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The Chemistry of Acyl and Sulphonyl Isocyanates, Isothiocyanates, and Isoselenocyanates

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The review presents the latest advances in the chemistry of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates. All the methods for the preparation of these compounds are examined and treated systematically. Their reactions and their physical properties are described and the problems of their structure and isomerisation are discussed. In conclusion the available literature data on the practical importance and applications of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates are presented.

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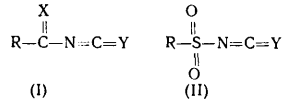
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I. INTRODUCTION

Organic isothiocyanates and isocyanates, first obtained towards the end of the last century, are assuming increasing importance at the present time. The enormous interest in this class of compounds is due to the fact that, by virtue of their reactivity, they have become important starting materials and intermediates for the synthesis of a wide variety of organic compounds, many of which have found practical applications. Organic isocyanates are essential for the synthesis of polymeric materials, synthetic fibres, medicinal preparations, insecticides, herbicides, fungicides, nematocides, photographic materials, and many other products.

In 1964 an International Symposium was held in Czechoslovakia on the chemistry of isocyanates [1]. Novel synthetic methods have been described in papers published recently[2-5] and new synthetic and practical applications have been found for organic isocyanates, isothiocyanates, and thiocyanates[6-7]. Reviews of the chemistry of isocyanates have been published[8-10].

The data on acyl isocyanates, isothiocyanates, and isoselenocyanates are scattered in many sources and information about them has not been compiled. The present review is an attempt to fill this gap. It deals with new data on the structure, methods of preparation, properties, and practical applications of acyl isocyanates, isothiocyanates, and isoselenocyanates, thioacyl isocyanates, sulphonyl isocyanates, and sulphonyl isothiocyanates with the general formulae (I) and (II):



(I) (II)

where X and Y can have the following significance: X = Y = O, X = Y = S, X = Y = Se, X = O and Y = S or Se, and X = S and Y = O or Se; R may be a halogen, alkyl, aryl, or an alkoxy- aryloxy-, or dialkylamino-group, etc.

The chemical properties of sulphonyl isocyanates [(II), Y = O] have been examined in Ulrich's review[10]. We shall deal only with those data on this class of compounds which were not included in Ulrich's review, but which are nevertheless of considerable interest.

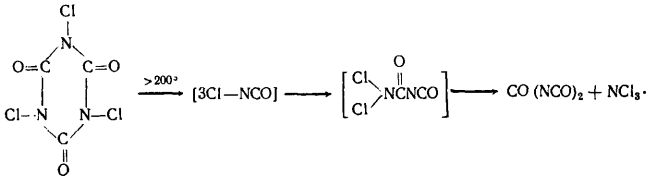
Of the two types of acyl isocyanates and isothiocyanates examined here, the first has been known for a long time, but recently there has been an increase of interest in these compounds. The chemistry of thioacyl isocyanates of the type R–C(=S)–N=C=O began to be studied in the last 4–5 years, while thioacyl isothiocyanates R–C(=S)–N=C=S and thioacyl isoseleno-

while thioacyl isothiocyanates R–C(=S)–N=C=S and thioacyl isoselenocyanates R–C(=S)–N=C=Se are still unknown. Acyl isoselenocyanates of the type R–C(=O)–N=C=Se have not been obtained in a pure form. Their existence has been demonstrated by conversion into selenourea derivatives. The first representatives of sulphonyl isothiocyanates $R-SO_2N=C=S$ have been obtained recently.

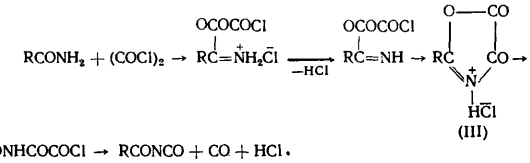
The review deals with papers published up to 1st June, 1967.

II. METHODS OF PREPARATION OF ACYL ISOCYANATES, ISTHIOCYANATES, AND ISOSELENOCYANATES

I. Carbonyl isocyanates. The simplest compound of this series, carbonyl diisocyanate O=C=N–C(=O)–N=C=O, was first obtained in 1966 by the thermal decomposition of trichloroisocyanuric acid at atmospheric pressure[11]. The reaction takes place via the intermediate formation of chloroisocyanate and *N*-dichloro-*N*-carbonylurea[12]:

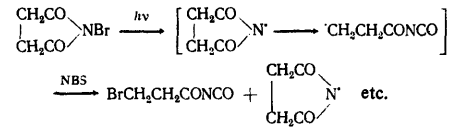


The corresponding chlorocarbonyl isothiocyanate ClCONCS and carbonyl di-isothiocyanate $CO(NCS)_2$ have not so far been obtained in a pure form. Their existence has been confirmed indirectly by the reactions of thiophosgene with lead thiocyanate, with subsequent conversion into thiourea derivatives[13,14]. The simplest acyl isocyanates have been obtained from the chlorides and salts of cyanic acid[15-24]. In recent years more convenient methods have been developed for the synthesis of acyl isocyanates. Recently a new and novel method has been proposed[25] for the synthesis of acyl isocyanates from unsubstituted amides and oxalyl chloride in dichloroethane with prolonged refluxing:



A ccording to the mechanism suggested for this reaction, *O*-acylation takes place in the first stage and is followed by intramolecular cyclisation with elimination of hydrogen chloride and the formation oxazolidin-4, 5-dione derivatives (III). On prolonged boiling, the latter are converted into acyl isocyanates with elimination of carbon monoxide and hydrogen chloride. In these reactions aromatic amides give yields of carbonyl isocyanates of 56–96%. Aliphatic amides react with somewhat greater difficulty, the yields of carbonyl isocyanates being 31–67%. The reaction of the amide of cyclopropanecarboxylic acid with oxalyl chloride takes place with opening of the cyclopropane ring and the formation of γ-chlorobutyryl isocyanate $ClCH_2CH_2CH_2CONCO$.[26] The possibility of preparing acyl isocyanates from acid amides and phosgene is mentioned in the patent of Waltmann and Wolf[27].

A method of preparation of acyl isocyanates by the rearrangement of cyclic *N*-bromo-imides was proposed by Johnson[28] and Martin[29]. Under the action of a catalyst (benzoyl peroxide, illumination) and in the presence of allyl halides, *N*-bromosuccinimide (NBS) forms the succinimide radical, which isomerises to the radical $^{\bullet}CH_2CH_2CONCO$, the latter being converted into β-bromopropionyl isocyanate under the action of NBS:



It has been shown[30] that this reaction does not take place with *N*-chloro- and *N*-iodo-succinimides but takes place smoothly in the case of *N*-bromoperfluoroglutarimine in the reaction with fully fluorinated olefins in the presence of benzoyl peroxide[31].

