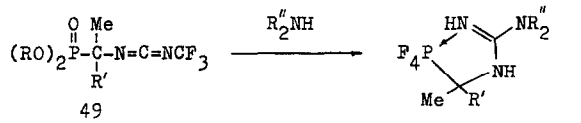
Perfluoroalkyl isocyanates treated with one mole of primary amine at 0°C produce unstable ureas **94** which are cleaved with excess amine giving a mixture of products [104] Reaction of perfluoroalkyl isocyanates with secondary amines involves both electrophilic centres and gives rise to alkylideneureas **95** [104] Similar products are obtained if methylene-bis-dialkylamines **96** are used [105]



Trifluoromethyl carbodiimides **49** react with ammonia exothermically giving cyanoguanidines **98** via the intermediate adducts **97** [106,107] Phosphorus-containing carbodiimides **49** react with secondary amines, the phosphorus coordination number being changed [108,109] The last reaction is unusual because the formation of hexacoordinated phosphorus compounds **99** is assumed from respective tetracoordinated phosphorus compounds

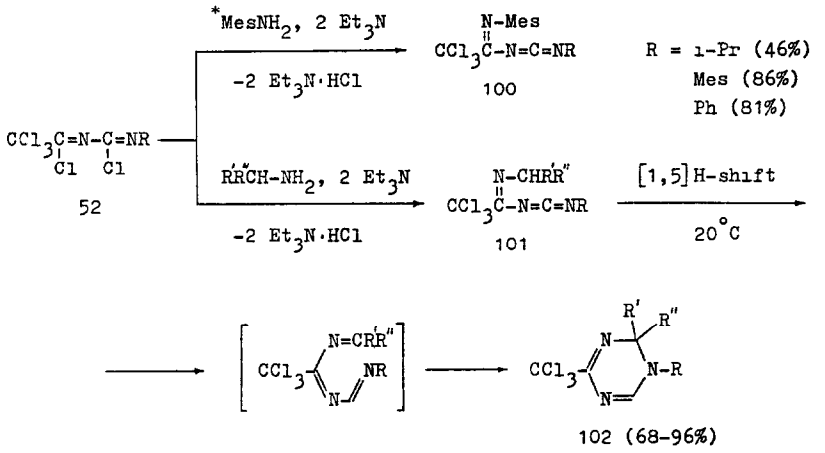


R = Alk, Ar, $(AlkO)_2P(O)C(Me)Alk$



R, R′, R″ = Alk

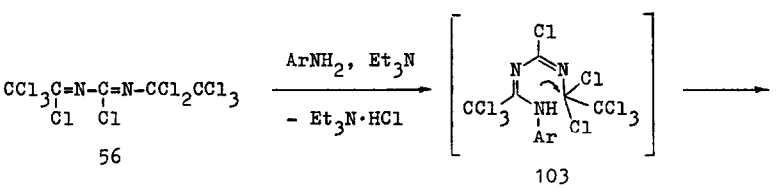
Dichlorodiazadienes **52** treated with equimolar quantity of mesidine in the presence of HCl acceptor (0°C, ether) are converted into imidoyl carbodiimides **100** [101] One should note that the application of this reaction is restricted to the use of sterically hindered aromatic amines because N-aryl imidoyl heterocumulenes without substituents in *ortho*-positions of the benzene ring are unstable and undergo easy conversion into cyclic products [110,111] Treatment of dichlorodiazadienes **52** with primary aliphatic amines also gives rise to imidoyl carbodiimides **101** However, in contrast with the carbodiimides **100**, the compounds **101** are unstable and after 30–50 minutes give substituted 1,2-dihydro-1,3,5-triazines **102** [112,113] The rearrangement of imidoyl carbodiimides **101** into triazines **102** is a 6π-electrocyclic reaction

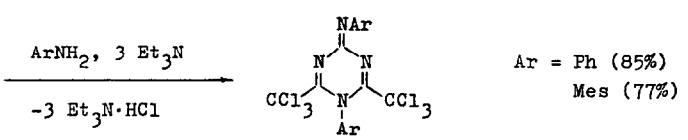


R = Ar
RR'CH = i-Pr, $PhCH_2$, c-C_6H_{11}

*Mes = 2,4,6-$Me_3C_6H_2$

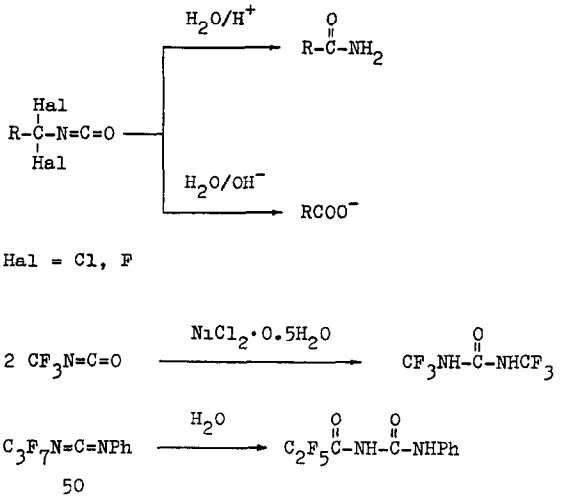
Perchlorodiazadiene **56**, the chlorotropic isomer of bis(perchloroethyl)carbodiimide, reacts with primary aromatic amines in the presence of a base under mild conditions (0–20°C, ether) yielding substituted 4-arylimino-1,3,5-triazines(1H) **104** [114] This reaction seems to be connected with intramolecular nucleophilic substitution in the primarily formed adduct **103**



