**Abstract**

The invention relates to a process for preparing a compound of formula (I) in which A is chlorine or 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazipin-5-yl; to intermediates used in this process; to the use of these intermediates; and to a process for the preparation of these intermediates. The compounds of formula (I) are valuable intermediates in the process of preparing pesticidal, especially insecticidal or acaricidal, formulations.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>GE</td>
<td>Georgia</td>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GN</td>
<td>Guinea</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GR</td>
<td>Greece</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>HU</td>
<td>Hungary</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>IE</td>
<td>Ireland</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IT</td>
<td>Italy</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>JP</td>
<td>Japan</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>KE</td>
<td>Kenya</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>CI</td>
<td>Cote d'Ivoire</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LR</td>
<td>Liberia</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LT</td>
<td>Lithuania</td>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LU</td>
<td>Luxembourg</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LV</td>
<td>Latvia</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MC</td>
<td>Monaco</td>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MD</td>
<td>Republic of Moldova</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td>MG</td>
<td>Madagascar</td>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>ML</td>
<td>Mali</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>MN</td>
<td>Mongolia</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td></td>
<td></td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
</tbody>
</table>
Process for preparing a 2-chloro-5-chloromethyl-thiazole compound

The invention relates to a process for preparing a known compound of the formula

![Chemical Structure](image)

I,

in which A is chlorine or 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazin-5-yl, which process comprises

a) reacting a compound of the formula

![Chemical Structure](image)

II,

in which X is a leaving group, if desired in the presence of a base, with a dehydrating agent, a halogenating agent and a sulfurizing agent to give the compound of the formula I, in which A is chlorine, or

b1) reacting a compound of the formula II, if desired in the presence of a base, with a dehydrating agent to give a compound of the formula

![Chemical Structure](image)

III,

in which X is as defined for the formula II, and

b2) reacting the compound thus obtainable of the formula III with a halogenating agent and a sulfurizing agent, if desired in the presence of a base or acid, to give the compound of the formula I, in which A is chlorine, or

c) reacting a compound of the formula

![Chemical Structure](image)

IV,

which is known or can be prepared in analogy to corresponding known compounds and in which X is as defined for the formula II, with a compound of the formula
which is known or can be prepared in analogy to corresponding known compounds and in
which either $R_1$ and $R_2$ together are oxo and $R_3$ is hydroxy, $C_1$-$C_6$alkoxy or $N(R_4)R_5$, $R_4$ and
$R_5$ being, independently of one another, hydrogen or $C_1$-$C_6$alkyl, or $R_1$, $R_2$ and $R_3$, independ-
ently of one another, are $C_1$-$C_6$alkoxy, to give a compound of the formula II and reacting
the compound thus obtainable of the formula II either in accordance with the process vari-
ant a) or in accordance with the process variant b1) / b2) to give the compound of the for-
mla I, in which $A$ is chlorine, or
d) preparing the compound of the formula I, in which $A$ is chlorine, either in accordance with
the process variant a) or in accordance with the process variant b1) / b2) or in accordance
with the process variant c) and reacting the compound thus obtainable of the formula I, in
which $A$ is chlorine, if desired in the presence of a base, with the known compound 3-me-
thyl-4-nitroimino-perhydro-1,3,5-oxadiazine or with the known tautomeric compound 3-me-
thyl-4-nitroamino-2,3-dihydro-6H-1,3,5-oxadiazine, respectively, to give the compound of
the formula I, in which $A$ is 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazin-5-yl;
to the compounds of the formulae II and III; to the use thereof; and to a process for the
preparation thereof.

The general terms used above and below, unless defined otherwise, are as defined below.

Suitable leaving groups $X$ are, for example, $C_1$-$C_6$alkoxy, halo-$C_1$-$C_6$alkoxy, $C_1$-$C_6$alkanoyl-
loxy, $C_1$-$C_6$alkylthio, halo-$C_1$-$C_6$alkylthio, $C_1$-$C_6$alkylsulfonloxy, halo-$C_1$-$C_6$alkylsulfonloxy,
phenylsulfonyloxy, tolylsulfonyloxy or halogen, preferably halogen, particularly bromine, or
preferably chlorine.

