

PATENT SPECIFICATION

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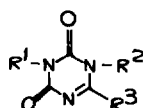
(54) TETRAHYDRO-1,3,5-TRIAZINE-2,6-DIONES, PROCESSES FOR THEIR PRODUCTION AND THEIR USE AS HERBICIDES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen-Bayerwerk, Germany (Federal Republic), do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to certain new tetrahydro - 1,3,5 - triazine - 2,6-diones, to processes for their production and to their use as herbicides.

It has been disclosed that hexahydro - 1,3,5 - triazine - 2,4,6 - triones display a certain herbicidal action (see German Offenlegungsschrift (German Published Specification) 1,927,921). However, their action is not always satisfactory.

The present invention provides, as new compounds, the tetrahydro - 1,3,5-triazine - 2,6 - diones of the general formula

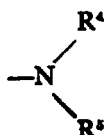


(I)

in which

R¹ is a saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbon radical, an araliphatic hydrocarbon radical or an aryl radical, each of which can carry one or more substituents selected from halogen, nitro, alkyl, alkoxy, alkylmercapto, aryl, aryloxy, halogenomethyl or arylmercapto,

R² is hydrogen, alkyl, cycloalkyl, aralkyl, aryl (which may be optionally substituted by chlorine), hydroxy, alkoxy, acyloxy, or an



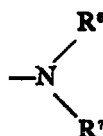
radical
 wherein

R⁴ and R⁵, which may be identical or different, are each hydrogen, alkyl or acyl

(both of which are optionally substituted by nitrile and/or hydroxyl and/or halogen),

or

5 R^4 and R^5 conjointly form alkylidene (which can carry one or more substituents selected from aryl, halogenoaryl, alkoxyaryl, nitroaryl and heterocyclic radicals), or cycloalkylidene, and R^3 is hydrogen, alkyl, halogenoalkyl, halogen, aryloxy or an



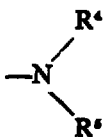
10 radical
wherein

R^6 and R^7 , which may be identical or different, are each hydrogen, alkyl, cycloalkyl, aralkyl, aryl, hydroxyl, amino or alkoxy

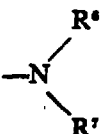
or

15 R^6 and R^7 conjointly with the nitrogen atom form a heterocyclic radical, or R^3 is alkoxy or alkylmercapto, provided that R^2 is not hydrogen.

Preferably, R^1 is straight-chain or branched C_1-C_{12} alkyl, which may be substituted by halogen, or a C_5-C_7 cycloalkyl, aralkyl or aryl radical which may be substituted by halogen, alkyl or trifluoromethyl; R^2 is hydrogen, C_1-C_4 alkyl, C_5-C_7 cycloalkyl, aralkyl, aryl or an



radical, wherein R^4 and R^5 are each hydrogen, alkyl or acyl or R^4 and R^5 conjointly form alkylidene (which may optionally carry one or more substituents selected from aryl, halogenoaryl, alkoxyaryl, nitroaryl and heterocyclic radicals) or cycloalkylidene; and R^3 is straight-chain or branched C_1-C_4 alkyl, alkoxy, alkylmercapto or an

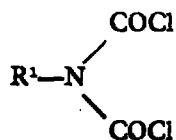


radical, wherein R^6 and R^7 are hydrogen, alkyl, hydroxyl, amino or alkoxy.

The compounds of this invention have been found to display strong herbicidal properties.

This invention also provides processes for the production of a tetrahydro - 1,3,5-triazine - 2,6 - dione of the formula (I) in which

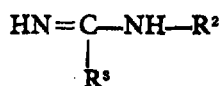
(a) a bis - (chlorocarbonyl) - amine of the general formula



(II),

in which

R^1 has the above-mentioned meaning,
is reacted with a compound of the general formula

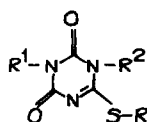


(III),

in which

R^2 and R^3 have the above-mentioned meaning,
or a salt thereof with an organic or inorganic acid, in the presence of an acid-binding
agent and optionally in the presence of a solvent, it being possible, when R^2 is hydroxyl
or amino, to protect this group by acylation or hydrazone formation and to liberate it
again after the reaction,

or (b) a compound of the general formula

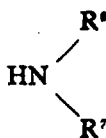


(IV),

in which

R^1 and R^2 have the above-mentioned meanings, and

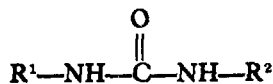
R is an alkyl radical which is optionally substituted, for example by carboxyl,
is reacted, optionally in the presence of a solvent and of an acid catalyst, with a com-
pound of the general formula



