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Acyl Isocyanates

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The methods of preparation and the reactions of acyl isocyanates are considered. The bibliography includes 197 references.

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I. INTRODUCTION

The advances in the chemistry of organic isocyanates have been reviewed fairly regularly[1-5] but these reviews dealt only with aryl and alkyl isocyanates. Recently new classes of compounds in which the isocyanate group is linked to silicon[6,7], phosphorus[6,8-13], difluorophosphoryl, fluorocarbonyl[14] and thioacyl[15-20], sulphonyl[21], etc. groups have been discovered and their properties investigated. The chemistry of each of these classes of isocyanates is fairly specific and requires a separate review. A recent review dealing with the chemistry of acyl and sulphonyl isocyanates, isothiocyanates, and isoselenocyanates[22] emphasises the similarity of the properties and not the specific features of the individual classes of isocyanates. Consequently reviews of such general type and those on specific branches of the chemistry of isocyanates are not mutually exclusive, supplementing one another. The inevitable repititions can be justified in each case by a new approach to the analysis of the literature data and new conclusions.

Such a special review on the chemistry of sulphonyl isocyanate was published recently[21] but the advances in the chemistry of acyl isocyanates have not as yet been reviewed.

Acyl isocyanates were obtained for the first time in 1862 by Schützenberger[23,24], i.e. 13 years after Würtz's discovery of organic isocyanates[24]; however, convenient methods for their synthesis became available only recently[26], which stimulated more extensive studies on these compounds.

Acyl isocyanates are chemically more reactive than the widely known[2,3] isocyanic acid esters. The presence of the additional acyl carbonyl group R—CONCO not only increases the reactivity but is also responsible for the ability of these compounds to undergo various reactions involving the formation of heterocycles.

In view of the above considerations, the author assumed that the present review, which deals with the syntheses, properties, and applications of acyl isocyanate and covers the literature up to January 1st, 1968, will be of interest and will stimulate further development of the chemistry of this interesting class of organic compounds.

II. METHODS OF SYNTHESIS OF ACYL ISOCYANATES

The available methods for the preparation of acyl isocyanates can be divided into two types: syntheses where the NCO group is already present in the starting materials and syntheses where it is produced in the course of the reaction.

1. Synthesis by the Reaction of Carboxylic Acid Chlorides with Cyanate Salts

Acetyl isocyanate, together with acetonitrile, was obtained by the reaction of silver cyanate[23,24] or mercury fulminate[27] with acetyl chloride. Under the same conditions, the reaction of silver cyanate and benzoyl chloride yields only benzonitrile[23]. The reaction of mercury fulminate with benzoyl chloride[28,29] or of silver fulminate with benzoyl bromide[30] followed by treatment of the reaction products with water led to the isolation of dibenzoylurea and a product melting at 107°C[28,29], which eventually proved to be (not until 1954) 3,5-diphenyl-1,2,4-oxadiazole[31].

Acetyl and benzoyl isocyanates were obtained in a pure form for the first time in 1903 by slow addition of silver cyanate to an excess of the chloride of the corresponding acid with rapid distillation of the isocyanate produced[32,33].

Billeter's method[32,33] was subsequently improved by Hill and Degnan[34-36] and then by Areus and Prydol[37,38] and until 1962 remained virtually the only method for the synthesis of acyl isocyanates[31,39-42]. In 1963 Steyermark proposed a more convenient method for the preparation of acyl isocyanates by the reaction of carboxylic acid halides with cyanic acid in the presence of organic bases. The yield of acyl cyanates reaches 90%, but in a number of cases the process is complicated by the formation of polymeric products[43,44].

2. The Reaction of Phosgene and Phosgene-Forming Compounds With Acid Amides

The first attempts to prepare acyl isocyanate from carboxylic acid amides were unsuccessful[45-47]. Later, Waltmann and Wolf[48-51] shows that in an autoclave at 150°C a mixture of the amide and phosgene or trichloromethyl formate and other phosgene-forming compounds (among which oxalyl chloride may also be included[52]) in the presence of pyridine forms acylcarbamoyl chloride, which on heating in benzene with calcium oxide yields acyl isocyanate. However, this method did not become as important in the synthesis of isocyanates as the reaction of amines with phosgene[2,3].

The reaction of acid amides with oxalyl chloride proved to be more promising for the synthesis of acyl isocyanates[26,47,53-70]:

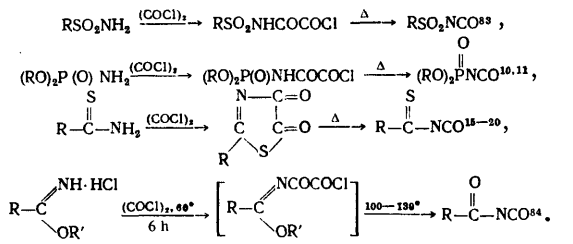
$$RCONH_2 + (COCl)_2 \xrightarrow{-2HCl,\,-CO} RCONCO.$$

The effect of oxalyl chloride on amides was investigated even earlier[71]: with a 1:2 reactant ratio, diacylurea was obtained[47,71,72], the thermal decomposition of which resulted in the formation of an amide, diacetamide, a

nitrile, cyanuric acid, and carbon dioxide[73], while with a 1:1 reactant ratio the products were 2-alkylideneoxazolidine-4,5-dione[47,74-78] and others.

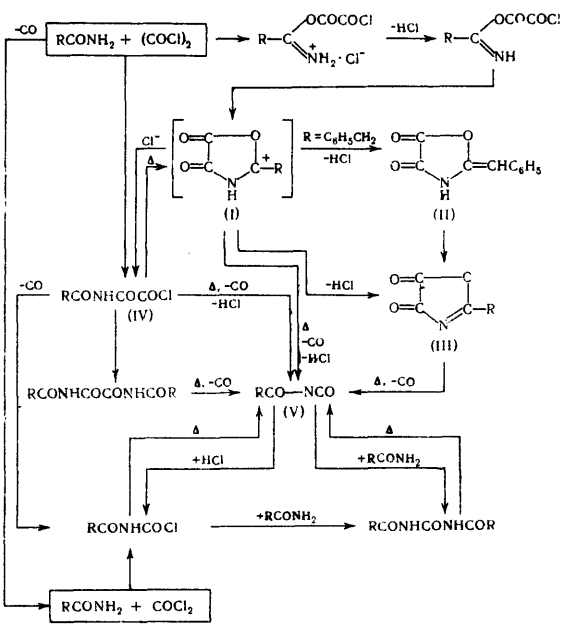
Speziale and Smith[26,47,55] showed that, when the products of the reaction of oxalyl chloride with amides are subjected to thermal decomposition in a vacuum at fairly low temperatures with simultaneous distillation of the decomposition products, aroyl isocyanates are obtained in high yields. The yield of aliphatic acyl isocyanates is usually lower, and in the case of propionyl isocyanate it amounted to only 0.8%[55].

The above method of preparation of aroyl isocyanates was improved by Neidlein[70]. After these investigations, there was a considerable increase of interest also in the chemistry of oxalyl chloride[79-82], which was successfully used in the synthesis of other classes of acyl isocyanates:



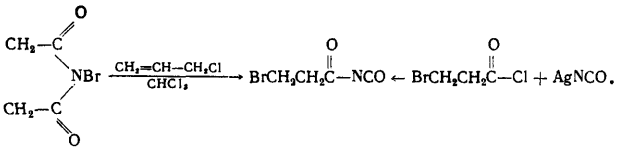
In the reaction of oxalyl chloride with carboxylic acid amides an *O*-aclyation product is probably formed initially and is then converted, with elimination of HCl and CO, either via the intermediate formation of compounds (II), (III), or (IV) or directly, into the acyl isocyanate (V). The low yield of alkanoyl isocyanates compared with that of aroyl isocyanates can probably be accounted for by the different stabilities of compounds (I). By analogy with 2-alkylideneoxazolidine-4,5-dione[76], aryl-containing compounds (I) are more resistant to attack by the chloride ion than their alkyl analogues (Scheme 1)[68].