Acyl isocyanates are formed in high yields (greater than 90%) in the reaction of acid chlorides with isocyanic acid in the presence of tertiary amines (B)[32]:

$$RCOCl + HNCO + B \rightarrow RCONCO + BH^+Cl^- .$$

A wide variety of acyl isocyanates derived from carboxylic acids and mono- and di-isocyanates of silicon $[R_nSi(NCO)_{4-n}]$ and phosphorus $[R_nP(NCO)_{3-n}]$ derivatives have been obtained by this method.

Azidoformyl isocyanate has been obtained by the slow decomposition of oxalyl diazine[33]:

$$(N_3CO)_2 \xrightarrow[-N_2]{} N_3CONCO .$$

The formation of arylaminoformyl isocyanate has been observed in the decomposition of the azides of aryloxamic acids in the presence of aromatic amines[34].

2. Carbonyl isothiocyanate. The first representative of acyl isothiocyanates was synthesised from acid chlorides and thiocyanate salts as early as the 1880's. In most cases the reaction was carried out in inert solvents[35,47]. Later acetonitrile and acetone began to be used[36-44]. So far this is the only method for the preparation of acyl isothiocyanates.

By the reaction of the chlorides of arylazochloroacetic acids with sodium thiocyanate, the corresponding isothiocyanates of arylazochloroacetic acids were synthesised in high yields[42]:

$$ArNHN=C(Cl)COCl + NaSCN \rightarrow ArNHNC(Cl)CONCS .$$

The carbonyl isothiocyanates of the furan[39,43,44], pyridine[45], and pyrazolone[14] series have been synthesised by the reaction of acyl chlorides with thiocyanate salts. Carbonyl isothiocyanates have been obtained by the reaction of acylamino-carboxylic acids with the diphenyl ester of isothiocyanatophosphoric acid in the presence of triethylamine in acetonitrile[46]. This reaction is of exceptionally great importance in the synthesis of peptides. The formation of ethoxycarbonyl isothiocyanate was observed on heating *NN*- diethoxycarbonylthiourea up to the melting point.

Carbamoyl isothiocyanate can be obtained by the reaction of thiocyanic and isocyanic acids at a low temperature[48,49].

3. Thiocarbonyl isocyanates. These compounds have been investigated only in recent years [50-53]. So far however they have not been isolated in a pure form because of their exceptional reactivity. Their formation and existence in solutions have been demonstrated experimentally. Thiocarbonyl isocyanates are obtained by the thermal degradation of thiazolidin-4, 5-dione, which can in turn be synthesised by the reaction of thioamides with oxalyl chloride [54].

4. Carbonyl isoselenocyanates. These compounds were synthesised for the first time in 1937 by the reaction of acid chlorides with potassium selenocyanate in acetone solution [55,56]:

$$RCOCl + KSeCN \rightarrow RCONCSe + KCl.$$

However, they have not been isolated in pure form. Their existence has been demonstrated by conversion into the corresponding carbonylselenoureas. When an attempt was made to prepare the isoselenocyanates of arylazochloroacetic acid, the corresponding selenocyanates were isolated [42].

5. Sulphonyl isocyanates. Recently Smith and coworkers [57] put forward a method for the preparation of organic disulphonyl isocyanates by direct combination of phosgene with disulphonamides in nitrobenzene at 170–180°C. The yields are 54–67%:

$$R(SO_2NH_2)_2 \xrightarrow[170-180^\circ]{COCl_2} R(SO_2NCO)_2,$$

where R= $-(CH_2)_4-$, $-(CH_2)_6-$, or 1,5-naphthyl.

Ulrich and coworkers [58] synthesised a number of arylsulphonyl isocyanates in high yields by the reaction of arylsulphonamides with an excess of phosgene in the presence of butyl isocyanate as the catalyst. Treatment of *p*-aminobenzenesulphonamide with phosgene in nitrobenzene leads to various products, depending in the reaction temperature: *p*-(chloroformamide) benzenesulphonamide formed at 0°C is converted into *p*-isocyanatobenzenesulphonamide at 90°C and into *p*-isocyanatobenzenesulphonyl isocyanate at 150°C [57]. Benzenesulphonamide reacts with phosgene in 1, 2, 4-trichlorobenzene solution in an atmosphere of nitrogen to form benzenesulphonyl isocyanate [59]. When benzenesulphonamide was allowed to react with a four-fold excess of axalyl chloride in dichlorobenzene solution, benzenesulphonyl isocyanate was obtained in 81% yield [60].

Recently a method has been proposed for the preparation of sulphonyl isocyanates from 1-arylsulphonyl-3-alkylureas and alkylenedi(arylsulphonyl)ureas and phosgene at 120–180°C in non-polar solvents [58]:

$$RC_6H_4SO_2NHCONHAlk \xrightarrow[-HCl]{COCl_2} \underset{90\%}{RC_6H_4SO_2NCO} + AlkNCO.$$

Not long ago a method was described [61] for the preparation of sulphuryl di-isocyanate and chlorosulphuryl cyanate by the reaction of cyanogen chloride with sulphur trioxide at 200–250°C in the presence of iron, cobalt, nickel, chromium, molybdenum, copper, and aluminium salts:

$$ClCN + SO_3 \xrightarrow{200-250^\circ} ClSO_2NCO + SO_2(NCO)_2.$$

Chlorosulphonyl isocyanate can be completely converted by pyrolysis into sulphuryl di-isocyanate. The method proposed is dinstinguished by its simplicity, high yields of the final products, and the possibility of achieving a continuous synthesis.

6. Sulphonyl isothiocyanates. When dipotassium salts of sulphonyliminodithiocarbonic acids [62-66] were allowed to react with phosgene in benzene, carbon tetrachloride, or methylene chloride at a low temperature, sulphonyl isothiocyanates were obtained in yields up to 88% [65,66]:

$$RSO_2NC(SK)_2 + COCl_2 \rightarrow RSO_2NCS + COS + 2KCl,$$

where R=alkyl or aryl.

Phosgene can be replaced by the chloroformic ester, phosphorus pentachloride, thionyl chloride, and sulphuryl chloride [62-64]. On standing, sulphonyl isothiocyanates dimerise spontaneously.