(V),

in which

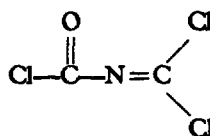
R^6 and R^7 have the above-mentioned meanings,
or (c) a compound of the general formula



(VI),

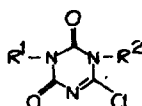
in which

R^1 and R^2 have the above-mentioned meanings,
is reacted with chlorocarbonylisocyanide of the formula



(VII),

optionally in the presence of an acid-binding agent and of a solvent, to give a com-
pound of the general formula



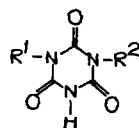
(VIII),

in which

R^1 and R^2 have the above-mentioned meanings,
and this compound is optionally reacted with a compound of the formula $R^3-\text{H}$, in
the presence of an acid-binding agent, or with a compound of the formula $R^3-\text{M}$,
in which

M is an alkali metal atom or a magnesium halide moiety
and

R^3 in each case has the above-mentioned meaning,
or (d) a compound of the general formula



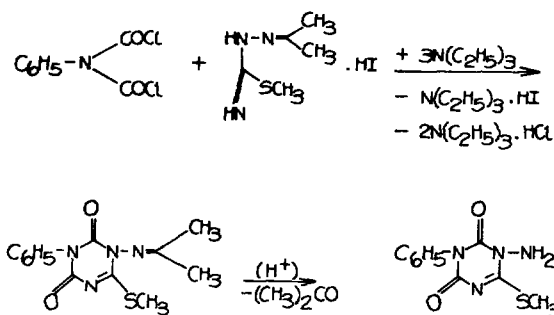
(IX)

in which

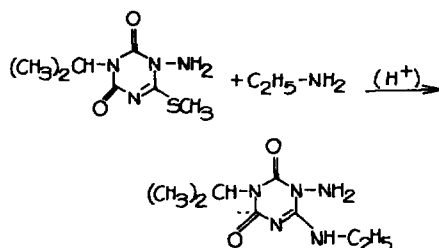
R^1 and R^2 have the above-mentioned meanings, is reacted with an inorganic acid halide, optionally in the presence of a solvent to give a compound of the general formula (VIII) above, which is then optionally reacted with a compound of the formula R^3-H in the presence of an acid-binding agent, or with a compound of the formula R^3-M as defined above.

Surprisingly, the tetrahydro - 1,3,5 - triazine - 2,6 - diones according to the invention display a substantially greater herbicidal activity than the hexahydro - 1,3,5-triazine - 2,4,6 - triones known from the state of the art. The compounds according to the invention thus represent an enrichment of the art.

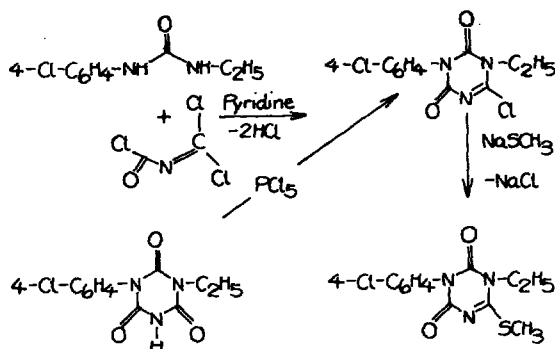
If, in accordance with process variant (a), *N* - phenyl - bis(chlorocarbonyl)-amine and acetone - *S* - methyl - isothiosemicarbazone hydroiodide are used in the presence of triethylamine, and the splitting reaction is subsequently carried out in a weakly acid solution, the course of the reaction can be represented by the following equation:



If, according to process variant (b), 1 - isopropyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione and ethylamine are used in the presence of *p* - toluenesulphonic acid as the catalyst, the course of the reaction can be represented by the following equation:



If, according to process variant (c), *N* - (4 - chlorophenyl) - *N'* - ethylurea, chlorocarbonylisocyanide dichloride and sodium thiomethylate are used or if, according to process variant (d), 1 - (4 - chlorophenyl) - 3 - ethyl - hexahydro - 1,3,5-triazine - 2,4,6 - trione, phosphorus pentachloride and sodium thiomethylate are used, the course of the reactions can be represented by the following equation:



The bis - (chlorocarbonyl) - amines (II) which can be used according to the invention are in part already known (see Synthesis 1970, page 542—543); the compounds which have not yet been described in the literature can be produced analogously.