Scheme 1



For this reason the aryl compound decomposes only on heating in a vacuum and compound (V) is formed in a high yield. The alkyl derivative of compound (I) decomposes already under the reaction conditions with formation of compound (IV), which then enters into a number of side processes (Scheme 1)[66].

The method of preparation of β-bromopropionyl isocyanate by the rearrangement of *N*-bromosuccinimide is in a class by itself[85-88]:



The reaction takes place only in the presence of chloroform or bromoform and certain halogeno-olefins (allyl chloride and bromide, methylallyl chloride, 2,3-dibromopropene, 3-bromo-2-t-butylpropene) in the presence of benzoyl peroxide. In the presence of crotyl bromide, 1-bromopropene, ααα-trichlorotoluene, and a number of other olefins the reaction does not occur. The maximum yield of β-bromopropionyl isocyanate (70%) is attained on refluxing in chloroform for 4 h equimolar amounts of *N*-bromosuccinimide, allyl chloride, and a catalytic amount of benzoyl peroxide[88]. The product was also isolated in 16% yield in the photochemical bromination of 1,4-*endo*-oxocyclohexane with *N*-bromosuccinimide in carbon tetrachloride. The reaction is of a radical type; this type of rearrangement does not occur with either chloro- or iodo-succinimides[86].

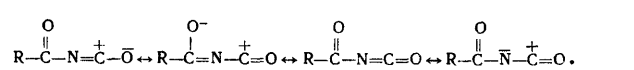
III. PROPERTIES OF ACYL ISOCYANATES

1. Physical Properties

Acyl isocyanates are colourless or yellowish liquids or low-melting solids which can be distilled in a vacuum. They have a sharp odour, and are readily hydrolysed by atmospheric moisture; they dissolve in the majority of organic solvents. Their infrared spectra[89,90] contain absorption bands at 2244 ± 1 cm^{-1} (asymmetric vibrations of the O=C=N group) and 1430 cm^{-1} (symmetrical vibrations of the O=C=N group); the bands at 1740 and 1050 cm^{-1} correspond to the vibrations of the C=O and C–N bonds in the group R–C(O)–N=; the bands due to the deformation vibrations of O=C=N and NC=O groups are located respectively at 632 and 570 cm^{-1}.

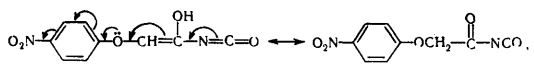
2. Chemical Properties

The characteristic features of the chemical properties of acyl isocyanates are a result of the charge and electron density distribution in the group CONCO, which may be described by the resonance of the following valence structures[91,92]:



Hence it follows that, in contrast to alkyl and aryl isocyanates[93,94], acyl isocyanate are, firstly, more reactive and, secondly, are capable of undergoing not only 1,2-cycloaddition[95,96] but also 1,4-cycloaddition[91,92,97-99] reactions. In some cases the presence of the acyl group may be the cause of other more special properties of acyl isocyanates. Thus the surprisingly effective transmission

of the influence of substituents on the reactivity of aryloxyacetyl isocyanates may be accounted for by the possibility of their tautomerism[68]:

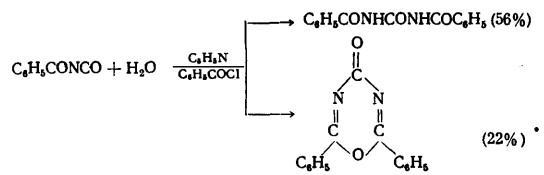


which evidently cannot occur in the case of aryloxyethyl isocyanates.

A. Reactions at Oxygen–Hydrogen and Sulphur–Hydrogen Bonds

The reaction with water of acetyl isocyanate[27], β-bromopropionyl isocyanate, etc.[85,86] yields the corresponding amides and carbon dioxide, the conversion of benzoyl isocyanate being to the extent of 75% into the amide and to the extent of 25% into dibenzoylurea[32].

In 1*N* sodium hydroxide solution benzoyl isocyanate forms only benzamide[37], while in a mixture with aqueous pyridine and benzoyl chloride it gives 56% of dibenzoylurea and 22% of 4-oxo-2,6-diphenyl-1,3,5-oxadiazine[31]. The last product is formed also under anhydrous conditions when the reaction is catalysed by an *N*-substituted pyridinium salt[92,100].



Acids react with acyl isocyanates with much greater difficulty. Thus the reaction with dialkyl phosphites takes place only in the presence of sodium ethoxide or catalytic amounts of triethylamine at 80–90°C over a period of 4 h.[101] The reaction of hydrogen chloride with acyl isocyanates gives the corresponding acylcarbamoyl chlorides[27,48-51].

The reaction of alcohols with acyl isocyanates has been most thoroughly investigated. It has been shown that they react more vigorously than phenols[66], giving good yields of acyl carbamates[26,27,32,38,55-57,60,64,66,68,85,88,101-104].

Polyhydric alcohols form with acyl isocyanates products corresponding to different degrees of addition—monoacyl, diacyl, etc. carbamates[88,102,105,106].

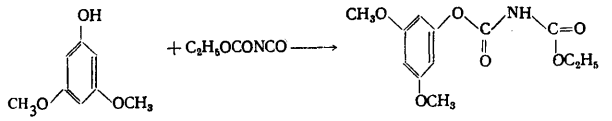
It has been erroneously assumed that the reaction of acetyl isocyanate with glycol gives a bis-addition product, while benzoyl isocyanate forms only the monoaddition product even when present in an excess. Later it was shown[106] that, regardless of their structure, acyl (and aroyl) isocyanates react with polyhydric alcohols to form as a rule polyaddition products, while with phenols monoaddition products are obtained. Thus, regardless of their structure, the reactant ratio, and the presence or absence of water in the reaction medium, the reaction of acyl (and aroyl) isocyanates with glycerol yields only products of addition to all three hydroxy-groups. Monoaddition could be achieved only by the action of 2,4-dichlorophenoxyacetyl isocyanate on isopropylidene-glycerol with subsequent ethanolysis of the product[106].

The presence in the alcohols of other functional groups—halogen atoms[55,57,66,88,102,105,107] and nitrile[88,102], carbonyl[88], carboxy-[102], dimethylamino-[57], xanthogenyl and dithiocarbamoyl groups[107,108], or unsaturated carbon–carbon bonds[55,57,66,88,102]—does not usually alter the normal course of their addition to acyl isocyanates.

However, if the alcohol molecule contains another functional group where the electron density at the constituent atom is higher than at the oxygen atom, for example NH_2, then the acyl isocyanate reacts preferentially with this group rather than with the hydroxy-group. The reaction with ethanolamine takes place stepwise in this way[39,105,106]:

$$HOCH_2CH_2NH_2 \xrightarrow{RCONCO} RCONHCONHCH_2CH_2OH \xrightarrow{RCONCO} \rightarrow RCONHCONHCH_2CH_2OCONHCOR.$$

Alkoxycarbonyl isocyanates react with 3,5-disubstituted phenols in two ways, depending on the electron-donor properties of the substituents: if the substituents are powerful donors (R_2N), then the isocyanate adds to a carbon atom of the aromatic ring (see Russ. p. 133), but if their electron-donor properties are less pronounced (OCH_3), then normal addition to the OH group takes place[109]:



Oximes, which are more basic than phenol[110], react with acyl isocyanates just as vigorously as alcohols and at room temperature form as a rule stable crystalline acyl carbamoyloxyoximes[111-113]:

$$\rangle C{=}N{-}OH + RCONCO \xrightarrow{20^\circ} RCONHCOON{=}C\langle .$$

However, the corresponding derivatives of acetaldoxime can be obtained only at 0°C, since at 20°C they readily decompose[111].