Ulrich [67,68] proposed a method for the synthesis of sulphonyl isothiocyanates by the reaction of sulphonylthioureas and phosgene:

$$RSO_2NHCNHR + COCl_2 \rightarrow RSO_2NCS + RNCO.$$
$$\quad\quad\quad

asymmetric stretching vibrations of sulphonyl isocyanates differ little from those in the spectra of alkyl and aryl isocyanates.

Nevertheless we believe that in acyl isothiocyanates ($R-\overset{\overset{O}{\|}}{C}-N=C=S$ and $RSO_2N=C=S$) there is slight interaction (or inductive effect) between $R-C=O$, $-SO_2-$, and $-N=C=S$ groups. It is expressed in an increase of the proportion of the mesomeric dipolar structure $R-C(\bar{O})=\overset{+}{N}=C=S$, in an increase of the double-bond character of the bond involving the nitrogen atom, and in a slight displacement of the stretching-vibration bands of the N=C=S and C=O groups towards longer wave lengths. Thus, whereas the stretching vibration frequency $\nu_{(as)}$ for CH_3NCS is 2110 cm^{-1} it is 1980–1950 cm^{-1} for CH_3CONCS, 2095 cm^{-1} for C_6H_5NCS, 1970–1930 cm^{-1} for C_6H_5CONCS, and 1905 cm^{-1} for $C_6H_5SO_2NCS$. [10,73,76-78]

IV. THE STRUCTURE AND ISOMERISATION OF ACYL ISOCYANATES, ISOTHIOCYANATES, AND ISOSELENOCYANATES

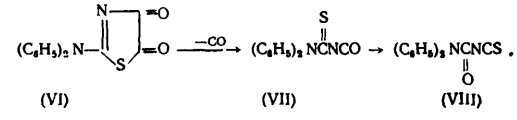
It is known that, in the synthesis of acyl isocyanates, isothiocyanates, and isoselenocyanates by the double decomposition reaction of acid halides with isocyanate, selenocyanate, and isothiocyanate salts, there is a possibility of the formation of compounds (IV) and (V):

$$\underset{}{AcHal} + MXCN \rightarrow \underset{(IV)}{AcNCX} + \underset{(V)}{AcXCN},$$

where M=K, Pb, Na, or NH_4 and X=O, S, or Se. The reasons for the preferential formation of compounds (IV) or (V) have not been adequately elucidated so far [79,80]. Some authors state that compounds (IV) form preferentially during the double decomposition process [81,82] while others isolated compounds (V) [83].

We believe that the preferential formation of acyl isothiocyanates relative to acyl thiocyanates is associated with the fact that, as a result of the mesomerism $^-S-C^-\equiv N \rightleftharpoons S=C=N^-$, it is easier for thiocyanate ions, on energy grounds, to form compounds (IV) rather than compounds (V) (according to Pauling [84], the energy of formation of the C–N bond is 67.7 kcal $mole^{-1}$, that of the C–S bond is 62 kcal $mole^{-1}$, the electronegativity of nitrogen is –3, and that of sulphur –2.5). Furthermore, there are literature data showing that the fraction of acyl thiocyanate which does form isomerises to acyl isothiocyanate under the action of thiocyanate salts [78].

The isomerisation of thioacyl isocyanate to acyl isothiocyanate was first observed for diphenylaminothiocarbonyl isocyanate obtained by the thermal decomposition of 2-diphenylaminothiazolidin-4,5-dione [51]:



(VI) (VII) (VIII)

Infrared absorption spectroscopic data showed that, in the decomposition of product (VI), there appears in the infrared spectrum an absorption band with $\nu_{(as)}$ (NCO)= 2230 cm^{-1}, which is characteristic of structure (VII). On further heating, the 2230 cm^{-1} band vanishes and is replaced by an absorption frequency at 1970 cm^{-1}, characteristic of the NCS group [compound (VIII)]. The mechanism of the conversion of compound (VII) into compound (VIII) proposed by the authors, including the formation of intermediates, was confirmed for other examples by chemical reactions involving tracer atoms. [53,85]

V. CHEMICAL REACTIONS OF ACYL ISOCYANATES, ISOTHIOCYANATES AND ISOSELENOCYANATES

Acyl isocyanates, isothiocyanates, and isoselenocyanates enter into the majority of chemical reactions characteristic of alkyl and aryl isocyanates, isothiocyanates, and isoselenocyanates. However, there are also differences, which are described below.

1. Reaction with Water and Alkalis

Carbonyl isocyanates react with water to form acid amides, carbon dioxide, and dicarbonyl ureas [18]. Carbonyl isothiocyanates are hydrolysed by water, also with formation of acid amides and carbon sulphide oxide [13]. They react more vigorously with alkalis, giving almost quantitative yields of acid amides. The hydrolysis of acyl isothiocyanates was investigated in detail by Elmore and Ogle [40,86]. The hydrolysis of sulphonyl isocyanates was studied recently by Smith [57]. By comparing the ease of hydrolysis of aliphatic and aromatic acyl isothiocyanates, Elmore and Ogle [87] established that phosphonyl isothiocyanates occupy an intermediate position between aliphatic and aromatic acyl isothiocyanates:

$$AlkCONCS > (RO)_2PONCS > ArCONCS.$$

2. Reactions with Aromatic and Aliphatic Alcohols and Mercaptans

Acyl isocyanates, isothiocyanates, and isoselenocyanates react with alcohols and mercaptans to form the corresponding urethanes, thiourethanes, and dithiourethanes. This reaction has been frequently studied with carbonyl isocyanates [26,88-92], carbonyl isothiocyanates [36,40,93,94], and sulphonyl isocyanates [59,95,96]. The preparation of urethanes by the reaction of carbonyl isocyanates with alcohols, glycols, and phenols constitutes a qualitative test for alcohols and phenols [88,89]. According to kinetic data, the formation of urethanes is a monomolecular reaction [93]. It takes place readily both at primary and sterically hindered alcohols and phenols [88,89,95]. The reaction of sulphonyl isocyanates with alcohols (2-methyl-2-propanol, 3-ethyl-3-pentanol) in toluene solutions takes place instantaneously even at 0°C.

3. Reactions with Ammonia, Amines, Aminonitriles, Amides, Substituted Hydrazines, Hydrazides, and Oximes

The reaction of acyl isocyanates, isothiocyanates, and isoselenocyanates with ammonia and amines has been thoroughly investigated and takes place smoothly both in polar solvents and in solvents of low polarity on heating [37,39-45,97-100]. The reactions of amines and diamines with carbonyl isocyanates [101-105], carbonyl isothiocyanates [86,97-100,106-117], thiocarbonyl isocyanates [52], carbonyl selenocyanates [55,118], and sulphonyl isocyanates [119-124] have been described.