The following may be mentioned as examples: N - methyl - (bis - chlorocarbonyl) - amine, N - ethyl - (bis - chlorocarbonyl) - amine, N - propyl - (bis - chlorocarbonyl) - amine, N - isopropyl - (bis - chlorocarbonyl) - amine, N - sec. - butyl - (bis - chlorocarbonyl) - amine, N - tert. - butyl - (bis - chlorocarbonyl) - amine, N - octyl - (bis - chlorocarbonyl) - amine, N - dodecyl - (bis - chlorocarbonyl) - amine, N - cyclopropyl - (bis - chlorocarbonyl) - amine, N - cyclohexyl - (bis - chlorocarbonyl) - amine, N - cyclooctyl - (bis - chlorocarbonyl) - amine, N - benzyl - (bis - chlorocarbonyl) - amine, N - (4 - chlorobenzyl) - (bis - chlorocarbonyl) - amine, N - (4 - methylbenzyl) - (bis - chlorocarbonyl) - amine, N - phenyl - (bis - chlorocarbonyl) - amine, N - (4 - methylphenyl) - (bis - chlorocarbonyl) - amine, N - (4 - ethylphenyl) - (bis - chlorocarbonyl) - amine, N - (3 - chlorophenyl) - (bis - chlorocarbonyl) - amine, N - (4 - chlorophenyl) - (bis - chlorocarbonyl) - amine, N - (3,4 - dichlorophenyl) - (bis - chlorocarbonyl) - amine, N - (2,4 - dichlorophenyl) - (bis - chlorocarbonyl) - amine, N - (4 - bromophenyl) - (bis - chlorocarbonyl) - amine, N - (3 - nitrophenyl) - (bis - chlorocarbonyl) - amine, N - (4 - methoxyphenyl) - (bis - chlorocarbonyl) - amine, N - (4 - methoxy - 3 - chlorophenyl) - (bis - chlorocarbonyl) - amine, N - (3 - trifluoromethyl - phenyl) - (bis - chlorocarbonyl) - amine and N - (2 - chloro - 5 - trifluoromethylphenyl) - (bis - chlorocarbonyl) - amine.

The compounds of the formula (III) which can be used according to the invention are already extensively known; those that have not yet been described in the literature can be produced according to known processes (see, for example, Houben-Weyl, Methoden der organischen Chemie (Methods of Organic Chemistry), 4th edition, volume VIII, pages 170—193, volume IX, pages 884—915 and volume XI/2, pages 38—69). The following may be mentioned as examples: formamidine hydrochloride, acetamidine hydrochloride, isobutyramidine hydrochloride, butylamidine hydrochloride, O - acetyl - acetamidoxime, O - acetylpropionamidoxime, S - methyl - isothiurea sulphate, N,S - dimethyl - isothiurea hydroiodide, N - ethyl - S - methyl - isothiurea hydroiodide, N - butyl - S - ethyl - isothiurea hydroiodide, N - benzyl - S - methyl - isothiurea hydroiodide, N - cyclohexyl - S - methyl - isothiurea hydroiodide, N - phenyl - S - ethyl - isothiurea hydroiodide, N - (4 - chlorophenyl) - S - methyl - isothiurea hydroiodide, acetone - S - methyl - isothiosemicarbazone hydroiodide, methyl ethyl ketone - S - ethyl - isothiosemicarbazone hydroiodide, acetaldehyde - S - methyl - isothiosemicarbazone hydroiodide, propionaldehyde - S - methyl - isothiosemicarbazone hydroiodide, phenylacetaldehyde - S - methyl - isothiosemicarbazone hydroiodide, cyclohexanone - S - methyl - isothiosemicarbazone hydroiodide, 4 - chlorobenzaldehyde - S - methyl - isothiosemicarbazone hydroiodide, 3,4 - dichlorobenzaldehyde - S - methyl - isothiosemicarbazone hydroiodide, 3 - nitrobenzaldehyde - S - methyl - isothiosemicarbazone hydroiodide, 4 - methoxybenzaldehyde - S - methyl - isothiosemicarbazone hydroiodide, furfuraldehyde - S - methyl - isothiosemicarbazone hydroiodide, 1 - isopropylidene - acetamidrazone, 1 - isopropylidene - propionamidrazone and 1 - methyl - S - methyl - isothiosemicarbazide hydroiodide.

The 4 - alkyl - mercapto - tetrahydro - 1,3,5 - triazine - 2,6 - diones (IV) which can be used according to the invention have not previously been described in the literature; however, they can be produced according to process variant (a). The following may be mentioned as examples:

- 1 - methyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6-dione, 1 - ethyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5-triazine - 2,6 - dione, 1 - tert. - butyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - benzyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (3,4 - dichlorophenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - tert. - butyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - benzyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (3,4 - dichlorophenyl) - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - tert. - butyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - tert. - butyl - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1,3 - diisopropyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - tert. - butyl - 3 - isopropyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 3 - isopropyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - isopropyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 3 - methylamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - tert. - butyl - 3 - methylamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 3 - methylamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - methylamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 3 - hydroxy - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - tert. - butyl - 3 - hydroxy - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - cyclohexyl - 3 - hydroxy - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - hydroxy - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - isopropyl - 3 - amino - 4 - carboxymethylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione and 1 - isopropyl - 3 - ethyl - 4 - carboxymethylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione.