The reactivity of oximes depends to a considerable degree on the steric configuration of the substituent in the *cis*-position relative to the hydroxy-group and to a lesser extent on the bulk of the *trans*-substituent and the electronic effects of the substituents. For this reason, ketoximes are less reactive than aldoximes and among the latter the *syn*-isomer is the more reactive[112].

The reaction of acyl isocyanates with *syn*- and *anti*-benzaldoximes yields only *syn*-acylcarbamoylbenzaldoxime[111].

Mercaptans react with acyl isocyanates less vigorously than their oxygen analogues, forming the corresponding thiolocarbamates[26,56,58,66]:

$$R{-}SH + R'CONCO \xrightarrow{20^\circ} R'CONHCOSR.$$

The reaction of terephthaloyl di-isocyanate with thiophenol yields terephthaloyl bis(phenylthiolocarbamate)[98].

B. Reactions at Nitrogen–Hydrogen Bonds.

Ammonia and primary and secondary amines react vigorously with acyl isocyanates at room temperature with formation of the ureides of the corresponding acids[26,32,38,39,42,57,68,84,85,88,101,103]. With increase of the basicity of the amines, their reactivity also rises[67,68].

By virtue of the exceptional ease and completeness of this reaction, it is frequently used to identify new acyl isocyanates[27,43,47,56,59]. Bis-acyl isocyanates also react readily with amines[98].

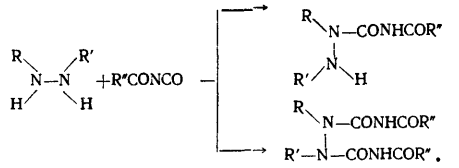
Polyfunctional compounds containing, apart from the amino-group, multiple bonds[68] and HO,[39,105,114] NO_2,[67,114] Me_2N,[67] COOEt, COOH,[114] and other groups form primarily ureides. When the molecule contains two amino-groups or an amino-group and a hydroxy-group, initially one NH_2 group reacts completely[39,106], and then, in the presence of an excess of acyl isocyanate, addition to the second NH_2 or OH group takes place[105,106,114].

Hydroxylamine and its derivatives react with acyl isocyanates in the same way as other amino-alcohols with formation of hydroxy- or alkoxy-ureas [40,62,69,114]:

$$RO{-}NH_2 + R'CONCO \rightarrow RONHCONHCOR'.$$

The reaction takes place readily not only with the free bases [62,69,114] but also with hydroxylammonium salts in the presence of pyridine [40].

Like other diamines [32,105,114], *hydrazine and its derivatives* can react with acyl isocyanates to form two series of compounds [32,38,61,115,116]:



However, the mode of reaction depends little on the reactant ratio; the decisive factors here are the nature of the acyl isocyanate and the substituents and the nitrogen atoms of the hydrazine. Hydrazine hydrate contains two equivalent (as regards nucleophilic properties) nitrogen atoms and therefore its reaction with benzoyl isocyanate yields only 1,6-dibenzoylurea [38].

The basicities of the two nitrogen atoms in arylhydrazines are not the same and therefore the nitrogen atom furthest removed from the aryl group enters into the reaction [38].

The structure of 4-benzoyl-1-phenylsemicarbazide obtained for the first time in this way by Billeter [32] was subsequently demonstrated by Arcus and Prydal [38], who showed at the same time that 4-nitro- and 2,4-dinitrophenylhydrazines also react. The reaction with terephthaloyl di-isocyanate takes place similarly but involves two isocyanate groups [98].

Thus aroyl isocyanates [32,38,98] form with hydrazine monoaddition products. In contrast to them, acyl isocyanates tend to form diadducts [32,61,69,115,116].

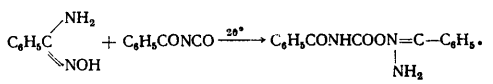
However, α-halogenoacyl isocyanates react with phenyl- and 4-nitrophenyl-hydrazines to form both di- and monoaddition products, the yield of which varies with the reaction ratio [115].

The more reactive aryloxyacetyl isocyanates readily form in high yields (similarly to aroyl isocyanates) predominantly monoadducts with phenyl- and 4-nitrophenylhydrazines [61,69]. In contrast to the latter, the reactions with 2,4-dinitrophenylhydrazine of all acyl isocyanates, regardless of their structure, result only in monoaddition products [115].

The reaction of aldehyde and ketone hydrazones with acyl isocyanates in molar proportions of 1:1 results in ready formation of the corresponding 4-acylsemicarbazones [117,118] and the reaction in proportions of 2:1 yields of diadducts, which probably have the structure of 3-alkylideneamino-1,5-diacylbiuret [119]:

$$R_2C{=}NNH_2 + 2R'CONCO \rightarrow R'CONHCON(N{=}CR_2)CONHCOR'.$$

Initially it was postulated that the reaction of acyl isocyanates with *amidoximes* results in the formation of *N*-(acylcarbamoyl)amidoximes [120], but NMR and infrared spectroscopic measurements showed that the addition is exclusively to the oxygen atom:

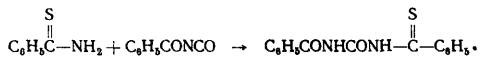


Acyl isocyanates react with *acid amides* with greater difficulty than with the compounds examined above, containing N–H, O–H, or S–H bonds. The reaction takes place on heating and leads to the formation of the corresponding diacylureas [27,28,30,32,45,71,121–123].

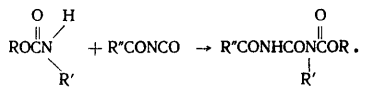
Sulphonamides form with acyl isocyanates *N*-sulphonyl-*N'*-acylureas [32,124]:

$$R{-}SO_2NH_2 + R'CONCO \rightarrow R'CONHCONHSO_2R.$$

The reaction of *thiobenzamide* and benzoyl isocyanate on refluxing in benzene yields *N*-benzoyl-*N'*-thiobenzoylurea [125]:



Carbamates react with acyl isocyanates more readily than carboxylic acid amides, forming in all cases, in contrast to aryl isocyanates [126–128], the corresponding acyl allophanates [61,69,114,129]:



Ureas [35] *and thioureas* [36] react with acyl isocyanate, forming respectively acylbiurets and acylthiobiurets [33–36,39].

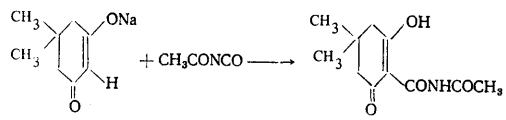
Hydrazoic acid reacts vigorously with acyl isocyanates giving high yields of acylcarbamoyl azides which are stable at room temperature [130,131]:

$$N{\equiv}N{=}N{-}H + RCONCO \rightarrow RCONHCON_3.$$

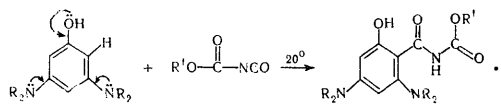
The reaction with terephthaloyl di-isocyanate takes place similarly [98].