Aliphatic and aromatic amines react with acyl isocyanates almost quantitatively. Aromatic polynitroamines do not enter into the condensation reaction [106].

Thiobenzoyl isocyanate does not react with ammonia and methylamine hydrochloride[52]. Amino-acids[40,86], carboxylic acid amino-esters[114], and heterocyclic bases[111,112] react similarly to aromatic amines. The acylureas and acyl thioureas obtained from them are widely used for the synthesis of heterocyclic compounds[111-114].

The mechanism of the reaction of acyl isocyanates and acyl isothiocyanates with amines was studied using as an example the reaction of sulphonyl isocyanates with primary and secondary amines in the presence of tertiary amines[119]. It has been shown that the mechanism proposed by Baker and Gaunt[125], according to which the reaction takes place via an intermediate donor–acceptor complex of the isocyanate with the tertiary amine, is entirely suitable for this process:

$$RSO_2NCO + R_3N \longrightarrow \left[RSO_2N=C-O^- \;\; \underset{+}{NR_3} \right] \xrightarrow{R''NH_2} RSO_2NHCONHR''.$$

α-Aminonitriles and their substituted derivatives react with acyl isocyanates and acyl isothiocyan tes similarly to amines. The reaction usually leads to the formation of thioureas, thiazole, and mercaptoimidazole[126]. Aminoacetamide enters into similar reactions but less vigorously[127]. (Ethoxycarbonyl) carbonyl isothiocyanate reacts with α-amino-nitriles similarly to benzoyl isothiocyanate, with formation of thiazole and imidazole derivatives[128].

Tri(dimethylamino)phosphine reacts with benzoyl isothiocyanate to form the corresponding thiourea[129]. Similarly, dimethylsulphoxylidene reacts with acyl isocyanates and isothiocyanates to give dimethylsulphoxylideneureas and dimethylsulphoxylidenethioureas[130].

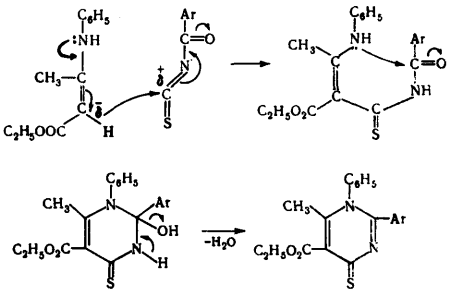
The reaction of acyl isocyanates with ureas and substituted thioureas in ether or benzene leads to the formation of biurets and thiobiurets RCONHCONHCNHR (where X= O or S) in high yields[16]. These compounds exhibit powerful physiological activity. Acyl isocyanates, isothiocyanates, and isoselenocyanates react with substituted hydrazines to form the corresponding 4-acyl-1-substituted semicarbazides and thiosemicarbazides[37,131-133] and selenosemicarbazides[134]. With thiocarbonyl isocyanate, substituted hydrazines form triazolone derivatives[52].

Unsubstituted hydrazine reacts with acyl isocyanates and isothiocyanates to form symmetrically substituted hydrazines[131] and sometimes, depending on the conditions, triazole derivatives[131]. The reaction of acyl isothiocyanates with acid hydrazides is similar to the reaction with substituted hydrazines; it has been investigated in detail using as an example the hydrazide of isonicotinic acid in alcohol, dioxan, and acetonitrile solutions. The resulting 1-isonicotinoyl-4-acylthiosemicarbazides exhibit high bacteriostatic activity[37,132,135].

The reaction of acetaldehyde-ammonia with carbonyl isothiocyanates was studied by Elmore and Ogle[136], who established that the product is 1,1-di[alkoxycarbonyl (thioureido)] ethane. The interaction of acyl isocyanates and isothiocyanates with oximes was investigated by Gheorghiu and coworkers[137,138]. However, the reaction mechanism was not elucidated. It has been shown that the reaction is exceptionally complicated, involving the formation of numerous products. Thus benzamide, benzonitrile, benzoylurea, benzoylcyanamide, carbon oxide sulphide, sulphur and other products have been isolated in the reaction of benzoyl isothiocyanate with aldoximes and ketoximes.

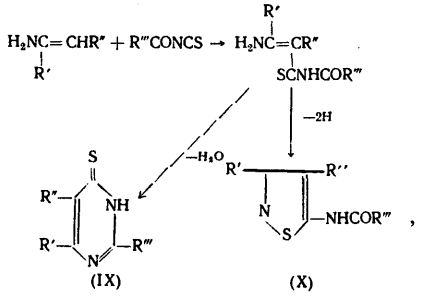
4. Reactions with Compound Containing an Active Hydrogen Atom

Acyl isocyanates and isothiocyanates react comparatively readily with organic compounds containing activated hydrogen atoms. An example is the reaction of acyl isothiocyanates with an $\alpha\beta$-unsaturated amino-ester, for example the β-anilinocrotonic ester[139]. It has been established that the primary product of this reaction is β-anilino-α-benzoyl thiocarbonyl crotonate[140]. However, when the latter is heated in ether or tetrahydrofuran, derivatives of 4-thiopyrimidine are obtained in yields up to 70%:



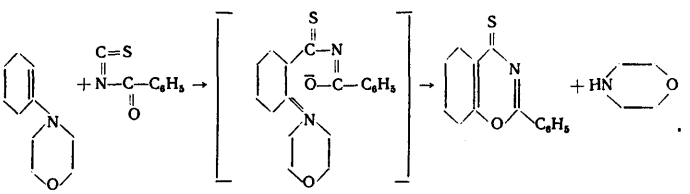
The reaction is general and can be applied both to $\alpha\beta$-unsaturated amino-esters and to various acyl isocyanates and isothiocyanates. The yield of the final product depends significantly on the nature of the substituent in the aromatic ring: electron acceptors increase and electron donors decrease the yield and favour the formation of side products.

In the reaction of carbonyl isocyanates with aliphatic amines, amino-esters, and diamines with the amino-group at the double bond, there is a possibility of the formation of pyrimidine (IX) and isothiazole (X) derivatives[141-144]:



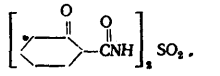
where R′ = NH_2, OC_2H_5.