The compounds of the formula (V) used as starting materials in process variant (b) are already known. As examples there may be mentioned: ammonia, methylamine, dimethylamine, ethylamine, isopropylamine, butylamine, diethylamine, benzylamine, hydrazine, hydroxylamine, O - methylhydroxylamine and N,O - dimethyl - hydroxylamine.

The compounds of the formula (VI), employed as starting materials in process variant (c), are already extensively known; the compounds that have not previously been described in the literature can be prepared according to known processes. As examples there may be mentioned: N,N' - dimethyl - urea, N - methyl - N' - isopropyl - urea, N - methyl - N' - tert. - butyl - urea, N - methyl - N' - benzyl - urea, N - methyl - N' - cyclohexyl - urea, N - methyl - N' - phenyl - urea, N,N' - diethyl - urea, N - ethyl - N' - isopropyl - urea, N - ethyl - N' - tert. - butyl - urea, N - ethyl - N' - benzyl - urea, N - ethyl - N' - cyclohexyl - urea, N - ethyl - N' - phenyl - urea, N,N' - diisopropyl - urea, N - methoxy - N' - isopropyl - urea, 1 - isopropylidene - 4 - methyl - semicarbazone, 1 - isopropylidene - 4 - isopropyl - semicarbazone, 1 - isopropylidene - 4 - tert. - butyl - semicarbazone, 1 - isopropylidene - 4 - cyclohexyl - semicarbazone, 1 - isopropylidene - 4 - phenyl - semicarbazone, 1 - benzylidene - 4 - methyl - semicarbazone, 1 - benzylidene - 4 - isopropyl - semicarbazone, 1 - benzylidene - 4 - tert. - butyl - semicarbazone, 1 - benzylidene - 4 - cyclohexyl - semicarbazone, 1 - benzylidene - 4 - phenyl - semicarbazone, 1 - cyclohexylidene - 4 - methyl - semicarbazone, 1 - cyclohexylidene - 4 - isopropyl - semicarbazone, 1 - cyclohexylidene - 4 - tert. - butyl - semicarbazone, 1 - cyclohexylidene - 4 - cyclohexyl - semicarbazone, 1 - cyclohexylidene - 4 - phenyl - semicarbazone, 1 - methylamino - 4 -

methyl - semicarbazide, 1 - methylamino - 4 - isopropyl - semicarbazide, 1 - methylamino - 4 - tert. - butyl - semicarbazide, 1 - methylamino - 4 - cyclohexyl - semicarbazide and 1 - methylamino - 4 - phenyl - semicarbazide.

Chlorocarbonylsuiphenyl chloride, which is used as a starting material in process variant (c), is already known (see German Patent Specification 1,224,720).

The compounds R^3-H or R^3-M employed in process variants (c) and (d), and in which M is preferably Li, Na, K, MgCl, MgBr or MgI, are already known. As examples there may be mentioned: methyl lithium, methyl-magnesium bromide, ethylamine, ethyllithium, butyl-lithium, sodium methylate, sodium ethylate, sodium thioamine, sodium thioethylate, ammonia, methylamine, propylamine, isopropylamine, dimethylamine, diethylamine, hydrazine, methyl - hydrazine, 1,1 - dimethylhydrazine, hydroxylamine, O - methyl - hydroxylamine and N,O - dimethyl - hydroxylamine.

The compounds of the formula (IX) which can be used according to process variant (d) are already largely known; the compounds that have not yet been described in the literature can be prepared according to known processes. As examples there may be mentioned: 1 - methyl - 3 - isopropylidene - amino - hexahydro - 1,3,5-triazine - 2,4,6 - trione, 1 - isopropyl - 3 - isopropylideneamino - hexahydro - 1,3,5-triazine - 2,4,6 - trione, 1 - tert. - butyl - 3 - isopropylideneamino - hexahydro - 1,3,5-triazine - 2,4,6 - trione, 1 - cyclohexyl - 3 - isopropylideneamino - hexahydro - 1,3,5-triazine - 2,4,6 - trione, 1 - benzyl - 3 - isopropylideneaminohexahydro - 1,3,5-triazine - 2,4,6 - trione, 1 - phenyl - 3 - isopropylideneamino - hexahydro - 1,3,5-triazine - 2,4,6 - trione, 1 - (3,4 - dichlorophenyl) - 3 - isopropylideneamino - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - isopropyl - 3 - methyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - tert. - butyl - 3 - methyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - cyclohexyl - 3 - methyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - phenyl - 3 - methyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - ethyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - cyclohexyl - 3 - ethyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - phenyl - 3 - ethyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - isopropyl - 3 - isopropyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - tert. - butyl - 3 - isopropyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - cyclohexyl - 3 - isopropyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - phenyl - 3 - isopropyl - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - tert. - butyl - 3 - methylamino - hexahydro - 1,3,5 - triazine - 2,4,6 - trione, 1 - cyclohexyl - 3 - methylamino - hexahydro - 1,3,5 - triazine - 2,4,6 - trione and 1 - phenyl - 3 - methylamino - hexahydro - 1,3,5 - triazine - 2,4,6 - trione.