C. Reactions at Carbon–Hydrogen Bonds and with Grignard Reagents

The carbon–hydrogen bond can be readily involved in the reaction with acyl isocyanates if the electron density at the carbon atom is sufficiently high. This reaction usually gives acylamides [109,132]. Thus in the synthesis of tetracycline an acetylcarbamoyl substituent was introduced into dimedone with the aid of acetyl isocyanate [132]:



Ethoxycarbonyl isocyanate enters into a similar reaction with somewhat greater difficulty [132]. Thus the reaction with 3,5-di(dialkylamino)phenol yields 2,4-dialkylamino-6-hydroxybenzoyl carbamates [109]:



The reaction of a *Grignard reagent* with acyl isocyanates also gives diacylamines together with a number of other products, the mechanism of the formation of which is still obscure [133]:

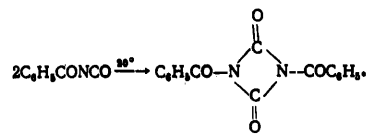
$$RMgX + C_6H_5CONCO \xrightarrow{20^\circ} C_6H_5CONHCOR + C_6H_5COR + C_6H_5CONHCONHCOC_6H_5 + C_6H_5CONHCONH_2 + C_6H_5CONH_2 + C_6H_5CONHCOC_6H_5.$$

The composition of the reaction products depends on the ratio and order of addition of the starting materials and the nature of the organic group and the halogen in the organomagnesium compound.

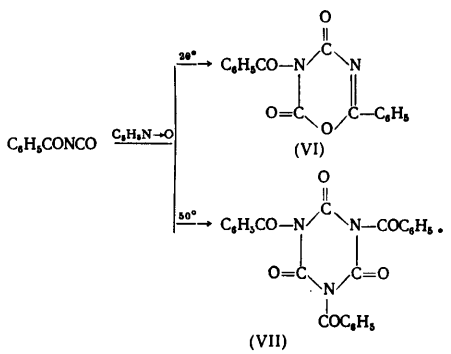
D. 1,2- and 1,4-Cycloaddition Reactions

a. Dimerisation and trimerisation of acyl isocyanates. Both 1,2- and 1,4- cycloaddition reactions are characteristic of acyl isocyanates[99] and therefore in the presence of the usual catalysts for the polymerisation of isocyanates (pyridine[134], triethylamine[135], and others) two series of dimers and the corresponding trimers are formed[92,95,100].

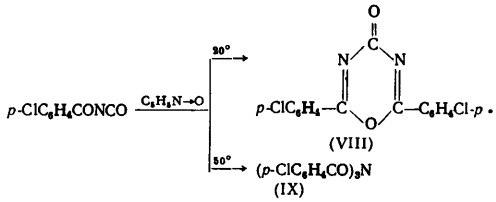
By treating benzoyl isocyanate with pyridine, Neidlein[95] obtained 82% yield of the benzoyl isocyanate dimer (1,3-dibenzoyluretidine-2,4-dione):



By the action of pyridine 1-oxide on benzoyl isocyanate at 20° and 50°C, Tsuge and Mizuguchi[92,100] obtained respectively the isomeric dimer [5-benzoyl-4,6-dioxo-2-phenyl-1,3,5-oxadiazine (VI)] and trimer [tribenzoyl isocyanurate (VII) (m.p. 162°C)]:



The polymerisation reaction is influenced not only by temperature but also by the nature of the catalyst and the substituent in the benzene ring[92,100]. Thus when *p*-chlorobenzoyl isocyanate is treated with pyridine 1-oxide at 20°C, the product is 2,6-di-(*p*-chlorophenyl)-4-oxo-1,3,5-oxadiazine (VIII), while at 50°C tri-(*p*-chlorobenzoyl)amine (IX) is formed:



Similarly at 50°C *p*-nitrobenzoyl isocyanate yields tri-(*p*-nitrobenzoyl)amine together with a small amount of 2,6-di-(*p*-nitrophenyl)-4-oxo-1,3,5-oxadiazine.

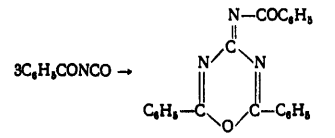
In the presence of tin tetrachloride benzoyl and *p*-methoxybenzoyl isocyanate are converted into the corresponding trimers.

Triethylamine converts benzoyl isocyanate at 50°C into the dimer (VI); at 80°C 2,4-diphenyl-6-oxo-1,3,5-oxadiazine is formed together with a small amount of tribenzoylamine and triphenyl-*s*-triazine.

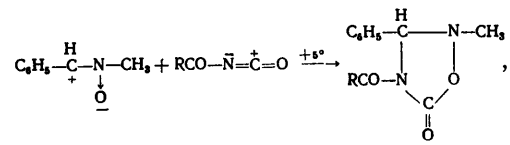
Under these conditions, *p*-methoxybenzoyl isocyanate forms a trimer and *p*-chloro- and *p*-nitro-benzoyl isocyanates are converted into the corresponding 6-oxo-1,3,5-oxadiazines.

Regardless of the nature of the substituent in the acyl isocyanate, *N*-substituted pyridinium salts in all cases lead to the formation of the same products—2,6-diaryl-4-oxo-1,3,5-oxadiazines[92,100].

Phospholen oxides convert benzoyl isocyanate into 4-benzamido-2,6-diphenyl-1,3,5-oxadiazine[136]:

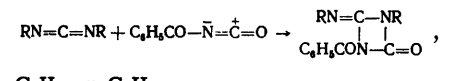


b. 1,2-Cycloaddition reactions. The reaction of *N-methyl benzaldoxime* with acyl isocyanates yields 1,2-cycloaddition products—4-acyl-2-methyl-3-phenyl-1,2,4-oxadiazolidin-5-one[95,99]:



where R = C_6H_5 or CH_2Cl.

Carbodi-imides add to benzoyl isocyanate with formation of 1-benzoyl-4-phenylimino-1,3-uretidin-2-one[95,99]:

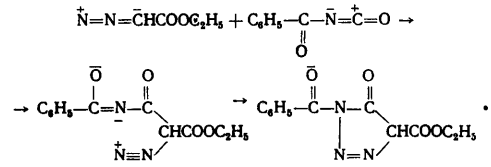


where R = C_6H_5 or C_6H_{11}.

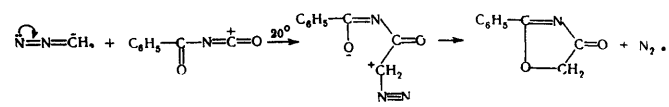
1,3-Dienes (butadiene, isoprene, 2,3-dimethylbutadiene, cyclopentadiene, etc.) react with acyl isocyanates similarly to carbodi-imides, forming the corresponding β-lactams[96]:



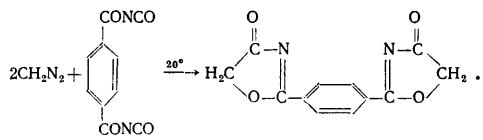
Diazoacetic ester, which may be regarded as a 1,3-dipole, forms with benzoyl isocyanate the ethyl ester of 1-benzoyl-5-oxotriazole-4-carboxylic acid. Probably the reaction takes place in two stages: initially an adduct is formed, which then undergoes intramolecular cyclisation[91]:



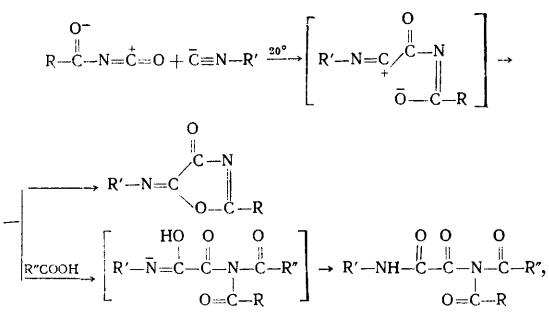
c. 1,4-Cycloaddition reactions. In contrast to diazoacetic ester, *diazomethane* reacts with benzoyl isocyanate as a 1,1-dipole[91], which results in the formation of 2-phenyl-4-oxazolone. Here too the initially formed adduct undergoes subsequently intramolecular cyclisation[97-99]:



Similarly the reaction of terephthaloyl di-isocyanate with diazomethane readily yields 1,4-di-(4-oxo-Δ^3-oxazolin-2-yl)benzene[98]:



Isonitriles, which are also 1,2-dipoles[91,99,137], react with acyl isocyanates to give 2-aryl(alkyl)-5-aryl(alkyl)-imino-oxazolin-4-ones. The reaction evidently takes place as in the preceding cases, via an intermediate adduct, which, in the absence of other reactants, undergoes subsequent intramolecular cyclisation[91]. However, when the reaction mixture contains an acid, the latter probably prevents the cyclisation of the intermediate, forming a second intermediate which is subsequently converted into a linear mixed amide[138]:

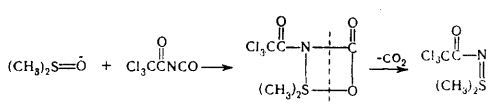


where R = R′ = R″ = C_6H_5 or C_6H_{11}.