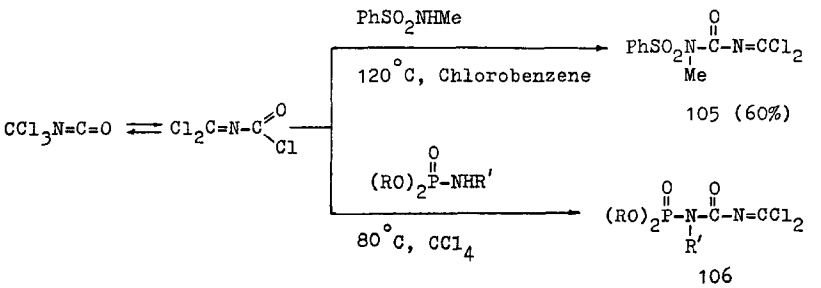


104

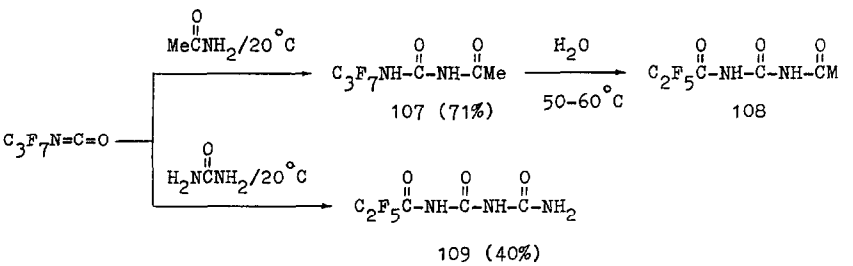
3 2 3 *Hydrolysis* Hydrolysis of 1,1-dihaloalkyl isocyanates, depending on its conditions (acid or alkaline medium), gives rise to carboxylic acids, their salts or amides [3-5,14,18] A careful hydrolysis of trifluoromethyl isocyanate with the use of hydrated salts produces bis(trifluoromethyl)urea [14] Hydrolysis of perfluoroalkyl carbodiimide **50** leads to N-phenyl-N′-perfluoropropionylurea [84]



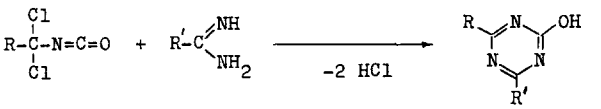
3 2 4 *Reactions with other protic nucleophiles* Trichloromethyl isocyanate, which exists predominantly in the iminocarbonyl chloride form, reacts with N-monosubstituted amides of benzenesulfonic acid and dialkyl phosphoric acid in boiling organic solvents, giving N-(dichloromethylidene)ureas **105** and **106**, respectively [115]



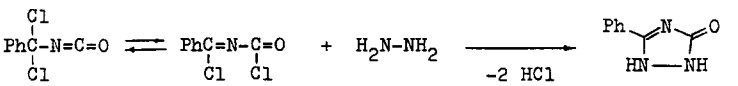
Perfluoropropyl isocyanate reacts with acetamide and urea even at ambient temperature [116] In the first case the addition product, urea **107**, is formed which hydrolyses easily giving diacyl-urea **108** In the second case, even with the excess of isocyanate, only one amino group reacts and hydrolysis of α-CF_2-group cannot be avoided As a result, perfluoropropionyl biuret **109** is obtained

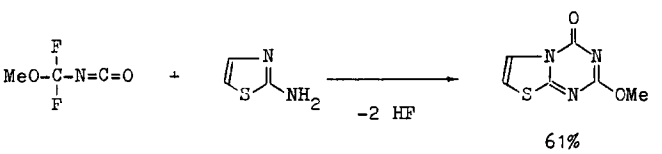


Reactions of 1,1-dihaloalkyl isocyanates with bifunctional nucleophiles such as amidines, hydrazines, guanidines and hydroxylamines provide convenient approaches for the synthesis of various heterocyclic compounds [68,102,117-121]