Suitable dehydrating agents are, for example, thionyl chloride, triphenylphosphine / triethyl-
amine, triphenylphosphine / azodicarboxylic ester, phosphorus oxytrichloride, phosphorus
oxytrichloride / amine base, phosgene, phosgene / triethylamine, diphosgene, diphosgene / tri-
ethylamine, triphosgene, triphosgene / triethylamine, di-2-pyridylsulfite, benzenesulfonyl
chloride, toluenesulfonyl chloride or toluenesulfonyl chloride / quinoline, preferably thionyl
chloride or phosphorus oxytrichloride, in particular thionyl chloride.
Suitable halogenating agents are, for example, elemental chlorine, thionyl chloride, poly(sulfur dichloride), sulfur dichloride, sulfonyl chloride, phosphorus trichloride, phosphorus pentachloride or mixtures of two or more than two of these compounds, preferably thionyl chloride, sulfur dichloride or a mixture of these two compounds, particularly sulfur dichloride or a mixture of thionyl chloride and sulfur dichloride.

Suitable sulfurizing agents are, for example, elemental sulfur, poly(sulfur dichloride) or sulfur dichloride, preferably sulfur dichloride.

Preferably, reagents are used which simultaneously act as halogenating agents and sulfurizing agents, such as poly(sulfur dichloride) or sulfur dichloride, preferably sulfur dichloride.

The reactions described above and below are carried out, as required, in the absence or presence of a suitable solvent or diluent or a mixture of the same, with cooling, at room temperature or with heating, for example in a temperature range from about -80°C to the boiling temperature of the reaction medium, preferably from about -60°C to about +200°C, in a closed vessel, under atmospheric, elevated or reduced pressure, in an inert-gas atmosphere and/or under anhydrous conditions. Particularly advantageous reaction conditions are described below and can be taken, in particular, from the preparation examples.

**Variant a)**

The reaction partners can be reacted with one another without addition of a solvent or diluent. However, the addition of an inert solvent or diluent or a mixture of the same can also be advantageous, its amount not being critical. Examples of solvents or diluents of this type are in particular: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene, tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; ethers, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; ketones, such as acetone, methyl ethyl ketone or methyl isobutyl ketone; amides, such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphorotriamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as
dimethyl sulfoxide. Preferably, the reaction is carried out without addition of an inert solvent or diluent, but in the presence of a, preferably great, excess of the dehydrating agent, if this is liquid at the reaction temperature.

The reaction can be carried out, if desired, in the presence of a base as catalyst. Suitable bases for facilitating the reaction are, for example, alkali metal hydroxides or alkaline earth metal hydroxides, alkali metal hydrides or alkaline earth metal hydrides, alkali metal amides or alkaline earth metal amides, alkali metal alkanolates or alkaline earth metal alkanolates, alkali metal acetates or alkaline earth metal acetates, alkali metal carbonates or alkaline earth metal carbonates, alkali metal dialkylamides or alkaline earth metal dialkylamides or alkali metal alkylsilylamides or alkaline earth metal alkylsilylamides, alkylamines, alkylenediamines, free or N-alkylated, saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides or carbocyclic amines. Examples of such bases are sodium hydroxide, sodium hydride, sodium amide, sodium methanolate, sodium acetate, sodium carbonate, potassium tert-butanolate, potassium hydroxide, potassium carbonate, potassium hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropyl-ethyl-amine, triethylendiamine, cyclohexylamine, N-cyclohexyl-N,N-dimethyl-amine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine, benzyl-trimethyl-ammonium hydroxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The reaction can also be carried out in a two-phase mixture, for example a mixture of an organic solvent and an aqueous solution of a base, if desired in the presence of a phase transfer catalyst, for example a crown ether or a tetraalkylammonium salt.

The reaction is advantageously performed in a temperature range from about 0°C to about 150°C, preferably from about 20°C to about 100°C, preferably at the reflux temperature of the reaction mixture.