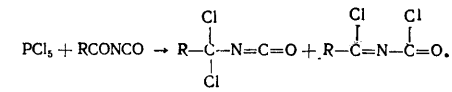
Di-isonitriles react similarly. 1,4-Di-isocyanobenzene and 1,4- and 1,3-di-isocyanocyclohexanes readily react with benzoyl isocyanate to form a mixture of the *cis*- and *trans*- isomers respectively of 5,5′-(*p*-phenylenedinitrilo)bis(2-phenyl-2-oxazolin-4-one and 5,5′-[1,3(or 1,4)-cyclohexylenedinitrilo)bis(2-phenyl-2-oxazolin-4-one[137].

E. Substitution Reactions

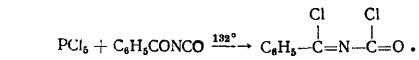
a. Reactions with elimination of CO from the isocyanate group. The reaction of *dimethyl sulphoxide* with dichloroacetyl isocyanate at 20°C in ether and with trichloroacetyl isocyanate (mixture refluxed in acetonitrile) gives high yields of the corresponding *N*-acylsulphimines[139]. By analogy with sulphonyl isocyanates[140], the reaction of acyl isocyanates probably takes place via 1,2-cycloaddition with subsequent elimination of carbon dioxide:



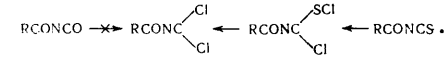
b. Reactions with elimination of an oxygen atom. *Phosphorus pentachloride chlorinates* acyl isocyanates in different ways depending on the nature of the acyl group, but this always involves only the elimination of one oxygen atom from the acyl carbonyl[141,142]. On prolonged heating with phosphorus pentachloride, mono-, di-, and tri-chloro acetyl isocyanates form a mixture of αα-dichloroalkyl isocyanate and α-chloroalkylidenecarbamoyl chloride:



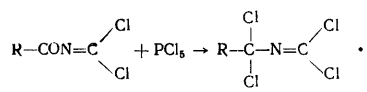
Under these conditions, benzoyl isocyanate yields only α-chlorobenzylidenecarbamoyl chloride[141,142]:



More extensive chlorination of benzoyl isocyanate could not be achieved[141]. The dichlorides of *N*-acylisonitriles have been obtained by the chlorination of acyl isothiocyanates[141-146]:



On heating with phosphorus pentachloride, the dichlorides yield products corresponding to more extensive chlorination of acyl isocyanates[141,142]:



IV. APPLICATIONS OF ACYL ISOCYANATES

Higher (stearyl, palmityl, etc.) acyl isocyanates have been patented as agents for imparting water-repellent properties to textiles[48-51]. The possibility of using acyl isocyanates for the synthesis of polymers[147] and for the identification of alcohols[88] is being investigated. Acyl isocyanates are used in preparative organic chemistry for the synthesis of a wide variety of different classes of compounds: ureides[42,56,57,59,104,114,121-124,148], acyl carbamates[60,102,104,108,115,149-156], acyl thiolcarbamates[58,157], acylbiurets[34-36], acyl alkoxyureas[40,158], acyl allophanates[68,129], acylsemicarbazides[61,69,115], acylcarbamoyliminophosphoranes[130], *N*-alkylidene-1-aminohydantoins[117], 1,5-diaryl-3-hydroxy-1,2,4-triazoles[38], benzoxazines[109], and other heterocyclic compounds[108,159,160] with biological activity[148,150-156,161,162-179]. Halogenoacyl carbamates obtained in this way have been patented as stabilisers for photographic emulsions[104].

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During the period when this review was being dealt with by the editors, the following papers were published.

1. *On the methods of preparation*: from oxalyl chloride and imino-esters[180,181] or chloroimino-esters[182] of carboxylic acids or the amides of chrysanthemic acid[183] and from trifluoroacetic anhydride and isocyanic acid[184].

2. *On chemical reactions*: with hydrazines[185,186], alcohols, mercaptans and amines[187-189], enamines[190], ethyleneimine[191], 2-aminothiazoles[192], *N*-(trimethylsilyl)-dialkylamines[193], hydroperoxides[194], substituted ketens[195], perchloric acid[196], and dienes[197].

REFERENCES

1. J. H. Saunders and R. J. Slocombe, Chem. Rev., **43**, 203 (1948).
2. A. A. Blagonravova and G. A. Levkovich, Uspekhi Khim., **24**, 93 (1955).