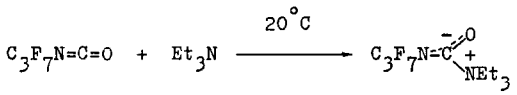
R = CCl_3, Ph
R' = Alk, Ar, AlkS, ArNH

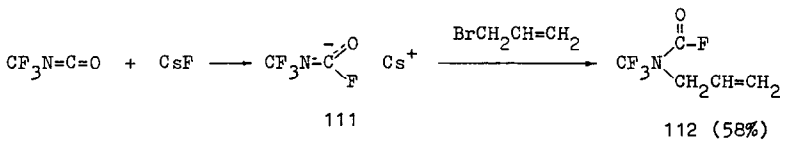




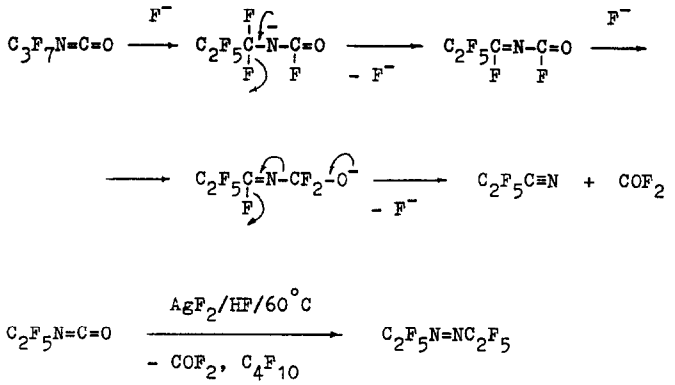
3 3 *Reactions with aprotic nucleophiles*

Perfluoroalkyl isocyanates give, with tertiary amines and alkali metal fluorides, reactive adducts **110**, **111** which may be used for synthesis [122-124] For example, alkylation of the adduct **111** yields the carbamoyl fluoride **112** [124]

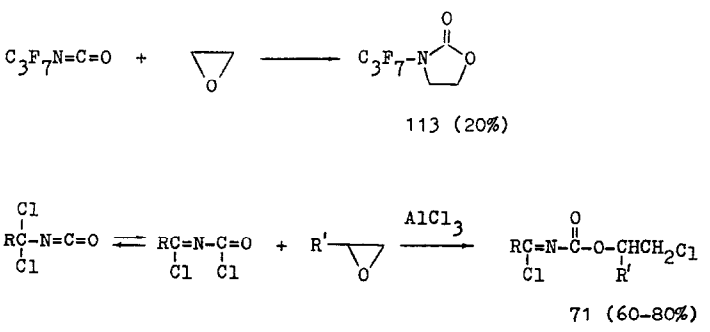




Under forcing conditions (300°C), alkali metal fluorides catalyse the cleavage of perfluoroalkyl isocyanates giving nitriles [125] Heating of perfluoroalkyl isocyanates with silver(II) fluoride in the presence of hydrogen fluoride as a catalyst yields perfluoroazoalkanes [19]

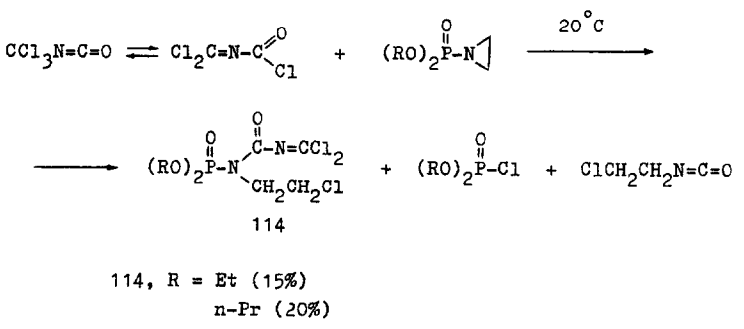


Perfluoroalkyl isocyanates under forcing conditions (180°C, autoclave) in the presence of tetraethyl ammonium bromide as a catalyst, react with oxiranes producing 2-oxazolidones, for example, **113** [122] 1,1-Dichloroalkyl isocyanates treated with oxiranes give alkylidene carbamates **71** [96,126] The last reaction is performed by heating (100°C) in the presence of a Lewis acid



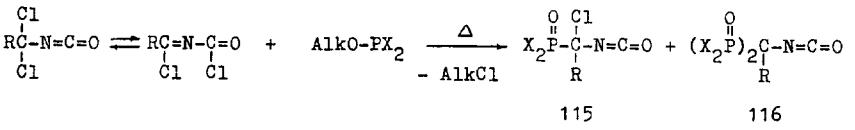
R = Cl , Alk, Ar; R' = H, Alk, Ar

Trichloromethyl isocyanate reacts with N-phosphoryl aziridines under mild conditions with opening of the aziridine ring giving N-phosphorylated alkylideneureas **114** and products of their cleavage [127]



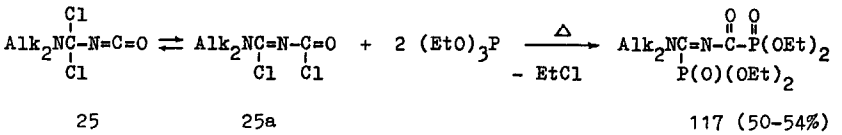
114, R = Et (15%)
n-Pr (20%)