Amongst the inorganic acid halides which can be used in process variant (d), thionyl chloride, phosgene, phosphorus oxychloride or phosphorus pentachloride are preferred.

Possible diluents for process (a) are all inert organic solvents, especially hydrocarbons, such as petroleum ether, benzene, toluene and xylene; ethers, such as diethyl ether, diisopropyl ether and dioxane; and acid amides, such as dimethylformamide and dimethylacetamide.

All customary acid-binders can be used as acid-binding agents: the alkali metal hydroxides, alkali metal carbonates, alcoholates and tertiary amines are preferred. Particularly suitable are sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, potassium tert. - butylate, pyridine, triethylamine, triethylene-diamine, dimethylaniline and diisopropyl ethylamine.

The reaction temperatures can be varied over a fairly wide range. In general, the reaction is carried out between 0° and 50° C, preferably between 20° and 40° C.

In carrying out the process variant (a), 1 mole of the compound (III) is generally employed per mole of bischlorocarbonylamine (II), and 2—4 moles of acid-binder are generally added to neutralise the acid produced. The reaction takes place exothermically. The resulting salts are removed by filtration or by extraction by shaking with water, the organic phase is evaporated and the residue is recrystallised.

Any desired organic solvents can be used as diluents in process variant (b). Preferred solvents are alcohols, such as isopropanol or tert. - butanol; carboxylic acids, such as formic acid and glacial acetic acid; and ethers, such as diethyl ether or dioxane.

Any desirable inorganic and organic acids can be added as catalysts; however, the oxygen acids of phosphorus, carboxylic acids, sulphonic acids, or mixtures thereof are preferred. Phosphoric acid, glacial acetic acid, trichloroacetic acid, benzenesul-

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benzyl - 3 - ethyl - 4 - ethylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - phenyl - 3 - amino - 4 - ethyl - tetrahydro - 1,3,5 - triazine - 2,6 - dione. 1-phenyl - 3 - benzylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine-2,6 - dione, 1 - phenyl - 3 - amino - 4 - ethylamino - tetrahydro - 1,3,5 - triazine-2,6 - dione, 1 - phenyl - 3 - amino - 4 - hydrazino - tetrahydro - 1,3,5 - triazine-2,6 - dione. 1 - phenyl - 3 - ethyl - 4 - hydroxylamino - tetrahydro - 1,3,5 - triazine-2,6 - dione, 1 - (4 - chlorophenyl) - 3 - amino - 4 - methylmercapto - tetrahydro-1,3,5 - triazine - 2,6 - dione, 1 - (4 - chlorophenyl) - 3 - amino - 4 - ethylamino-tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (3,4 - dichlorophenyl) - 3 - amino-4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (3,4 - dichlorophenyl) - 3 - ethyl - 4 - hydroxylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (4 - methylphenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5-triazine - 2,6 - dione, 1 - (4 - methylphenyl) - 3 - hydroxy - 4 - ethyl - tetrahydro-1,3,5 - triazine - 2,6 - dione, 1 - (4 - methoxyphenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (4 - methoxyphenyl) - 3-amino - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione, 1 - (3 - trifluoromethylphenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine-2,6 - dione, and 1 - (3 - trifluoromethylphenyl) - 3 - ethyl - 4 - ethylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione.

The active compounds according to the invention display strong herbicidal properties and can therefore be used for combating weeds. By weeds, in the broadest sense, there are to be understood all plants which grow in locations where they are not desired. Since the active compounds influence plant growth in different ways, they can be employed as selective herbicides. At higher concentrations (for instance 25 kg/ha), the active compounds according to the invention are suitable for the total combating of weeds.