3. R.G. Arnold, J.A. Nelson, and J.J. Verbanc, Chem. Rev., 57, 47 (1957).
4. J.H. Saunders and K.C. Frisch, "Polyurethanes, Chemistry and Technology. Part I", New York, Interscience, 1962.
5. C.V. Wilson, Org. Chem. Bull., 35, No. 2, 3 (1963).
6. G.S. Forbes and H. Anderson, J. Amer. Chem. Soc., 62, 761 (1940).
7. J. Goubeau and D. Paulin, Chem. Ber., 93, 1111 (1960).
8. H. Anderson, J. Amer. Chem. Soc., 64, 1757 (1942).
9. A.V. Kirsanov and N.N. Zhmurova, Zhur. Obshch. Khim., 27, 1002 (1957).
10. L.I. Samarai and G.I. Derkach, Zhur. Obshch. Khim., 35, 755 (1965).
11. L.I. Samarai and G.I. Derkach, Zhur. Obshch. Khim., 36, 1433 (1966).
12. K. Utvary, E. Freundlinger, and B. Gutmann, Monatsh, 97, 348 (1964).
13. A.C. Haven, Jnr., J. Amer. Chem. Soc., 78, 842 (1956).
14. O. Glemser, U. Biermann, and M. Fild, Chem. Ber., 100, 1082 (1967).
15. J. Goerdeler and H. Schenk, Chem. Ber., 98, 2954, 3831 (1965).
16. J. Goerdeler and H. Schenk, Chem. Ber., 99, 782 (1966).
17. H. Schenk, Chem. Ber., 99, 1258 (1966).
18. J. Goerdeler and K. Jones, Chem. Ber., 99, 3572 (1966).
19. R. Weiss, Chem. Ber., 100, 865 (1967).
20. J. Goerdeler and R. Weiss, Chem. Ber., 100, 1627 (1967).
21. H. Ulrich, Chem. Rev., 65, 369 (1965).
22. M.O. Lozinskii and P.S. Pel'kis, Uspekhi. Khim., 37, 840 (1968) [Russ. Chem. Rev., No. 5 (1968)].
23. K. Schützenberger, Compt. rend., 54, 154 (1862).
24. K. Schützenberger, Annalen, 123, 271 (1862).
25. A. Würtz, Annalen, 71, 326 (1849).
26. A.J. Speziale and L.R. Smith, J. Org. Chem., 27, 3742 (1962).
27. R. Scholl, Ber., 23, 3505 (1890).
28. A.F. Holleman, Ber., 23, 2998 (1890).
29. A.F. Holleman, Rec. Trav. chim., 10, 65 (1891).
30. H. Wieland and A. Hochtlen, Annalen, 505, 237 (1933).
31. R.H. Terss and W.E. McEwen, J. Amer. Chem. Soc., 76, 580 (1954).
32. O.C. Billeter, Ber., 36, 3213, 3218 (1903).
33. O.C. Billeter, German P. 275 215; Chem. Abs., 8, P3350[9] (1914).
34. A.J. Hill and W.M. Degnan, J. Amer. Chem. Soc., 62, 1595 (1940).
35. A.J. Hill and W.M. Degnan, US P. 2 379 486 (1945); Chem. Abs., 40, P175[6] (1946).
36. A.J. Hill and W.M. Degnan, US P. 2 398 003 (1946); Chem. Abs., 40, 3772[9] (1946).
37. C.L. Arcus and B.S. Prydal, J. Chem. Soc., 4018 (1954).
38. C.L. Arcus and B.S. Prydal, J. Chem. Soc., 1091 (1957).
39. H.G. Steinman, G.O. Dook, and H. Eagle, J. Amer. Chem. Soc., 66, 192 (1944).
40. W.A. Lott, J. Bernstein, and B. Stearns, US P. 2 999 110 (1961); Chem. Abs., 56, 7213g (1962).
41. T. Lieser and K. Macura, Annalen, 548, 226 (1941).
42. K. Hasspacher, BRD P. 1 204 220 (1965); Chem. Abs., 3378g (1966).
43. P.R. Steyermark, US P. 3 155 700 (1964); Chem. Abs., 62, 445a (1965).
44. P.R. Steyermark, J. Org. Chem., 28, 586 (1963).
45. K. Schmidt, J. prakt. Chem., 5, 63 (1872).
46. R. Greenhalgh, B.P. 488 036 (1938); Chem. Abs., 33, 178[3] (1939).
47. A.J. Speziale and L.R. Smith, J. Org. Chem., 28, 1805 (1963).
48. E. Waltmann and E. Wolf, German P. 566 603 (1936).
49. E. Waltmann and E. Wolf, Canad. P. 420 235 (1944); Chem. Abs., 38, 3990[8] (1944).
50. E. Waltmann and E. Wolf, US P. 2 173 029 (1939); Chem. Abs., 34, 642[4] (1940).
51. E. Waltmann and E. Wolf, US P. 2 346 202 (1944); Chem. Abs., 38, 4958[1] (1944).
52. H. Staudinger, Ber., 41, 3566 (1908).
53. M. Sulzbacher, Manuf. Chemist, 34, 264 (1963).
54. A.J. Speziale and L.R. Smith, Org. Synth., 46, 16 (1966).
55. A.J. Speziale, L.R. Smith, and J.E. Fedder, J. Org. Chem., 30, 4306 (1965).
56. A.J. Speziale and L.R. Smith, US P. 3 213 135; Chem. Abs., 64, 3353f (1966).
57. A.J. Speziale and L.R. Smith, US P. 3 261 865 (1966); Chem. Abs., 65, 15284d (1966).
58. K.A. Nuridzhanyan and N.P. Bulanova, USSR P. 179 301 Byul. Izobret., No. 5, 9 (1966).
59. K.A. Nuridzhanyan, N.P. Bulanova, and G.Ya. Ermolenko, USSR P. 176 885 (1964); Byul. Izobret., No. 25, 19 (1965).
60. K.A. Nuridzhanyan, N.P. Bulanova, and G.Ya. Ermolenko, USSR P. 179 300 (1964); Byul. Izobret, No. 5, 19 (1966).
61. K.A. Nuridzhanyan, N.P. Bulanova, L.M. Nesterova, L.D. Stonov, and L.A. Bakumenko, USSR P. 189 421 (1965); Byul. Izobret., No. 24, 22 (1966).
62. K.A. Nuridzhanyan, L.M. Nesterova, and N.P. Bulanova, USSR P. 192 797 (1966); Byul. Izobret., No. 6, 24 (1967).
63. K.A. Nuridzhanyan, L.M. Nesterova, and N.P. Bulanova, USSR P. 201 379 (1966); Byul. Izobret., No. 18 (1967).
64. K.A. Nuridzhanyan and G.V. Kuznetsova, USSR P. 216 700 (1967); Byul. Izobret., No. 15, 16 (1968).
65. K.A. Nuridzhanyan, L.M. Nesterova, and N.E. Mironova, USSR P. 232 245 (1967); Byul. Izobret., No. 1, 24 (1969).
66. K.A. Nuridzhanyan, N.P. Bulanova, and L.M. Nesterova, Zhur. Org. Khim., 3, 349 (1967).
67. K.A. Nuridzhanyan, N.P. Bulanova, and L.M. Nesterova, Zhur. Org. Khim., 3, 345 (1967).
68. K.A. Nuridzhanyan, G.V. Kuznetsova, N.P. Bulanova, and A.M. Nesterova, Symposium, "Biologicheskie Akitivnye Soedineniya (Zhurnal Organicheskoi Khimii)" [Biologically Active Compounds (Journal of Organic Chemistry)], Izd. Akad. Nauk SSSR, 1968, p. 290.
69. K.A. Nuridzhanyan, L.M. Nesterova, and N.P. Bulanova, Symposium, "Biologicheskie Akitivnye Soedineniya (Zhurnal Organicheskoi Khimii)" [Biologically Active Compounds (Journal of Organic Chemistry)], Izd. Akad. Nauk SSSR, 1968, p. 297.
70. R. Neidlein, Chem. Ber., 97, 3476 (1964).
71. M.J. Bornwater, Rec. Trav. chim., 31, 118 (1912).
72. O. Scherer, US P. 3 184 507 (1964); Chem. Abs., 60, 12608f (1964).
73. B.W. Stoughton, J. Org. Chem., 2, 514 (1938).