1,1-Dihaloalkyl isocyanates are widely used as electrophilic components of the Arbuzov reaction for the synthesis of α-phosphorylated alkyl isocyanates [128] Dichloromethyl and trichloromethyl isocyanates react with phosphites and halophosphites producing a mixture of isocyanates with various extents of phosphorylation **115**, **116**, depending on the conditions of the reaction and

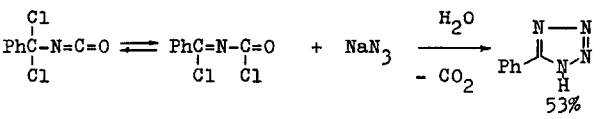


R = H, Cl X = Cl, F OAlk

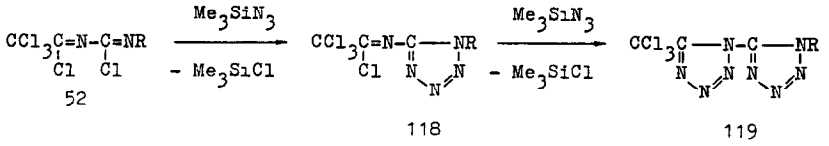
reagents ratio Reaction is performed on heating the reagent mixture, in the presence or absence of a catalytic amount of anhydrous iron(III) chloride [50,60 96,129-131] When dialkylaminodichloromethyl isocyanates **25** are used in Arbuzov reaction, phosphorylated formamidines **117** are obtained [56]



Phenyl dichloromethyl isocyanate reacts with sodium azide in aqueous acetone at 30°C to produce 5-phenyltetrazole [47,102] In anhydrous solvent this reaction gives rise to a complex mixture of heterocyclic products

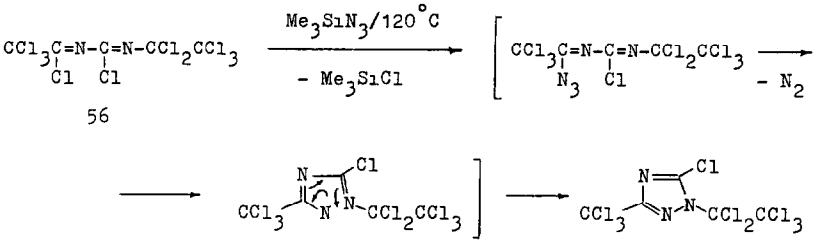


Dichlorodiazadienes **52**—chlorotropic isomers of 1,1-dichloroalkyl carbodiimides—in contrast to the reactions of protic nucleophiles where they manifest themselves as latent carbodiimides (see 3 2 1 , 3 2 2), show the features of imidoyl chloride reactivity when treated with trimethylsilyl azide Initial reaction products (in boiling benzene) are the tetrazoles **118** Upon treatment with excess trimethylsilyl azide under forcing conditions (100°C, without solvent) bis-tetrazoles **119** are formed The reaction of trimethylsilyl azide with perchlorodiazadiene **56** is unusual and the substituted 1,2,4-triazole **121** is formed Authors believe that the reaction proceeds via the formation of the intermediate nitrene **120** [86,132]



52 118 119

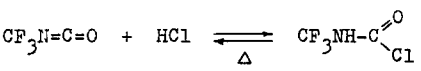
119, R = i-Pr (69%)
Ph (89%)



56 120 121 (95%)

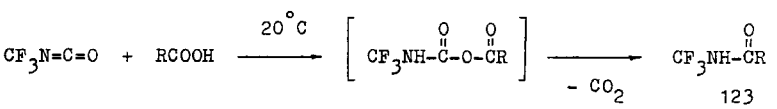
3 4 *Reactions with hydrogen halides, carboxylic and other acids*

Addition of hydrogen halides to the isocyanate group of 1,1-dihaloalkyl isocyanates is, as a rule, a reversible process Thus, hydrogen chloride easily adds to trifluoromethyl isocyanate to produce the carbamoyl chloride **122** which is stable only at temperatures below 0°C As was already mentioned (see 2 1 3), reaction of trichloromethyl isocyanate with hydrogen fluoride may be used for obtaining trifluoromethyl isocyanate [39,40]



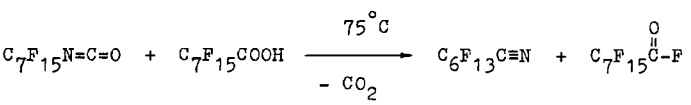
122

Trifluoromethyl isocyanate gives unstable adducts with carboxylic acids, these adducts undergo degradation even at 20°C giving amides **123** [133] The main reaction products from perfluoroalkyl isocyanates and perfluorocarboxylic acids or their anhydrides are nitriles and perfluoroacyl fluorides [134]