Benzoyl isothiocyanate readily reacts with 1-morpholinylcyclohexene in chloroform to form 2-aryl-5,6,7,8-tetrahydro-1,3-benzoxazine-4-thione[145]:

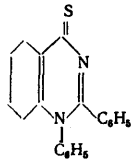


Similarly in the reaction with 1-morpholinylcyclohexene, sulphuryl di-isocyanate leads to the formation of the adduct

NN-di(2-morpholinyl-3,4,5,6-tetrahydrobenzoyl)sulphonamide, which is converted into *NN'*-di(2-oxohexahydrobenzoyl)sulphonamide on hydrolysis with 70% sulphuric acid[146]:

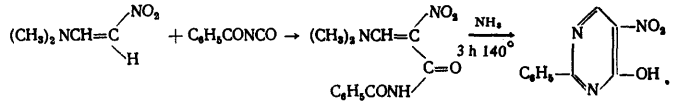


In a similar reaction with benzoyl isothiocyanate in ether 1-phenylaminocyclohexene gives 1,2-diphenyl-5,6,7,8-tetrahydroquinazolone-4-thione[140,147]:

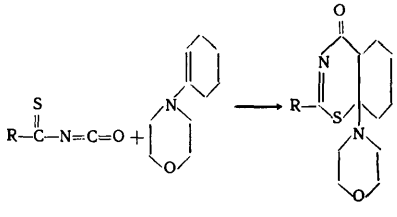


The above reactions involving the addition of acyl isocyanates and isothiocyanates to the β-carbon atom of primary and secondary enamines make possible the preparation by a new synthetic procedure of pyrimidine and quinazoline derivatives[147,148].

Acyl isocyanates readily add also to 1-dimethylamino--2-nitroethylene in benzene at 20°C with formation of *N*-benzoyl-β-dimethylamino-α-nitroacrylamide[149]. When the latter reacts with ammonia initially at 0°C and then at 140°C, it is converted over a period of 3 h into 4-hydroxy--5-nitro-2-phenylpyrimidine, which is otherwise difficult to obtain:



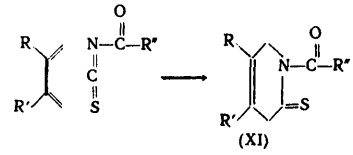
Thioacyl isocyanates react more vigorously with compounds containing active hydrogen atoms[151]. Thus, in the reaction of thioacyl isocyanates with 1-morpholinylcyclohexene in ether at 0°C and with 2,3-dihydropyran, the addition takes place in accordance with the 1,4-cycloaddition principle, with formation of 2-aryl-4a,5,6,7,8,8a-hexahydro-8a-morpholino-4*H*-1-benzothiazin-4-one,



and 2-aryl-8-oxa-1-thia-3-azabicyclo[4,4,0]dec-2-en-4-one.

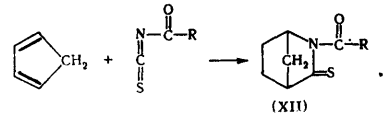
5. Acyl Isocyanates and Isothiocyanates in Diene Synthesis Reactions

The participation of acyl isocyanates and isothiocyanates in diene synthesis reactions has been investigated very little. The work of Arbuzov and Zobova deals with this question[150,151]. Using acetyl and benzoyl isocyanates and isothiocyanates as an example[150], they studied their interaction with a number of dienes: divinyl, isoprene, 2,3--dimethylbuta-1,3-diene, and cyclopentadiene. The reaction probably involves 1,4-addition with formation of 4(5)-substituted *N*-acyl-1,2,3,6-tetrahydro-2--thionopyridines (XI) in a yield of 40–45% in the presence of divinyl, isoprene, and 2,3-dimethylbuta-1,3-diene:



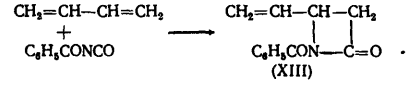
(XI)

and *N*-acyl-3-thiono-2-azabicyclo[2,2,1]hept-5-ene (XII) in a yield of about 50% in the presence of cyclopentadiene:



(XII)

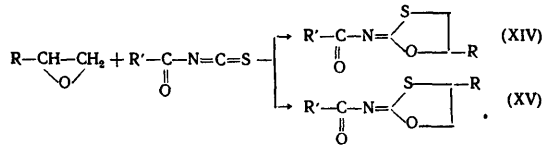
Benzoyl isocyanate reacts with 1,3-dienes to form 1,2--addition products[151] (XIII) in yields of 30–40%:



(XIII)

6. Reactions with Epoxides

In contrast to other isothiocyanates[152,153], acyl isothiocyanates react with the double bond of the thiono-group C=S of the isothiocyanate[154,155] to form two five-substituted derivatives of 1,3-oxathiolane-(XIV)or(XV):



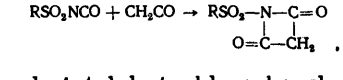
(XIV)

(XV)

However, in the case of 2,3-epoxy-1-phenoxypropane the reaction with acyl isothiocyanate takes place with formation of compound (XIV) only, as demonstrated rigorously by synthesis. The formation of compound (XIV) can be explained by the fact that in most addition reactions the epoxy-ring is opened on the side of the unsubstituted carbon atom because of the steric hindrance due to substituents.

7. Reactions with Ketens

The reactions of acyl isocyanates and isothiocyanates with ketens have been almost not investigated. It has been established recently that keten reacts very readily with sulphonyl isothiocyanate to form the corresponding *N*-sulphonylazetidinediones[156]:



where R = phenyl, *p*-tolyl, *p*-chlorophenyl, *p*-fluorophenyl, etc, and if the products are unstable, polymers derived from the latter, of the type $[-COCH_2CONSO_2R]_n$, are formed. Usually the reaction takes place in ether or methylene chloride at a temperature between - 30° and - 10°C. Sulphonyl isocyanates also react readily with vinyl ethers, keten acetals[157], and olefins of the type, $[RCH{=}CR']_2S$ at 20–170°C.[158] Both di-isocyanate groups of di-isocyanates react with keten to form bis-*N*-sulphonylazetidines[156].

8. Reactions of Acyl Isocyanates with Orthocarbonic Esters

Recently Biener [159] described an interesting reaction of sulphonyl isocyanates with orthocarbonic esters. This reaction makes it possible to obtain yields up to 90% esters of *N*-sulphonyl-*N*-alkylcarbonic acids which cannot be obtained otherwise:

$$R''SO_2NCO + R'(COR)_3 \rightarrow R''SO_2N(R)CO_2R + R'COOR .$$

Usually the reaction takes place at a low temperature in methylene chloride or chloroform and virtually reaches completion in 1–2 h. In reactions with sulphonyl di-isocyanates, either one or two isocyanate groups may be involved, with formation of various products.