74. R. Stolle and M. Luther, Ber., 53, 314 (1920).
75. G. S. Skinner and C. B. Miller, J. Amer. Chem. Soc., 75, 977 (1953).
76. G. S. Skinner and R. E. Ludwig, J. Amer. Chem. Soc., 78, 4656 (1956).
77. K. R. Markham and I. D. Rae, Australian J. Chem., 18, 1497 (1965).
78. G. S. Skinner and J. F. Perkins, J. Amer. Chem. Soc., 72, 5569 (1950).
79. L. I. Samarai, G. I. Derkach, and V. A. Bondar', "Tezisy IX Mendeleevskogo S'ezda, No. 2, Sektsiya Khimicheskikh Sredstv Regulirovaniya Rosta i Zashchity Rastenii" (Abstracts of the Ninth Mendeleev Congress, No. 2, Section of Chemical Agents for the Regulation of Plant Growth and Plant Protection), Izd. Nauka, Moscow, 1965, p. 49.
80. L. I. Samarai, V. A. Bondar', and G. I. Derkach, Zhur. Org. Khim., 1, 2004 (1965).
81. J. Goerdler and R. Sappelt, Chem. Ber., 100, 2064 (1967).
82. P. S. Stoffel, US P. 3 288 832; Chem. Abs., 66, 28509i (1967).
83. J. E. Franz and C. Osuch, J. Org. Chem., 29, 2592 (1964).
84. L. I. Samarai, V. P. Belaya, and G. I. Derkach, USSR P. 210 140; Byul. Izobret., No. 6, 21 (1968).
85. H. W. Johnson and D. E. Bublitz, J. Amer. Chem. Soc., 79, 753 (1957).
86. J. C. Martin and P. D. Bartlett, J. Amer. Chem. Soc., 79, 2533 (1957).
87. H. W. Johnson, Jnr., and D. E. Bublitz, J. Amer. Chem. Soc., 80, 3150 (1958).
88. H. W. Johnson, Jnr., H. A. Kreyssler, and H. L. Needles, J. Org. Chem., 25, 279 (1960).
89. H. Hoyer, Ber., 89, 2677 (1956).
90. G. Ostrogovich, R. Bacaloglu, and A. Nemes, Stiinte Chim., 10, 167 (1963); Chem. Abs., 61, 2939a (1964).
91. R. Neidlein, Chem. Ber., 97, 3476 (1964).
92. O. Tsuge and R. Mizuguchi, J. Chem. Soc. Japan, 86, 325 (1965); Chem. Abs., 63, 4299e (1965).
93. R. F. Curl, V. M. Nao, K. V. L. Sastry, and J. A. Hodgson, J. Chem. Phys., 39, 3335 (1963).
94. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow, 1947, p. 142.
95. R. Neidlein, Arch. Pharm., 297, 623 (1964).
96. B. A. Arbuzov and N. N. Zobova, Dokl. Akad. Nauk SSSR, 170, 1317 (1966).
97. J. C. Sheehan and P. T. Izzo, J. Amer. Chem. Soc., 71, 4059 (1949).
98. R. Neidlein and R. Bottler, Chem. Ber., 100, 698 (1967).
99. R. Neidlein, Angew. Chem., 76, 596 (1964).
100. O. Tsuge and R. Mizuguchi, J. Chem. Soc. Japan, Ind. Chem. Sect., 69, 939 (1966); Chem. Abs., 66, 85552s (1967).
101. G. I. Derkach, E. S. Gubnitskaya, and L. I. Samarai, Zhur. Obshch. Khim., 36, 1949 (1966).
102. S. Umemoto and H. Takamatsu, J. Pharm. Soc. Japan, 85, 875 (1965).
103. G. I. Derkach and V. I. Belaya, Zhur. Obshch. Khim., 36, 1942 (1966).
104. Belg. P. 659 938 (1965); Chem. Abs., 64, 8046c (1966).
105. K. A. Nuridzhanyan, N. I. Bulanova, and L. M. Nesterova, USSR P. 226 590 (1967); Byul. Izobret., No. 29, (1968).
106. K. A. Nuridzhanyan, N. I. Bulanova, and L. M. Nesterova, Zhur. Org. Khim. (in the Press).
107. K. A. Nuridzhanyan and N. P. Bulanova, Khim. Geterotsikl. Soed., 946 (1968).
108. K. A. Nuridzhanyan, N. P. Bulanova, and G. A. Pivovarov, Zhur. Org. Khim. (in the Press).
109. F. Effenberger and R. Niess, Angew. Chem., 79, 474 (1967).
110. C. van Hoodonk and L. Ginjaar, Chem. Ind., 1564 (1967).
111. K. A. Nuridzhanyan, L. M. Nesterova, A. F. Vasil'ev, and V. V. Negrebetskii, Zhur. Org. Khim., 5, 869 (1969).
112. K. A. Nuridzhanyan, L. M. Nesterova, A. F. Vasil'ev, and N. L. Aryutkina, Zhur. Org. Khim., 5, 874 (1969).
113. K. A. Nuridzhanyan and L. M. Nesterova, "Tezisy Konferentsii po Problemam Napravlennogo Izyskaniya Fiziologichesko Aktivnykh Soedinenii, Akad. Nauk SSSR, ASSR, Erevan, 1968" (Abstracts of the Conference on the Problems of the Controlled Utilisation of Physiologically Active Compounds, Academy of Sciences of the USSR and the Armenian SSR, Erevan, 1968) p. 113.
114. H. Takamatsu, S. Umemoto, T. Tatsumi, and T. Isozaki, Japanese P. 22 932 (1965); Chem. Abs., 64, 3432d (1966).
115. K. A. Nuridzhanyan and G. V. Kuznetsova, Zhur. Org. Khim. (in the Press).
116. K. A. Nuridzhanyan and G. V. Kuznetsova, USSR P. 235 011 (1967); Byull. Izobret., No. 5 (1969).
117. E. Haack and H. Berger, BRD P. 1 177 644 (1964); Chem. Abs., 61, 16075d (1964).
118. K. A. Nuridzhanyan, L. M. Nesterova, and N. E. Mironova, USSR P. 239 944 (1967); Byul. Izobret., No. 12 (1969).
119. K. A. Nuridzhanyan, L. M. Nesterova, and N. E. Mironova, USSR P. 235 013 (1967); Byul. Izobret., No. 5 (1969).
120. K. A. Nuridzhanyan, and L. M. Nesterova, USSR P. 235 012 (1967); Byul. Izobret., No. 5 (1969).
121. S. Umemoto, S. Ose, and H. Takamatsu, J. Pharm. Soc. Japan, 83, 753 (1963); Chem. Zentr., 2-1065 (1967).
122. H. Takamatsu, S. Umemoto, S. Kano, and T. Isozaki, Japanese P. 11 973 (1964); Chem. Abs., 61, 16015a (1964).
123. H. Takamatsu, S. Umemoto, H. Tatsumi, and K. Nakamura, Japanese P. 14 131 (1965); Chem. Abs. 64, 9637g (1966).
124. W. Allmuller, R. Weyer, and G. Korger, US P. 3 068 282 (1961); Chem. Abs., 55, 17579c (1961).
125. G. Goerdelor and H. Schenk, Chem. Ber., 99, 782 (1966).
126. P. Adams and F. A. Baron, Chem. Rev., 65, 577 (1965).
127. I. C. Kogan, J. Org. Chem., 26, 3004 (1961).
128. T. N. Ghosh and P. C. Guha, J. Indian Chem. Soc., 7, 263 (1930).
129. S. Umemoto and H. Takamatsu, J. Pharmac. Soc. Japan, 83, 917 (1963); Chem. Zentr., 3-1040 (1967).
130. R. Neidlein, Arch. Pharm., 299, 1003 (1966); Angew. Chem., 78, 333 (1966); Angew. Chem. Intern. Ed., 5, 314 (1966).
131. E. Lieber, R. L. Minnis, and C. N. R. Rao, Chem. Rev., 65, 377 (1965).
132. M. M. Shemyakin, Yu. A. Arbuzov, M. N. Kolosov, G. A. Shatenshtein, V. V. Onoprienko, and Yu. V. Kononova, Zhur. Obshch. Khim., 30, 542 (1960).