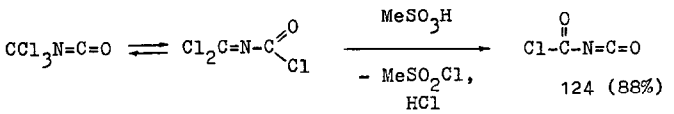


123

R = Me, CF_3

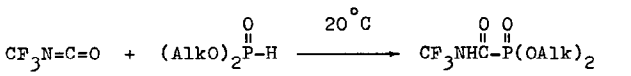


Reaction of 1,1-dichloroalkyl isocyanates with equimolar amounts of strong acids, such as trichloroacetic acid and methanesulfonic acid, is a convenient method for the synthesis of acyl isocyanates [135-137] For example, chlorocarbonyl isocyanate **124**, an important reagent in isocyanate chemistry, is obtained by treatment of trichloromethyl isocyanate with methanesulfonic acid in high yield [137,138]



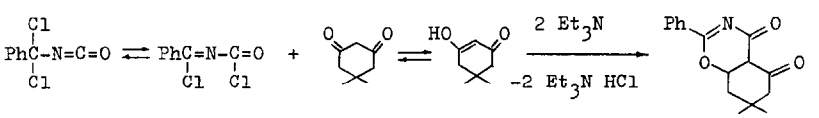
124 (88%)

Acidic phosphites add easily to the isocyanate group of perfluoroalkyl isocyanates giving carbamoyl phosphonates **125** [139]



125 (70-80%)

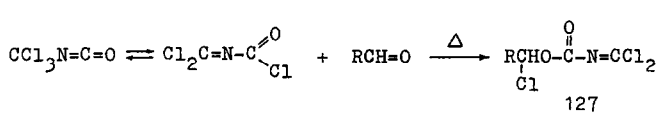
An example of the reaction of dichloroalkyl isocyanates with CH- acids is the reaction of phenyldichloromethyl isocyanate with dimedone, this proceeds under mild conditions (20°C, ether) giving the bicyclic oxazinone **126** [140]



126 (30%)

3 5 *Addition of* 1,1-*dihaloalkyl isocyanates to multiple bonds*

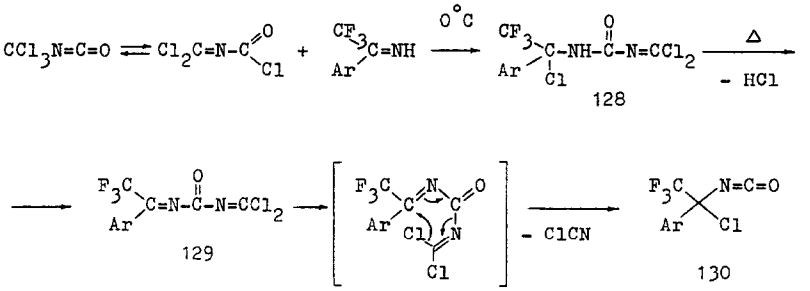
Trichloromethyl isocyanate adds to the aldehyde carbonyl group in boiling benzene, with pyridine as a catalyst, producing N-dichloromethylidene carbamates **127** [141] Ketones do not react in this way



127

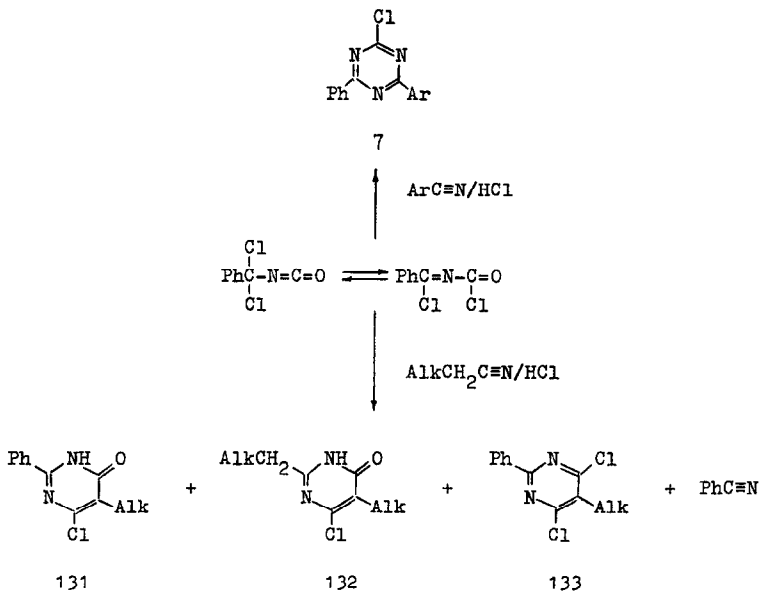
R = CCl_3 (60%)
Ph (57%)