The molar ratio, in which the compound II and the sulfurizing agent are used in the reaction and which is defined by the quotient "number of moles of compound II / number of moles of sulfurizing agent", is, in particular, between 0.5 and 1, preferably between 0.75 and 1, in particular between 0.9 and 1. The dehydrating agent is preferably used in great excess.

The reaction is preferably performed at atmospheric pressure.
The reaction time is not critical; the preferred reaction time is from about 1 to about 48 hours, in particular from about 12 to about 30 hours.

The product is isolated by conventional methods, for example by filtration, crystallization, distillation or chromatography or any suitable combination of these processes.

The yield which can be achieved is generally good. A yield of more than 40 % of the theoretical yield is achieved.

Preferred conditions for the reaction are described in Example H1.

**Variant b1)**

The reaction partners can be reacted with one another as such, i.e. without addition of a solvent or diluent, for example in the melt. However, for the most part, the addition of an inert solvent or diluent or a mixture of the same is advantageous, its amount not being critical. Examples of solvents or diluents of this type are those which are listed under variant a). Preferably, the reaction is carried out in an amide, particularly in N,N-dimethylformamide.

The reaction can be carried out, if desired, in the presence of a base as catalyst, for example of the type listed under variant a).

The reaction can also be carried out in a two-phase mixture, for example a mixture of an organic solvent and an aqueous solution of a base, if desired in the presence of a phase transfer catalyst, for example a crown ether or a tetraalkylammonium salt.

The reaction is advantageously performed in a temperature range from about -80°C to about +60°C, preferably from about -50°C to about +40°C.

The molar ratio, in which the compound II and the dehydrating agent are used in the reaction and which is defined by the quotient "number of moles of compound II / number of moles of dehydrating agent", is, in particular, between 0.5 and 1, preferably between 0.75 and 1, in particular between 0.9 and 1.

The reaction is preferably performed at atmospheric pressure.

The reaction time is not critical; the preferred reaction time is from about 1 to about 24 hours, in particular from about 5 to about 15 hours.
The product is isolated by conventional methods, for example by filtration, crystallization, distillation or chromatography or any suitable combination of these processes. The yield which can be achieved is generally very good. A yield of more than 80 % of the theoretical yield is achieved.

Preferred conditions for the reaction are described in Example H2.

**Variant b2)**

The reaction partners can be reacted with one another as such, i.e. without addition of a solvent or diluent, for example in the melt. However, for the most part, the addition of an inert solvent or diluent or a mixture of the same is advantageous, its amount not being critical. Examples of solvents or diluents of this type are those which are listed under variant a). Preferably, the reaction is carried out in a halogenated hydrocarbon, such as di - or, in particular, tetrachloromethane.

The reaction can be carried out, if desired, in the presence of a base as catalyst, for example of the type listed under variant a).

The reaction can also be carried out, if desired, in the presence of an acid as catalyst. Acids which are suitable for this purpose are, for example, strong organic carboxylic acids, such as unsubstituted or substituted, for example by halogen, C₃₋₄alkanecarboxylic acids, for example formic acid, acetic acid or propionic acid, sulfonic acids, such as methylsulfonic acid, p-toluene sulfonic acid or camphor-10-sulfonic acid, Lewis acids, such as boron trifluoride-diethyl ether complexes or boron trifluoride-dimethyl ether complexes, and mineral acids, such as sulfuric acid, hydrochloric acid or phosphoric acid.

The reaction can also be carried out in a two-phase mixture, for example a mixture of an organic solvent and an aqueous solution of a base or acid, if desired in the presence of a phase transfer catalyst, for example a crown ether or a tetraalkylammonium salt.

The reaction is advantageously performed in a temperature range from about -50°C to about +160°C, preferably from about -20°C to about +60°C.

The molar ratio, in which the compound III and the sulfurizing agent are used in the reaction and which is defined by the quotient “number of moles of compound III / number of moles of
sulfurizing agent", is, in particular, between 0.5 and 1, preferably between 0.75 and 1, in particular between 0.85 and 0.95.

The reaction is preferably performed at atmospheric pressure.