133. J. W. McFarland and R. L. Harris, J. Org. Chem., 32, 1273 (1967).
134. H. L. Snape, J. Chem. Soc., 49, 254 (1886).
135. J. M. Lyon and R. H. Thompson, J. Chem. Soc., 1971 (1950).
136. L. A. McGrew, W. Sweeny, T. W. Campbell, and V. S. Foldi, J. Org. Chem., 29, 3002 (1964).
137. R. Neidlein, Arch. Pharm., 298, 124 (1965).
138. R. Neidlein, Z. Naturforsch., 19b, 1159 (1964).
139. R. Neidlein and E. Heukelbach, Arch. Pharm., 299, 64 (1966).
140. C. King, J. Org. Chem., 25, 352 (1960).
141. R. Neidlein and W. Haussmann, Tetrahedron Letters, 2423 (1965).
142. R. Neidlein and W. Haussmann, Chem. Ber., 99, 239 (1966).
143. Zh. M. Ivanova, G. I. Derkach, and N. A. Kirsanova, Zhur. Obshch. Khim., 34, 3516 (1964).
144. Zh. M. Ivanova, N. A. Kirsanova, and G. I. Derkach, Zhur. Org. Khim., 1, 2186 (1965).
145. R. Neidlein and W. Haussmann, Arch. Pharm., 300, 609 (1967).
146. E. Kuehle, B. Anders, and G. Zumach, Angew. Chem. Intern. Ed., 6, 649 (1967); Angew Chem., 79, 663 (1967).
147. W. Haussmann, R. Neidlein, and H. Ringsdorf, Kolloid Z., 212, 32 (1966).
148. K. A. Nuridzhanyan, L. D. Stonov, L. A. Bakumenko, and N. P. Bulanova, USSR P. 181 443; Byul. Izobret., No. 9 (1966).
149. K. A. Nuridzhanyan, N. P. Bulanova, and S. S. Babayan, USSR P. 1 209 052 (Applied for 4th Jan., 1968).
150. B. F. Brookes, D. H. Godson, and E. L. Leafe, B. P. 1 071 975 (1966); Chem. Abs., 64, 11134h (1966).
151. Dutch P. 6 411 807; Chem. Abs., 64, 4995b (1966).
152. Belg. P. 654 121; Chem. Abs., 64, 19491c (1966).
153. W. A. Robertson, J. Fraser, and P. G. Clinch, B. P. 982 235 (1965); Chem. Abs., 62, 16145b (1965).
154. D. K. Lewis, Nature, 213, 205 (1967).
155. J. Fraser, P. G. Hinch, and R. C. Reay, J. Sci. Food Agric., 16, 615 (1965).
156. K. Engel and K. Phaehler, US P. 2 221 914; Chem. Abs., 42, 1549[4] (1941).
157. K. A. Nuridzhanyan, L. D. Stonov, L. A. Bakumenko, and N. P. Bulanova, USSR P. 178 237; Byul. Izobret., No. 2 (1966).
158. J. Bernstein, K. A. Losee, and M. A. Dolliver, US P. 3 121 113 (1964); Chem. Abs., 60, 11940h (1964).
159. K. A. Nuridzhanyan and G. V. Kuznetsova, Khim. Geterotsikl. Soed. (in the Press).
160. K. A. Nuridzhanyan and N. P. Bulanova, USSR P. 230 164 (1967); Byul. Izobret., No. 34 (1968).
161. K. A. Nuridzhanyan, L. M. Nesterova, N. P. Bulanova, A. D. Stonov, L. A. Bakumenko, N. M. Usacheva, and E. I. Bystrova, Khim. v Selsk. Khoz., 374 (1968).
162. L. M. Semikolennykh, M. G. Katsnel'son, and V. B. Del'nik, Med. Prom. SSSR, No. 10, 15 (1965).
163. H. Takamatsu, S. Umemoto, S. Kano, and T. Isozaki, Japanese P. 11972 (1964); Chem. Abs., 61, 16015a (1964).
164. P. Adams, M. Hill, and B. R. Juliano, US P. 3 282 998 (1966); Chem. Abs., 66, 10621w (1967).
165. N. Duschinsky, US P. 2 560 522 (1951); Chem. Abs., 46, 3568g (1952).
166. Dutch P. 6 506 881 (1965); Chem. Abs., 64, 17445c (1966).
167. P. Gold-Aubert and L. Toribo, Arch. Sci., 16, 405 (1963).
168. H. Rochnert, J. prakt. Chem., 32, 265 (1966).
169. Y. Matsuo, J. Pharm. Soc. Japan, 83, 480 (1963); Chem. Abs., 59, 7401c (1963).
170. B. Rada, D. Blaskovic, J. Gut, and F. Sorm, Acta Virol. (Prague), 7, 152 (1963).
171. H. E. Thompson, C. P. Swanson, and A. G. Norman, Bot. Gaz., 107, 476 (1946); Chem. Abs., 41, 3903d (1947).
172. P. Poignant and D. Pillon, "Symposium on a New Herbicides", Second Edition, Paris, 1965, p. 1; Chem. Abs., 65, 12796b (1966).
173. D. Pillon and P. Poignant, French P. 1 392 499 (1965); Chem. Abs., 63, 8258h (1965).
174. N. N. Mel'nikov and Yu. A. Baskakov, "Khimiya Gerbitsidov i Regulyatorov Rosta Rastenii" (The Chemistry of Herbicides and Plant Growth Regulators), Goskhimizdat, Moscow, 1962.
175. H. J. Gerjovich and R. S. Johnson, Swed. P. 337 681; Chem. Abs., 54, 25543b (1960); BRD P. 971 511 (1959); US P. 2 762 696 (1956); Chem. Abs., 51, 3911h (1957); B. P. 769 613 (1957); Chem. Abs., 51, 9077h (1957).
176. J. Lehureau and P. Poignant, French P. 1 327 761; Chem. Abs., 59, 12706f (1963); Supplement 83 764 (1964); Chem. Abs., 64, 644 (1966).
177. K. A. Nuridzhanyan, L. D. Stonov, E. I. Bystrova, and N. P. Bulanova, USSR P. 182 436; Byul. Izobret., No. 1 (1966).
178. K. A. Nuridzhanyan, E. A. Dvoichenkova, G. V. Solov'eva, N. M. Golyshin, L. M. Nesterova, V. G. Blinova, and N. N. Bulanova, USSR P. 191 262; Byul. Izobret., No. 3 (1967).
179. US P. 2 801 200; Chem. Abs., 51, 15 877 (1957); BRD P. 981 812; Chem. Abs., 51, 9078 (1957).
180. L. I. Samarai, V. P. Belaya, and G. I. Derkach, USSR P. 210 140 (1966); Byul. Izobret., No. 6, 21 (1968).
181. L. I. Samarai, V. P. Belaya, O. V. Vishnevskaya, and G. I. Derkach, Zhur. Org. Khim., 4, 720 (1968).
182. H. H. Hoerhold and H. Eibisch, Chem. Ber., 102, 1080 (1969).
183. T. Sasaki, S. Eguchi, and M. Ohno, Tetrahedron, 25, 2145 (1969).
184. W. C. Firth, Jnr., J. Org. Chem., 33, 441 (1968).
185. O. Tsuge, T. Itoh, and S. Kanemasa, J. Chem. Soc. Japan, 89, 69 (1968).
186. O. Tsuge, S. Kanemasa, and M. Tashiro, Tetrahedron, 24, 5205 (1968).
187. A. J. Speziale and L. R. Smith, US P. 3 335 301 (1962); Chem. Abs., 69, 10 209 (1968).
188. A. J. Speziale and L. R. Smith, US P. 3 337 600 (1965); Chem. Abs., 67, 99 841 (1967).
189. A. J. Speziale and L. R. Smith, US P. 3 406 192 (1965); Chem. Abs., 70, 28 609 (1969).
190. R. Nast, K. Ley, and U. Eholzer, BRD P. 1 248 056 (1965); Chem. Abs., 68, 87 305 (1968).
191. French P. 1 513 142 (1966); Chem. Abs., 70, 77 966 (1969).
192. P. J. Islip, B. P. 1 126 134 (1967); Chem. Abs., 70, 47 437 (1969).
193. J. Matsuda, K. Itoh, and G. Ishii, J. Chem. Soc., C, 701 (1969).
194. G. A. Razuvaev, N. M. Lapshin, and N. V. Balukova, Zhur. Org. Khim., 4, 73 (1968).

195. J. C. Martin and P. G. Gott, US P. 3 394 132 (1966); Chem. Abs., **69**, 59 256 (1968).
196. J. L. Chaille and S. F. Reed, Jnr., US P. 3 440 280 (1960); Chem. Abs., **70**, 2999 (1969).
197. B. A. Arbuzov, N. N. Zobova, and E. G. Yarkova, Izd. Akad. Nauk SSSR, Ser. Khim., 1114 (1969).

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