The reaction of trichloromethyl isocyanate with aryltrifluoromethyl ketimines is a preparative method for the synthesis of 1-chloroalkyl isocyanates **130** [142,143] The initially formed adduct **128** eliminates hydrogen chloride in boiling toluene giving N,N-bis(alkylidene)ureas **129** The latter eliminate chlorocyanogen in the presence of acidic (HCl) or basic (Et_3N) catalysts and yield 1-chloroalkyl isocyanates **130**



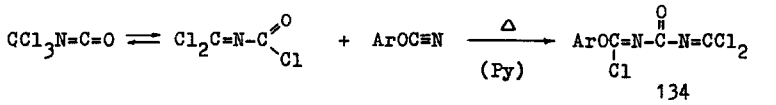
130, Ar = Ph (70%)
p-MeC_6H_4 (30%)
p-$MeOC_6H_4$ (50%)
p-ClC_6H_4 (55%)
p-$CF_3C_6H_4$ (75%)

Phenyldichloromethyl isocyanate reacts with aromatic nitriles at 100°C in the presence of hydrogen chloride yielding substituted 1,3,5-triazines **7** With aliphatic nitriles a mixture of products is obtained including substituted 4(3H)-pyrimidones **131**, **132**, and substituted pyrimidine **133** [22]



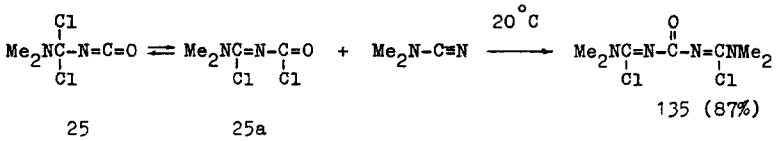
As was mentioned above (see 2 1 2), the reaction of trichloromethyl isocyanate with trichloroacetonitrile is a convenient method for the synthesis of perchloroethyl isocyanate [33]

Trichloromethyl isocyanate is added to the C≡N bond of aryl cyanates to produce bis(alkylidene)ureas **134** in boiling benzene in the presence of a basic catalyst [144] Dialkylaminodichloromethyl isocyanates **25** are added to dialkyl cyanamides under mild conditions giving bis(alkylidene)ureas **135** [49]



134

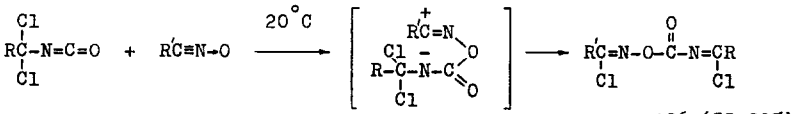
134, Ar = Ph (70%)



25 25a

135 (87%)

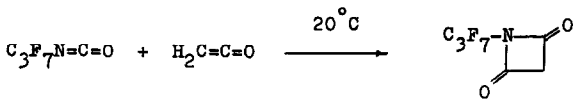
Alkyl(aryl) isocyanates are known[145] to react with nitrile oxides with difficulty to produce [2+3]-cycloaddition compounds 1,1-Dichloroalkyl isocyanates, in contrast with isocyanates, react with nitrile oxides easily in the presence of catalytic amount of tertiary amine to give linear products O-(alkylideneaminocarbonyl)hydroxamoyl chlorides **136** [146] One should note that 1,1-dichloroalkyl isocyanates existing in equilibrium with their iminocarbonyl chloride form, for example, $ArCCl_2N{=}C{=}O \rightleftarrows ArCCl{=}N{-}C(O)Cl$, do not react in this way even under forcing conditions



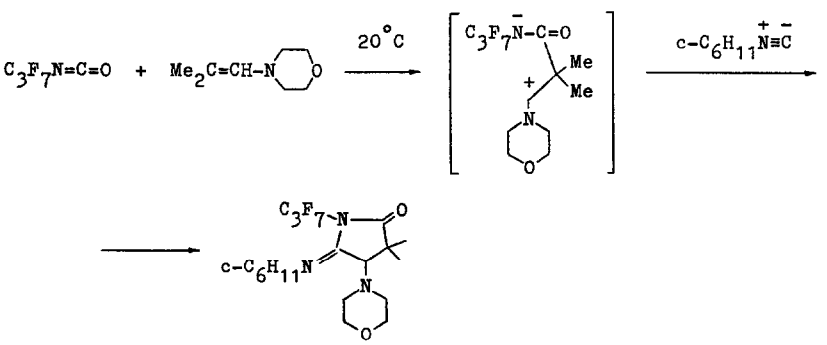
136 (58-89%)

R = CCl_3, CF_3
R' = Ar, PhC(O)

Perfluoroalkyl isocyanates react with ketenes at ambient temperature via [2+2]-cycloaddition producing azetidinediones **137** [116] Reactions of perfluoroalkyl isocyanates with both enamines and isonitriles also proceed easily but isolation of the products is difficult However, stable imino-pyrrolidones, for example **138**, may be prepared by reaction of perfluoroalkyl isocyanates with enamines and isonitriles [122]