The active compounds according to the invention can be employed in the case of, for example, the following plants: dicotyledons, such as mustard (*Sinapis*), cress (*Lepidium*), cleavers (*Galium*), chickweed (*Stellaria*), camomile (*Matricaria*), gallant soldier (*Galinsoga*), goosefoot (*Chenopodium*), annual nettle (*Urtica*), groundsel (*Senecio*), cotton (*Gossypium*), beets (*Beta*), carrots (*Daucus*), beans (*Phaseolus*), potatoes (*Solanum*) and coffee (*Coffea*); monocotyledons, such as timothy (*Phleum*), bluegrass (*Poa*), fescue (*Festuca*), goosegrass (*Eileusine*), fox-tail (*Setaria*), ryegrass (*Lolium*), cheat (*Bromus*), barnyard grass (*Echinochloa*), maize (*Zea*), rice (*Oryza*), oats (*Avena*), barley (*Hordeum*), wheat (*Triticum*), millet (*Panicum*) and sugar cane (*Saccharum*).

The active compounds are particularly suitable for the selective combating of weeds in cotton, maize, cereals and carrots.

The active compounds according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid or liquefied gaseous diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes, toluene, benzene or alkyl naphthalenes, chlorinated aromatic or aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes of methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly polar solvents, such as dimethyl formamide, dimethyl sulphoxide or acetonitrile, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal temperatures and pressures, for example aerosol propellants, such as halogenated hydrocarbons, for example Freon (registered trade mark).

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, or ground synthetic minerals, such as highly-dispersed silicic acid, alumina or silicates.

Preferred examples of emulsifying and foam-forming agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acids esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates, alkyl sulphates and aryl sulphonates as well as albumin hydrolyzation products; and pre-

ferred examples of dispersing agents include lignin sulphite waste liquors and methyl cellulose.

The active compounds according to the invention can be present in the formulations as a mixture with other active compounds.

The formulations generally contain from 0.1 to 95 per cent by weight, preferably from 0.5 to 90 percent by weight of active compound.

The active compounds can be used as such, in the form of their formulations or in the application forms prepared therefrom, such as ready-to-use solutions, emulsions, suspensions, powders, pastes and granules. They can be used in the customary manner, for example by watering, spraying, atomising, sprinkling and dusting.

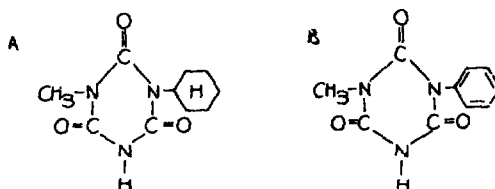
They can be used either by the post-emergence process or by the pre-emergence process. The amount of active compound employed can fluctuate within fairly wide ranges. It depends essentially on the nature of the desired effect. In general, the amounts used are between 0.1 and 20 kg of active compound/ha, preferably between 0.5 and 15 kg/ha.

The present invention also provides a herbicidal composition containing as active ingredient a compound of the present invention in admixture with a solid or liquefied gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

The present invention also provides a method of combating weeds which comprises applying to the weeds or a weed habitat a compound of the present invention alone or in the form of a composition containing as active ingredient a compound of the present invention in admixture with a diluent or carrier.

The present invention further provides crops protected from damage by weeds by being grown in areas in which immediately prior to and/or during the time of the growing a compound of the present invention was applied alone or in admixture with a diluent or carrier. It will be seen that the usual methods of providing a harvested crop may be improved by the present invention.

The herbicidal activity of the compounds of this invention is illustrated in the following test Examples. The compounds of this invention are each identified by the number of the corresponding preparative Examples hereinafter; the known compounds, used for comparison, are as follows:



Example A.

Post-emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the above stated amount of solvent, the above stated amount of emulsifier was added and the concentrate was then diluted with water to the desired concentration.

Test plants, which had a height of 5—15 cm, were sprayed with the preparation of the active compound in such a way that the amounts of active compound per unit area shown in the table were applied. Depending on the concentration of the spray liquor, the amount of water used was between 1,000 and 2,000 l/ha. After three weeks, the degree of damage to the plants was determined and characterised by the values 0—5, which had the following meaning:

- 0 no effect
- 1 a few slightly burnt spots
- 2 marked damage to leaves
- 3 some leaves and parts of stalks partially dead
- 4 plant partially destroyed
- 5 plant completely dead.