9. Acyl Isocyanates in the Grignard Reaction

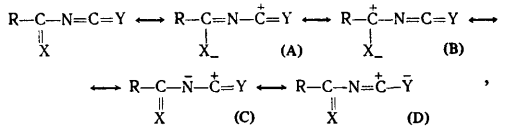
The Grignard reaction was studied in detail by McFarland between benzene- and *p*-toluene-sulphonyl isocyanates and alkyl- and aryl-magnesium bromides (or iodides) in ether at a low temperature. *N*-Sulphonamides are obtained in yields up to 88% when isocyanate or isothiocyanate is added to the Grignard reagent:

$$RSO_2NCO + R'MgX \xrightarrow[H^+,\ H_2O]{\text{ether}} RSO_2NHCOR' .$$

When the Grignard is added to the isocyanate or isothiocyanate, the reaction is accompanied by side processes and the yields of *N*-sulphonamides fall by a factor of 4–5. When the reaction is carried out with an excess of the Grignard reagent and the mixture is refluxed, the yield of the final product is appreciably reduced [160].

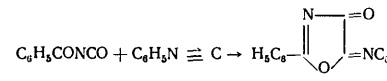
10. Acyl Isocyanates and Isothiocyanates in Reactions with Compounds Containing the C=N Bond

a. Reactions with isonitriles. The reactions of acyl isocyanates and isothiocyanates and thioacyl isocyanates with isonitriles and carbodi-imides can be regarded as dipolar 1,4-addition and dipolar 1,2-interaction [51,161]. In various reactions acyl isocyanates and isothiocyanates can be represented by dipolar structures:



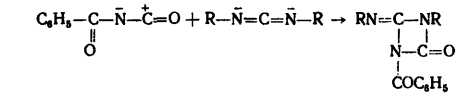
where Y, X=O, S, Se.

Benzoyl isocyanate reacts with phenylisonitrile in benzene with formation of 5-phenylimino-oxazolin-4-one in 96% yield:

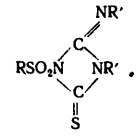


When isonitriles react with acyl isocyanates in the presence of carboxylic acids, intramolecularly acylated mixed amides of the type RNHCOCON(COR')COR", which are otherwise difficult to obtain, are formed in yields up to 90%. [162] Thiobenzoyl isocyanate and benzylmercapto-thiobenzoyl isocyanate react with the isonitrile in methylcyclohexane or toluene more vigorously, forming respectively 2-phenyl- and 2-benzylmercapto-5-phenylimino thiazolidin-4-one in 70–85% yield [51,53,161]. Di-isonitriles react with acyl isocyanates and isothiocyanates similarly, with formation of di-imino-thiazolin-4-ones [161,163].

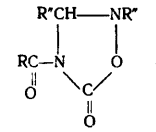
b. Reactions with carbodi-imides. It is known that compounds with cumulated double bonds (for example carbonylsulphonyl isocyanates and isothiocyanates) readily enter into dipolar 1,2-cycloaddition reactions. Thus benzoyl isocyanate reacts with carbodi-imide in a 1 : 1 benzene–ether mixture with formation of 4-imino--1,3-diazetidin-2-one in a yield up to 70% [53,161,164]:



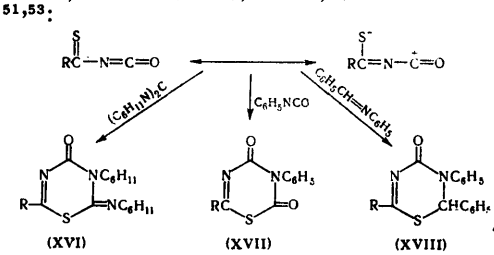
Under similar conditions [68,165] sulphonyl isothiocyanates give rise to quantitative yields of 2-imino-1,3-diazetidin-4--thione:



Another example of dipolar 1,2-addition may be the reaction of acyl isocyanates with *N*-ethylbenzaldoxime in a 1 : 1 benzene–ether solution, which leads to the formation of 1,2,4-oxadiazolidin-5-one in a yield up to 90% [161]:

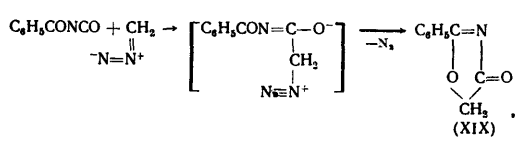


In view of the very pronounced nucleophilic properties of the sulphur atom in thioacyl isocyanates compared with the oxygen atom of acyl isocyanates, the former are more reactive. In addition reactions they probably have the dipolar structure (A) and this accounts for their interaction with carbodi-imides, isocyanates, and benzylideneamine by a 1,4-cycloaddition mechanism with formation of the corresponding substituted six-membered heterocyclic compounds—2-imino-1,3,5-thiadiazin-4-one (XVI), 1,3,5--thiadiazin-2, 4-dione (XVII), and 1,3,5-thiadiazin-4-one (XVIII) [51,53]:



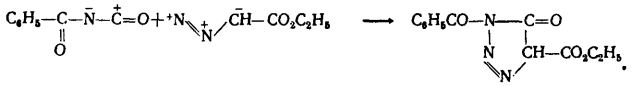
11. Reactions of Acyl Isocyanates and Isothiocyanates with Diazo-alkanes

The reactions of acyl isocyanates and isothiocyanates with diazo-alkanes began to be studied recently. It has been shown that benzoyl isocyanate reacts with diazomethane to form 2-phenyl-oxazol-4-one in yields up to 70% [166]. The mechanism of this reaction may be regarded as addition of diazomethane to the polarised carbonyl bond of the isocyanate in the first stage with subsequent elimination of nitrogen and formation of 2-phenyloxazol-4-one (XIX):

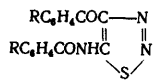


The structure of the latter has been demonstrated by hydrolysis and the formation of the amide of benzoylglycolic acid.

Benzoyl isocyanate reacts readily with ethyl diazoacetate, with formation of the ethyl ester of 1-benzoyl--1,2,3-triazol-5-one-4-carboxylic acid [167,168]:



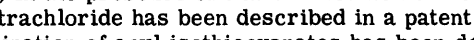
Acyl isothiocyanates react with diazomethane, ethyldiazoacetate, diazoacetamide, ω-diazoacetophenone etc. [168-172] with formation of 1,2,3-thiadiazole derivatives. Substituted ω-diazoacetophenone derivatives react with benzoyl isothiocyanate to form 5-acetamide-4-benzoyl--1,2,3-thiadiazole:



Usually these reactions take place at 100°C and are virtually complete in 30–120 min [172]. The nature of the substituent in the diazoacetophenone molecule has a significant influence on the rate of the addition reaction. With electron-acceptor substituents, the reaction takes place very slowly or not at all, while electron-donor substituents accelerate the process [170].