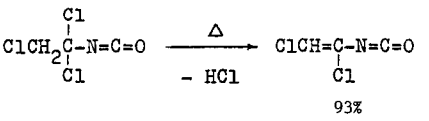
137 (77%)

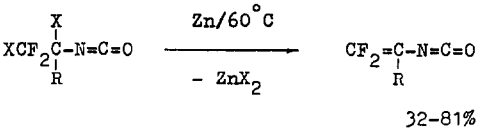


138 (37%)

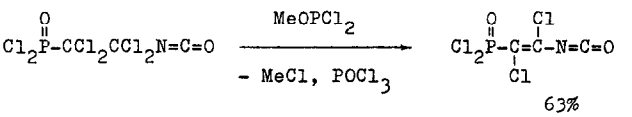
3 6 *Elimination of hydrogen halides and halogens*

1,1-Dihaloalkyl isocyanates with hydrogen atoms in the β-position may be converted into vinyl isocyanates by dehydrohalogenation Thus, 1,1,2-trichloroethyl isocyanate heated to 140°C in the presence of a catalyst (calcium chloride or activated charcoal) gives 1,2-dichlorovinyl isocyanate in high yield [37] Dehalogenation of perhaloalkyl isocyanates may be performed by treatment with zinc in diglyme or tetrahydrofuran[10,147] or with methyl dichlorophosphite [43]

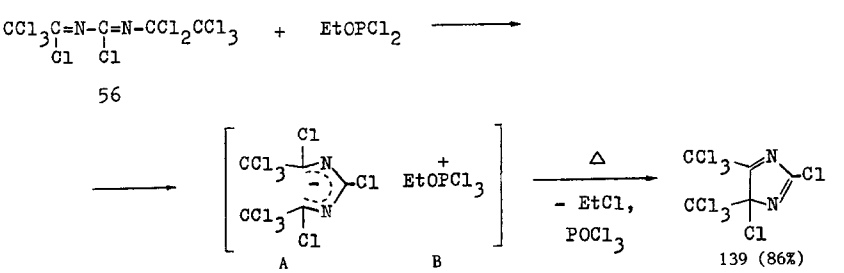




X = Cl, Br
R = F, CF_3

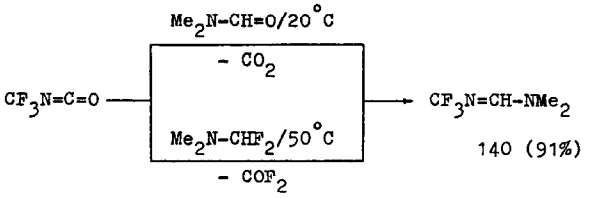


Dechlorination of perchlorodiazadiene **56**—the chlorotropic isomer of bis(perchloroethyl)-carbodiimide—proceeds unusually Treated with ethyl dichlorophosphite, this compound eliminates two chlorine atoms in the 1,5-positions and undergoes cyclization producing substituted 4H-imidazole **139** This reaction is supposed to proceed via halophilic conversion to form an intermediate ionic pair AB, with subsequent elimination of anion Cl^- and cyclization to the final product [86,87] Instead of ethyl dichlorophosphite, triphenyl phosphine or zinc (in diglyme) may be used as dechlorinating agents

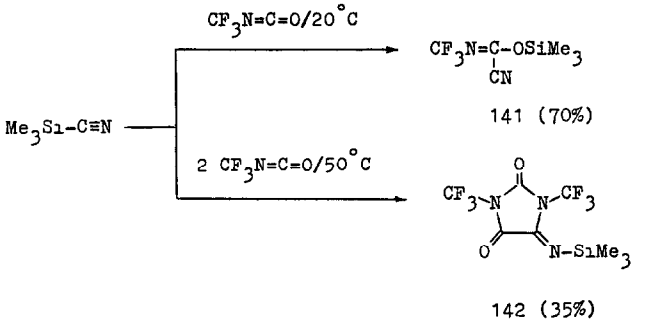


3 7 *Other conversions*

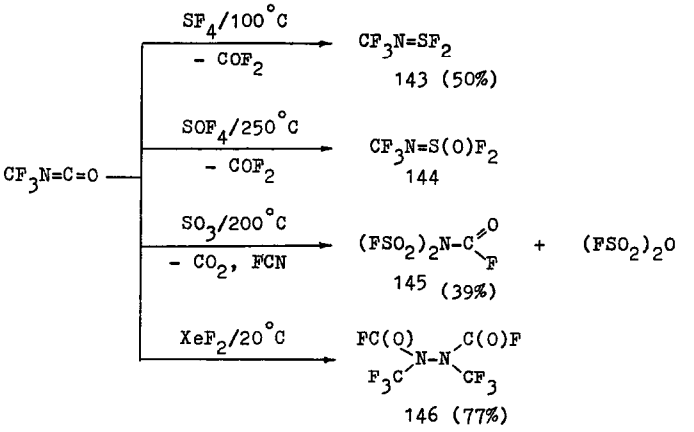
Trifluoromethyl isocyanate reacts with dimethylformamide smoothly to produce the formamidine **140** in high yield [148] Compound **140** is also obtained in the reaction of trifluoromethyl isocyanate with 1,1-difluorotrimethylamine [149]