The active compounds, amounts used and results can be seen from the table which follows:

Table A
Post-emergence test

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Table A (continued)

Active compound No.	Amount of active compound used kg/ha	Post-emergence test								
		Echino- chloa	Cheno- podium	Sina- pis	Galini- soga	Stell- aria	Mairi- caria	Carrots	Oats	Cotton Wheat Beans
77	1 0.5	5 3	5 5	5 3	5 5	5 5	5 5	4 3	5 4	2 2
76	1 0.5	5 3	5 4	5 3	5 5	5 4	5 3	4 3	3 2	2 1
101	1 0.5	5 5	5 5	5 5	5 5	5 5	5 5	5 5	5 5	4-5 4
103	1 0.5	5 4	5 5	5 5	5 5	5 5	5 5	3 2	5 5	4 2
87	1 0.5	5 3	5 5	5 5	5 5	3 3	5 3	4 3	5 5	4 3
93	1 0.5	4 3	5 5	5 5	5 5	5 4	4 3	4 3	5 5	3 2
90	1 0.5	5 4	5 5	5 5	5 5	5 5	5 5	5 4	5 5	3 2
104	1 0.5	5 5	5 5	5 5	5 5	5 5	5 5	4-5 4	5 5	4 4
105	1 0.5	5 5	5 5	5 5	5 5	5 5	5 4-5	4-5 3	5 5	4 3
A (known)	1 0.5	1 1	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
B (known)	1 0.5	2 1	2 1	4 4	0 0	0 0	1 0	2 2	0 0	0 0

(26)

(27)

14

1,397,888

14

Example B.

Pre-emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5 To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with the above stated amount of solvent, the above stated amount of emulsifier was added and the concentrate was diluted with water to the desired concentration. 5

10 Seeds of the test plants were sown in normal soil and, after 24 hours, watered with the preparation of the active compound. It was expedient to keep constant the amount of water per unit area. The concentration of the active compound in the preparation was of no importance, only the amount of active compound applied per unit area being decisive. After three weeks, the degree of damage to the test plants was determined and characterised by the values 0—5, which had the following meaning: 10

- | | | |
|----|--|----|
| 15 | 0 no effect | 15 |
| | 1 slight damage or delay in growth | |
| | 2 marked damage or inhibition of growth | |
| | 3 heavy damage and only deficient development or only 50% emerged | |
| | 4 plants partially destroyed after germination or only 25% emerged | |
| 20 | 5 plants completely dead or not emerged. | 20 |

The active compounds, the amounts applied and the results obtained can be seen from the following table:

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Table B

Active compound No.	Amount of active compound used, kg/ha	Pre-emergence test						
		Echino- chloa	Cheno- podium	Sina- pis	Lol- ium	Stell- aria	Galin- soga	Matri- caria
13	5 2.5	5 4	5 5	5 4	5 5	5 5	5 5	5 5
14	5 2.5	5 4	5 5	5 4	5 5	5 5	5 5	5 5
4	5 2.5	5 5	5 5	5 5	5 5	5 5	5 5	5 5
5	5 2.5	5 5	5 5	5 4-5	5 5	5 5	5 5	5 5
9	5 2.5	5 5	5 5	5 4-5	5 5	5 5	5 5	5 5
6	5 2.5	5 5	5 4	5 4-5	5 4-5	5 5	5 5	5 5
31	5 2.5	5 4	5 4-5	5 4-5	5 4	5 5	5 5	5 5
10	5 2.5	5 5	5 4	5 4-5	5 5	5 5	5 5	5 5

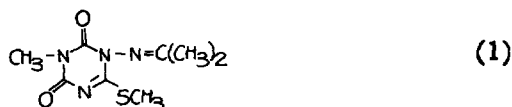
Cotton Wheat Buck Maize
sativa wheat

Table B (continued)

Pre-emergence test													
Active compound No.	Amount of active compound used, kg/ha	Echino-chloa	Chenopodium	Sinapis	Lolium	Stellaria	Galin-soga	Mari-caria	Avena fatua	Cotton	Wheat	Buck wheat	Maize
77	5 2.5	5 5	5 4	2 2	4-5 4	- -	5 5	5 5	4 3	3 2	3 2	3 3	3 2
76	5 2.5	5 5	5 5	5 5	5 5	- -	5 5	5 5	5 4	4 4	3 3	5 5	3 3
101	5 2.5	5 5	5 5	5 5	5 5	- -	5 5	5 5	5 5	4 4	3 2	5 5	4 3
103	5 2.5	5 5	5 5	4 4	5 4	- -	5 5	5 5	3 2	2 2	2 1	4 2	3 3
87	5 2.5	5 4	5 4	4 4	3 2	- -	5 5	5 5	3 3	4 3	3 2	4 3	3 2
93	5 2.5	5 5	5 5	5 5	4 4	- -	5 5	5 5	3 2	3 2	3 3	4-5 3	3 3
90	5 2.5	5 5	5 5	5 5	5 5	- -	5 5	5 5	5 4	4 3	4 4	5 5	3 3
104	5 2.5	5 5	5 5	5 5	5 5	- -	5 5	5 5	4 4	3 2	3 3	5 5	4 3
105	5 2.5	5 5	5 5	5 5	5 5	- -	5 5	5 5	5 5	2 2	3 3	4-5 3	4 3
A (known)	5 2.5	0 0	0 0	0 0	0 0	- -	0 0	0 0	0 0	0 0	0 0	0 0	0 0
B (known)	5 2.5	1 0	0 0	2 0	0 0	- -	4 3	4 2	1 0	0 0	0 0	2 1	1 0

The process of the present invention is illustrated in the following preparative Examples.