The reaction time is not critical; the preferred reaction time is from about 1 to about 24 hours, in particular from about 1 to about 15 hours.

The product is isolated by conventional methods, for example by filtration, crystallization, distillation or chromatography or any suitable combination of these processes.

The yield which can be achieved is generally good. A yield of more than 50 % of the theoretical yield can be achieved.

Preferred reaction conditions are described in Example H4.

**Variant c)**

(i) **Reaction of the compounds IV and V**

C₁₋₆alkoxy is either straight-chain, i. e. methoxy, ethoxy, propoxy, butoxy, pentyloxy or hexyloxy, or branched, for example isopropoxy, isobutoxy, sec-butoxy, tert-butoxy, isopentyloxy, neopentyloxy or isohexylloxy.

C₁₋₆alkyl is either straight-chain, i. e. methyl, ethyl, propyl, butyl, penty1 or hexyl, or branched, for example isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Preference is given to compounds V, in which R₁ and R₂ together are oxo and R₃ is C₁₋₆alkoxy, preferably C₁₋₆alkoxy, in particular methoxy or especially ethoxy.

The reaction partners can be reacted with one another without addition of a solvent or diluent. However, the addition of an inert solvent or diluent or a mixture of the same can also be advantageous, its amount not being critical. Examples of solvents or diluents of this type are those which are listed under variant a). Preferably, the reaction is carried out without addition of an inert solvent or diluent.
The reaction is advantageously performed in a temperature range from about 0°C to about 180°C, preferably from about 40°C to about 150°C, preferred at the reflux temperature of the reaction mixture.

The molar ratio, in which the compounds IV and V are used in the reaction and which is defined by the quotient "number of moles of compound IV / number of moles of compound V" is, in particular, between 0.1 and 1, preferably between 0.4 and 1, in particular between 0.5 and 0.8.

The reaction is preferably performed at atmospheric pressure.

The reaction time is not critical; the preferred reaction time is from about 1 to about 48 hours, in particular from about 5 to about 15 hours.

The product is isolated by conventional methods, for example by filtration, crystallization, distillation or chromatography or any suitable combination of these processes.

The yield which can be achieved is generally very good. A yield of more than 75 % of the theoretical yield is achieved.

Preferred conditions for the reaction are described in Example H3.

(ii) Reaction of the compounds II to give the compound I, in which A is chlorine

The reaction of the compounds II obtainable according to step (i) to give the compound I, in which A is chlorine, according to the variant c) is performed either as described under the variant a) or as described under the variant b1) / b2).

Variant d)

The preparation of the compound I, in which A is chlorine, according to the variant d) is performed either in accordance with the variant a) or in accordance with the variant b1) / b2) or in accordance with the variant c).

The reaction of the compound thus obtainable of the formula I, in which A is chlorine, with 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine or the tautomeric 3-methyl-4-nitroamino-2,3-dihydro-6H-1,3,5-oxadiazine, respectively, to give the compound I, in which A is 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazin-5-yl, according to the variant d) can be performed
in such a manner, that the reaction partners are reacted with one another as such, i.e. without addition of a solvent or diluent, for example in the melt. However, for the most part, the addition of an inert solvent or diluent or a mixture of the same is advantageous, its amount not being critical. Examples of solvents or diluents of this type are those which are listed under variant a). Preferably, the reaction is carried out in an amide, particularly in N,N-dimethylformamide.

The reaction can be carried out, if desired, in the presence of a base as catalyst, for example of the type listed under variant a).

The reaction is advantageously performed in a temperature range from about -20°C to about +180°C, preferably from about +10°C to about +100°C.

The reaction is preferably performed at atmospheric pressure.

The reaction time is not critical; the preferred reaction time is from about 1 to about 24 hours, in particular from about 3 to about 12 hours.

The product is isolated by conventional methods, for example by filtration, crystallization, distillation or chromatography or any suitable combination of these processes.

The yield which can be achieved is generally very good. A yield of more than 65 % of the theoretical yield is achieved.

Preferred conditions for the reaction are described in Example H5.

The compounds II and III are novel and are likewise subject-matter of the invention.