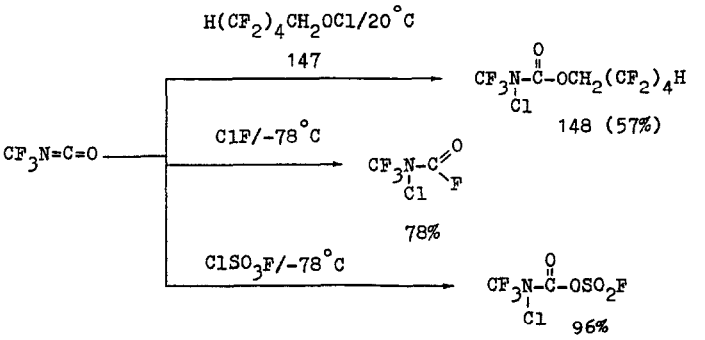
Trimethylsilyl cyanide adds to the C=O bond of trifluoromethyl isocyanate easily to produce the imidoyl cyanide **141** If trifluoromethyl isocyanate is in excess and reaction is performed in forcing conditions the heterocyclic product substituted imidazolidinedione **142** is obtained [14]



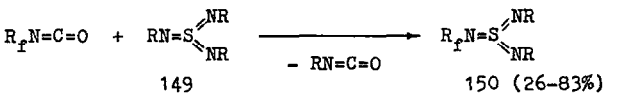
Trifluoromethyl isocyanate reacts with sulfur tetrafluoride and sulfur oxytetrafluoride to produce the compounds **143** and **144** respectively [14] The heating with sulfur trioxide leads to a mixture of products, one of them is N,N-bis(fluorosulfonyl)carbamoyl fluoride **145** [153] Fluorination of trifluoromethyl isocyanate with xenon difluoride in mild conditions gives rise to the substituted hydrazine **146** [14]



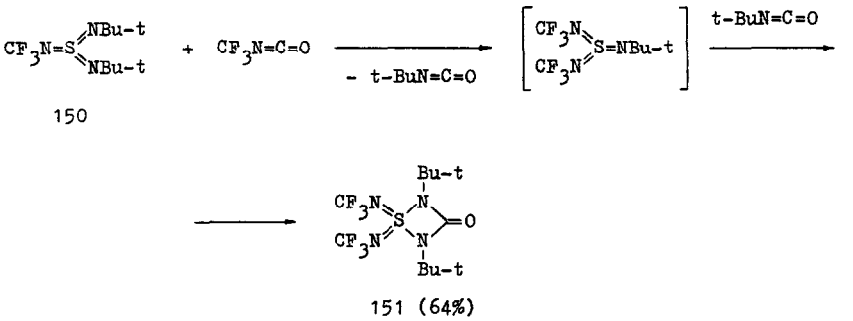
Trifluoromethyl isocyanate easily adds hypochlorite **147** to the N=C=O group to produce N-chlorocarbamate **148** [150] Chlorofluoride and chlorosulfonyl fluoride are added to trifluoromethyl isocyanate in mild conditions yielding derivatives of N-chlorocarbaminic acid [151]



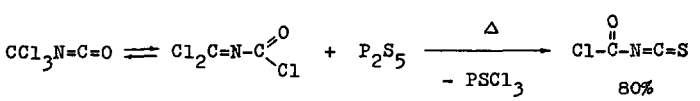
Perfluoroalkyl isocyanates react with sulfur trimides **149** in mild conditions (−60–10°C, ether) producing the compounds **150** [152] The latter give thiadiazetidinones **151** on heating (50°C) with excess perfluoroalkyl isocyanate [153]



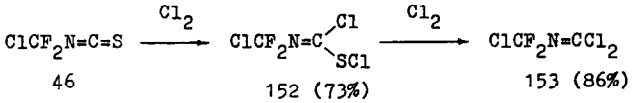
R = t-Bu, Me_3Si



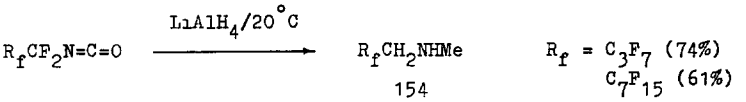
Trichloromethyl isocyanate converts smoothly into chlorocarbonyl isothiocyanate at boiling with phosphorus pentasulfide in toluene or chlorobenzene [78]



Isothiocyanate **46** adds chlorine to the C=S bond at 50°C to produce the sulfenyl chloride **152**, which may be chlorinated to yield the isocyanide dichloride **153** under forcing conditions (80°C), in the presence of catalytic amounts of iodine [74]



Perfluoroalkyl isocyanates are easily reduced yielding secondary amines **154** with lithium aluminium hydride [154]



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