12. Reaction of Acyl Isocyanates and Isothiocyanates with Chlorine

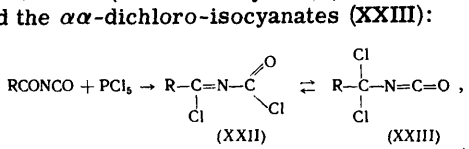
The chlorination of benzoyl isothiocyanates was first studied by Johnson and coworkers [173,174]. The chlorination of acyl isothiocyanates $CH_3(CH_2)_n$-CONCS (where n=2,6,10, 12, or 14) in the presence of titanium tetrachloride in carbon tetrachloride has been described in a patent [175]. The chlorination of acyl isothiocyanates has been described in detail in the papers of Derkach and coworkers [176,177], who established that the chlorination products are the sulphenyl chloride derivatives of the chlorides of N-acyliminocarbonic acids (XX) and the dichlorides of N-acyliminocarbonic acids (XXI):



The dichlorides (XXI) are valuable starting materials for the synthesis of new heterocyclic compounds [178].

13. Acyl Isocyanates and Acyl Isothiocyanates in Reactions with Phosphorus Pentachloride

The reaction of acyl isocyanates with phosphorus pentachloride was studied only by Neidlein and coworkers [178-182]. On prolonged heating in chlorobenzene of benzoyl isocyanate and phosphorus pentachloride in proportions of 1 : 1, the chloride of α-phenyl-α-chloroalkylidene carbamic acid forms. Aliphatic acyl isocyanates react with phosphorus pentachloride to form an equilibrium mixture of the chlorides of N-(α-chloroalkylidene)carbamic acids (XXII) and the αα-dichloro-isocyanates (XXIII):



where R = $ClCH_2$, Cl_2CH, Cl_3C, etc. The mode of reaction was confirmed by infrared spectroscopy [181].

14. Acyl Isocyanates and Acyl Isothiocyanates in Alkoxycarbonylation Reactions

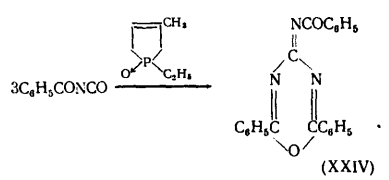
Acyl isothiocyanates readily enter into the alkoxycarbonylation of acylation reaction with phenoxides and phenyl sulphides. The presence in the phenoxide molecule of electronegative substituents facilitates the reaction [183]:



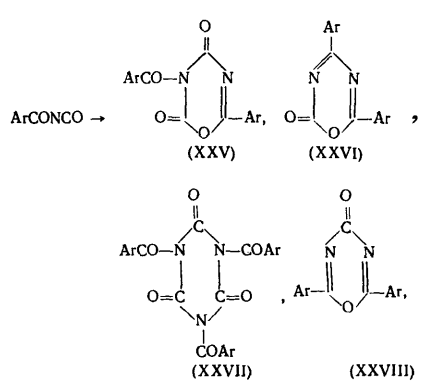
where Y = O or S and R′ = C_2H_5O, C_4H_9O, CH_3, C_6H_5, or C_2H_5S. It has been established that the acylating activity of acyl thiocyanates and isothiocyanates decreases in the series RCOSCN > RCONCS > ROCOSCN > ROCONCS > > RSCONCS. This reaction has found practical application in the synthesis of *OS*-di(alkoxycarbonyl)thiamine [78].

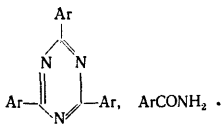
15. Dimerisation, Trimerisation, and Polymerisation of Acyl Isocyanates and Isothiocyanates

The first unsuccessful attempt to study the polymerisation of acyl isocyanates was undertaken in 1960. [184] The trimerisation of benzyol isocyanate under the action of a phospholene oxide in dry xylene with refluxing was studied by McGrew et al. [185]. On the basis of infrared absorption spectra and thermal and hydrolytic degradation of the reaction products, the authors attributed the structure of 4-benzoylimino-2,6-diphenyl-1,3,5-oxadiazine (XXIV) to the trimerisation product and proposed a mechanism for its formation:



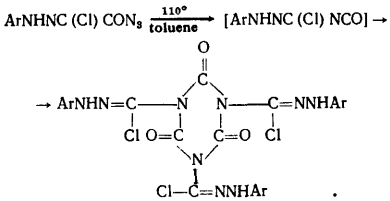
Japanese chemists [186,187] studied in detail the di- and tri-merisation of aroyl isocyanates in ether and cyclohexene in the presence of triethylamine, pyridine 1-oxide, and pyridinium salts as catalysts. They showed that the reaction is very complex. Depending on the conditions, the catalyst and the substituent in the aroyl isocyanate molecule, the products may be 5-aroyl-2-aryl-1,3,5--oxadiazin-4,6-dione (XXV), 2,4-diaryl-1,3,5-oxadiazin--6-one (XXVI), triaroyl isocyanurate (XXVII), 2,6-diaryl--1,3,5-oxadiazin-4-one (XXVIII), and also triaryl-s--triazine (XXIX) and aromatic acid amides (XXX):





(XXIX) (XXX)

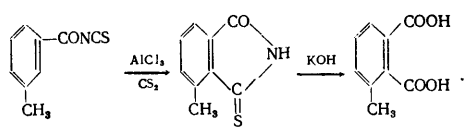
The present authors isolated the trimerisation products of arylazochloroacetyl isocyanates in an attempt to prepare the isocyanates of the arylhydrazones of chloroformaldehyde from arylazochloroacetyl azides [188,189]:



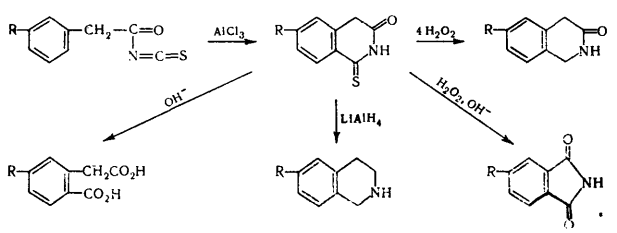
The isothiocyanates of iminocarboxylic acids readily dimerise in the light into quinazoline and *s*-triazine derivatives [190-192].