Preferred compounds II and III are those, in which X is halogen, especially bromine or in particular chlorine.

The process for preparing the compounds II and III is likewise subject-matter of the invention. The compounds II can be prepared, for example, as described under variant c), i.e. by reacting a compound IV with a compound V. The compounds III can be prepared, for example, as described under variant b1), i.e. by reacting a compound II with a dehydrating agent.
The use of the compounds II as intermediates in the process of the invention for preparing the compounds III or the compounds I and the use of the compounds III as intermediates in the process of the invention for preparing the compounds I are likewise subject-matter of the invention.

The invention relates to all those embodiments of the process, in which one starts from a compound, which can be used as a starting product or intermediate at any stage of the process, and carries out all or some of the missing steps, or in which one uses, or, in particular, forms under the reaction conditions, a starting material in the form of a derivative or salt and/or of its racemates or antipodes.

The invention relates in particular to the process described in the Examples H1 to H5.

Starting materials and intermediates used according to the invention for the preparation of the compounds I which are novel, a process for the preparation thereof and the use thereof as starting materials and intermediates for the preparation of the compounds I are likewise subject-matter of the invention; this relates in particular to the compounds II and III.

The compounds I are valuable intermediates in the process of preparing pesticidal, especially insecticidal or acaricidal, formulations.

The following examples illustrate the invention. They do not restrict the invention. Temperatures are given in degrees Celsius. The abbreviation "h" means hours.

**Preparation examples**

**Example H1: 2-chloro-5-chloromethyl-thiazole**

A mixture of 10.5 ml of thionyl chloride, 0.5 g of N-(2-chloroallyl)formamide and 0.44 g of sulfur dichloride is refluxed for 24 h. The reaction mixture is then concentrated on a rotary evaporator, and the residue is purified by flash chromatography on silica gel (mobile phase: dichloromethane). The title compound is obtained in this manner in a yield of 42 % (melting point: 35°).

**Example H2: 2-chloroallylisonitrile**
A solution of 2.5 g of thionyl chloride in 6 ml of N,N-dimethylformamide is added dropwise, with stirring, to a solution of 2.4 g of N-(2-chloroallyl)formamide in 40 ml of N,N-dimethylformamide, after cooling to -50°. 4.7 g of sodium carbonate are then added. The reaction mixture is stirred for 12 h at room temperature, diluted with 100 ml of water and extracted with pentane. The pentane extract dried over sodium sulfate gives the title compound, after distilling off the pentane at atmospheric pressure, in a yield of 81 % and in a purity of more than 80 % (impurity: N,N-dimethylformamide). The title compound can be further used without additional purification.

**Example H3: N-(2-chloroallyl)formamide**

A mixture of 37.2 g of 2-chloroallylamine and 43.7 g of ethyl formate is refluxed for 12 h. The reaction mixture is then concentrated on a rotary evaporator, and the residue is fractionally distilled under reduced pressure via a Vigreux column. The title compound is obtained in this manner (boiling point: 131° at 19 mbar; yield: 79 %).

**Example H4: 2-chloro-5-chloromethylthiazole**

a) 0.57 g of sulfur dichloride is added dropwise to a solution of 0.5 g of 2-chloroallyl isonitrile in 7.5 ml of tetrachloromethane at 0°. The reaction mixture is stirred for 4 h at 40°, the solvent is distilled off at atmospheric pressure and the residue is subjected to Kugelrohr distillation (20 mbar, 120-130°). The pure title compound is obtained in this manner in a yield of 12 %.

b) 0.4 g of thionyl chloride is added dropwise to a solution of 0.5 g of 2-chloroallylisonitrile in 7.5 ml of tetrachloromethane at 0°. After 5 minutes, 0.57 g of sulfur dichloride is added dropwise at 0°. The reaction mixture is stirred for 12 h at room temperature, the solvent is distilled off under atmospheric pressure, and the residue is subjected to a Kugelrohr distillation (20 mbar, 120-130°). The pure title compound is obtained in this manner in a yield of 52 %.

**Example H5: 5-(2-Chlorothiazol-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine**

A mixture of 1.62 g of 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine, 2.44 g of 2-chloro-5-chloromethyl-thiazole, 4.2 g of potassium carbonate and 25 ml of N,N-dimethylformamide is heated for 5 h at 60° and then filtered. The filtrate is evaporated in vacuo on a rotary evap-
erator, and the residue is purified by chromatography [silica gel; dichloromethane / methanol (95:5)]. This gives the title compound, which melts at 132-134°C, in a yield of 67%.
WHAT IS CLAIMED IS

1. A process for preparing a compound of the formula

\[
\text{\( \text{II}, \)}
\]

in which A is chlorine or 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazin-5-yl, which process comprises

a) reacting a compound of the formula

\[
\text{\( \text{II}, \)}
\]

in which X is a leaving group, if desired in the presence of a base, with a dehydrating agent, a halogenating agent and a sulfurizing agent to give the compound of the formula \( \text{I}, \) in which A is chlorine, or

b1) reacting a compound of the formula \( \text{II}, \) if desired in the presence of a base, with a dehydrating agent to give a compound of the formula

\[
\text{\( \text{III}, \)}
\]

in which X is as defined for the formula \( \text{II}, \) and

b2) reacting the compound thus obtainable of the formula \( \text{III}, \) with a halogenating agent and a sulfurizing agent, if desired in the presence of a base or acid, to give the compound of the formula \( \text{I}, \) in which A is chlorine, or

c) reacting a compound of the formula

\[
\text{\( \text{IV}, \)}
\]

which is known or can be prepared in analogy to corresponding known compounds and in which X is as defined for the formula \( \text{II}, \) with a compound of the formula
HC(R₁)(R₂)R₃ \quad V,

which is known or can be prepared in analogy to corresponding known compounds and in which either R₁ and R₂ together are oxo and R₃ is hydroxy, C₁-C₆alkoxy or N(R₄)R₅, R₆ and R₇ being, independently of one another, hydrogen or C₁-C₆alkyl, or R₁, R₂ and R₃, independently of one another, are C₁-C₆alkoxy, to give a compound of the formula II and reacting the compound thus obtainable of the formula II either in accordance with the process variant a) or in accordance with the process variant b1) / b2) to give the compound of the formula I, in which A is chlorine, or

d) preparing the compound of the formula I, in which A is chlorine, either in accordance with the process variant a) or in accordance with the process variant b1) / b2) or in accordance with the process variant c) and reacting the compound thus obtainable of the formula I, in which A is chlorine, if desired in the presence of a base, with the known compound 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine or with the known tautomeric compound 3-methyl-4-nitroamino-2,3-dihydro-6H-1,3,5-oxadiazine, respectively, to give the compound of the formula I, in which A is 3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazin-5-yl.

2. A process according to claim 1 for preparing the compound of the formula I, in which A is chlorine, wherein a compound of the formula II, in which X is a leaving group, is reacted, if desired in the presence of a base, with a dehydrating agent, a halogenating agent and a sulfurizing agent.

3. A process according to claim 2, wherein a compound of the formula II is used, in which X is chlorine.

4. A process according to claim 2, wherein the dehydrating agent is thionyl chloride.

5. A process according to claim 2, wherein the halogenating agent is thionyl chloride or sulfur dichloride.

6. A process according to claim 2, wherein the sulfurizing agent is sulfur dichloride.

7. A process according to claim 4, wherein thionyl chloride is used in excess.

8. A process according to claim 7, wherein the reaction is carried out at the reflux temperature of the reaction mixture.
9. A process according to claim 6, wherein the molar ratio, in which the compound II and the sulfurizing agent are used and which is defined by the quotient "number of moles of compound II / number of moles of sulfurizing agent", is between 0.5 and 1.