16. Acyl Isocyanates and Isothiocyanates in Intermolecular and Intramolecular Cyclisation Reactions

The intra- and inter-molecular cyclisation of acyl isothiocyanate was first studied in detail by Smith and Kan [193,194] and a novel method for the preparation of phenyl-substituted dicarboxylic acids was proposed on its basis:



It is noteworthy that the reaction does not take place with *p*-toluoyl, benzoyl, 3-methoxybenzoyl, 3,5-dimethoxybenzoyl, 3,4,5-trimethoxybenzoyl, and α-naphthoyl isothiocyanates. The cyclisation takes place smoothly when methyl groups are present in the *meta*-position with respect to the carbonyl isothiocyanate group (3-methyl, 3,5-dimethyl). Furthermore, it requires the presence of two free *ortho*-positions. When *m*-toluoyl isothiocyanate is used, the cyclisation takes place with formation of 2-methylphthalic acid only. The use of phenylacetyl isothiocyanate and its derivatives in a similar intramolecular cyclisation reaction opens up extensive possibilities for the synthesis of homophthalic acids and a number of heterocyclic compounds, in particular 1,2,3,4-tetrahydroisoquinoline and phthalimide:



In contrast to *m*-toluoyl isothiocyanate, *m*-tolylacetyl isothiocyanate cyclises exclusively in the para-position with respect to the methyl group with formation of 5-methyl-2a-thiohomophthalimide or 6-methyl-1-thio-1,2,3,4-tetrahydro-*2H*,*4H*-isoquinoline-1,3-dione†, 4-methylphthalimide and 4-methylhomophthalic acid being obtained from the latter.

3-Thienoyl isothiocyanate, βγ-saturated aliphatic carbonyl isothiocyanates and cyclohexen-1-ylacetyl isothiocyanate also undergo intermolecular cyclisation [193,194] Despite certain limitations, this reaction is of fundamental importance. It makes it possible to obtain a number of heterocyclic compounds, and from the latter substituted *ortho*-dicarboxylic acids, which are difficult to obtain.

17. Other Reactions of Acyl Isocyanates and Isothiocyanates

In 1966 Neidlein [195] described the reaction of carbonyl and sulphonyl isocyanates with hydrazoic acid under pressure in benzene solution, with cooling, leading to the formation of the azides of *N*-carbonyl- and *N*-sulphonyl-carbamic acids (XXXI) respectively:

$$AcNCO + HN_3 \rightarrow \underset{(XXXI)}{AcNHCON_3},$$

where Ac = RCO or p-$CH_3C_6H_4SO_2$.

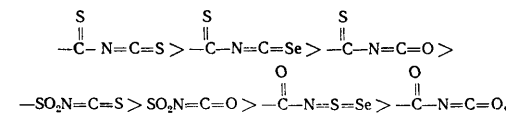
Carbonyl isothiocyanates react relatively smoothly also with dialkylsulphoxides to form *N*-acylsulphilimines [180]:

$$RCONCO + (R')_2SO \rightarrow RCONS(R')_2 + CO_2.$$

In a similar reaction sulphonyl di-isocyanates react with two moles of dimethylsulphoxide to form *NN*-sulphonylbis-(*SS*-dimethylsulphilimine) $(CH_3)_2S{=}N{-}SO_2{-}N{=}S(CH_3)_2$ in 54% yield. Chlorosulphonyl isocyanate gives rise to a 75% yield of *N*-chlorosulphonyl-*SS*-dimethylsulphilimine [196]:

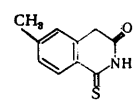
$$ClSO_2NCO + (CH_3)_2SO \rightarrow (CH_3)_2S{=}NSO_2Cl \xrightarrow[HCl]{H_2O} (CH_3)_2S{=}N{-}SO_3OH.$$

In our examination of the chemical properties of acyl isocyanates and isothiocyanates, we frequently mentioned the unequal activities of the latter in various chemical reactions. The data reviewed here make it possible to arrange thio(seleno)acyl and acyl iso(thio, seleno)cyanates in the following series of decreasing activity in various chemical reactions:



VI. APPLICATIONS OF ACYL ISOCYANATES, ISOTHIOCYANATES, AND ISOSELENOCYANATES

Above it was shown that acyl isocyanates, isothiocyanates, and isoselenocyanates are very reactive organic compounds. They enter into a wide variety of chemical reactions, yielding organic products which are valuable for syntheses and for practical applications: urethanes, thiourethanes, urea, thiourea, selenourea, semicarbazides, thiosemicarbazides, and selenosemicarbazides. Various

† 

(Ed. of Translation).

derivatives of heterocyclic compounds have been prepared from them: pyrimidine [101,103,114,117,139,140,143,144,148,149,297], thiazole [111,112,126-128], imidazole [46,116,184], triazole [52,131,166], triazine [52,114,185,188,189], isothiazole [143,144], benzoxazine [145], quinazoline [148], oxathiolane [154], oxazoline [161,163], thiazoline [53,161,163], thiazine [53], thiadiazine [51,53], thiadiazole [170-172], oxadiazine [185-187], isoquinoline [194], and others.

Acyl isocyanates and isothiocyanates have found wide application for the identification of alcohols [88] and amines [98,106] and also for the determination of the structure of nucleic acids and peptides [46,101,103,198]. They are used as copolymers [23,38,199]. Valuable rubbers and fire-resistant polyurethane foam plastics have been obtained on their basis [102].

Acyl isocyanates and isothiocyanates and derivatives based on them exhibit a wide spectrum of biological and chemotherapeutic activity. Compounds with pesticide activity have been found among them [200]. A number of the substances synthesised have been tested as antidiabetic agents [122,124] and depressants of the central nervous system [201].

Many organic substances synthesised using acyl isocyanates and isothiocyanates exhibit considerable antitubercular [202], hypoglycemic [121], anaesthetic [203], anticonvulsant [202,204], and hypnotic [16] activity.

After this review had been submitted for publication, the following papers appeared.

1. On the methods of synthesis of acyl isocyanates [205-210,250-253], acyl isothiocyanates [211,212,251,254], thioacyl isocyanates [85,213,248], sulphinyl isocyanates [214], sulphonyl isocyanates [215-217,255-257], and sulphonyl isothiocyanates [218,220].

2. On chemical reactions with alcohols [221,258-260], mercaptans [222], amines [223-230,261-267], amides [231], hydrazines [232,233,268,269], aziridines [234], compounds containing an active hydrogen atom [235-239,270,271], dienes [240,272-274], Grignard reagents [241], azomethines [242,243,275], chlorine [244,245], nitrosonium salts [246], phosphorus pentasulphide [247], hydrazoic acid [248,276], heterocyclic compounds [248,249], hydroperoxides [277], carboxylic acids [278], and sulphonic acids [279].

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