10. A process for preparing a compound of the formula

\[
\begin{align*}
&\quad \text{in which } X \text{ is a leaving group, which process comprises reacting a compound of the formula} \\
&\quad \text{X} \\
&\quad \text{N(\text{H})C(\text{H})O} \\
\end{align*}
\]

which is known or can be prepared in analogy to corresponding known compounds and in which X is as defined for the formula II, with a compound of the formula

\[
\begin{align*}
&\quad \text{HC(\text{R}_1)(\text{R}_2)\text{R}_3} \\
\end{align*}
\]

which is known or can be prepared in analogy to corresponding known compounds and in which either \(\text{R}_1\) and \(\text{R}_2\) together are oxo and \(\text{R}_3\) is hydroxy, \(\text{C}_1\text{-C}_5\text{alkoxy}\) or \(\text{N(\text{R}_4)\text{R}_5}\), \(\text{R}_4\) and \(\text{R}_5\) being, independently of one another, hydrogen or \(\text{C}_1\text{-C}_5\text{alkyl}\), or \(\text{R}_1\), \(\text{R}_2\) and \(\text{R}_3\), independently of one another, are \(\text{C}_1\text{-C}_5\text{alkoxy}\).

11. A process for preparing a compound of the formula

\[
\begin{align*}
&\quad \text{X} \\
&\quad \text{NC} \\
\end{align*}
\]

in which X is a leaving group, which process comprises reacting a compound of the formula

\[
\begin{align*}
&\quad \text{X} \\
&\quad \text{N(\text{H})C(\text{H})O} \\
\end{align*}
\]

in which X is as defined for the formula III, if desired in the presence of a base, with a dehydrating agent.

12. A compound of the formula
in which X is a leaving group.

13. A compound according to claim 12 of the formula II, in which X is chlorine.

14. A compound of the formula

\[
\begin{align*}
\text{II:} & \quad \begin{array}{c}
\text{X} \\
\text{N(H)C(H)O}
\end{array} \\
\text{III:} & \quad \begin{array}{c}
\text{X} \\
\text{NC}
\end{array}
\end{align*}
\]

in which X is a leaving group.

15. A compound according to claim 14 of the formula III, in which X is chlorine.

16. Use of a compound according to claim 12 of the formula II in a process according to claim 1 or claim 11.

17. Use of a compound according to claim 14 of the formula III in a process according to claim 1.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

<table>
<thead>
<tr>
<th>IPC</th>
<th>C07D277/32</th>
<th>C07D417/06</th>
<th>C07C233/13</th>
<th>C07C291/10</th>
</tr>
</thead>
</table>

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

<table>
<thead>
<tr>
<th>IPC</th>
<th>C07D</th>
<th>C07C</th>
</tr>
</thead>
</table>

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EP 0 446 913 A (TAKEDA CHEMICAL INDUSTRIES LTD) 18 September 1991 see claims</td>
<td>1-9</td>
</tr>
<tr>
<td>A</td>
<td>EP 0 260 560 A (BAYER AG) 23 March 1988 see the whole document</td>
<td>1-9</td>
</tr>
<tr>
<td>A</td>
<td>EP 0 580 553 A (CIBA GEIGY AG) 26 January 1994 see page 17, compound 1.3 see claims</td>
<td>1</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

**Date of the actual completion of the international search**

3 December 1996

**Date of mailing of the international search report**

10.12.1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340 2040, Tx: 31651 epo nl
Fax: (+31-70) 340 3016

Authorized officer

Henry, J
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>IL-A- 97565</td>
<td>29-06-95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-A- 4234864</td>
<td>24-08-92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA-A- 1306463</td>
<td>18-08-92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-B- 7116167</td>
<td>13-12-95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR-B- 9411458</td>
<td>15-12-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BG-A- 97962</td>
<td>25-04-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BR-A- 9302943</td>
<td>16-02-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA-A- 2100924</td>
<td>23-01-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN-A- 1084171</td>
<td>23-03-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CZ-A- 9301457</td>
<td>16-02-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HR-A- 931073</td>
<td>30-04-96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HU-A- 65131</td>
<td>28-04-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NZ-A- 248195</td>
<td>27-02-96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PL-A- 299755</td>
<td>05-04-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SK-A- 76493</td>
<td>08-06-94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZA-A- 9305263</td>
<td>09-02-94</td>
</tr>
</tbody>
</table>