Example 1.



15.6 g (0.1 mole) of N - methyl - bis - (chlorocarbonyl) - amine were dissolved in 100 ml of benzene and added dropwise, whilst stirring, to 27.3 g (0.1 mole) of acetone - S - methyl - iso - thio - semicarbazone hydroiodide suspended in 100 ml of benzene. Thereafter, 30.3 g (0.3 mole) of triethylamine in 50 ml of benzene were slowly added dropwise. The mixture was stirred for a further hour and the precipitate was filtered off. The precipitate was introduced into 100 ml of chloroform and 100 ml of water and extracted by shaking. The chloroform phase was separated off, dried over calcium chloride and evaporated *in vacuo*, together with the benzene filtrate.

The residue was recrystallised from isopropanol. 17.3 g (76%) of 1 - methyl - 3 - isopropylideneamino - 4 - methyl - mercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione were obtained as a colourless powder; melting point 130—132° C.

Example 2.



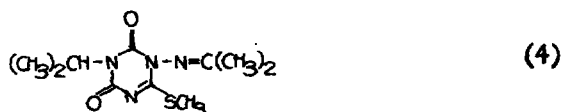
22.8 g (0.1 mole) of 1 - methyl - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 1) were dissolved in 250 ml of ethanol and warmed, with addition of a pinch of *p* - toluenesulphonic acid, for 5 hours to 50° C, whilst applying a vacuum of about 200 mm Hg. The mixture was evaporated *in vacuo* and the residue was recrystallised from ethanol. 18 g (96%) of 1 - methyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione were obtained as colourless needles; melting point 174—175° C.

Example 3.



18.8 g (0.1 mole) of 1 - methyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 2) were dissolved in 200 ml of isopropanol with addition of 6 g of glacial acetic acid and a pinch of *p* - toluenesulphonic acid and the mixture was saturated with methylamine gas at room temperature. The batch was left to stand for about 10 hours and was evaporated *in vacuo*, and the residue was recrystallised from isopropanol. 15 g (88%) of 1 - methyl - 3 - amino - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione were obtained as a colourless powder; melting point 225—227° C.

Example 4.



Analogously to Example 1, N - isopropyl - bis - (chlorocarbonyl) - amine (prepared analogously to Synthesis 1970, page 542—543; boiling point 66—67° C/12 mm

Hg) and acetone - S - methyl - isothio - semicarbazone hydroiodide, with addition of triethylamine, yielded 1 - isopropyl - 3 - isopropylideneamino - 4 - methylmercapto-tetrahydro - 1,3,5 - triazine - 2,6 - dione as a pale yellow powder of melting point 110—112° C.

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Example 5.

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Analogously to Example 2, 1 - isopropyl - 3 - isopropylidene - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 4) yielded 1 - isopropyl - 3 - amino - 4 - methylmercapto - 1,3,5 - triazine - 2,6 - dione as colourless needles of melting point 148—150° C.

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Example 6.



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Analogously to Example 3, 1 - isopropyl - 3 - amino - 4 - methylmercapto-tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 5) and methylamine yielded 1 - isopropyl - 3 - amino - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 195—196° C.

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Example 7.



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Analogously to Example 3, 1 - isopropyl - 3 - amino - 4 - methylmercapto-tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 5) and dimethylamine yielded 1 - isopropyl - 3 - amino - 4 - dimethylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 131—133° C.

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Example 8.

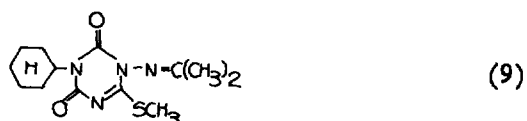


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Analogously to Example 3, 1 - isopropyl - 3 - amino - 4 - methylmercapto-tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 5) and ethylamine yielded 1 - isopropyl - 3 - amino - 4 - ethylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 122—123° C.

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Example 9.



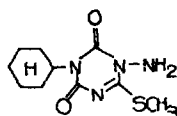
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Analogously to Example 1, N - cyclohexyl - bis - (chlorocarbonyl) - amine (prepared analogously to Synthesis 1970, page 542—543; boiling point 80—82°

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C/0.3 mm Hg) and acetone - S - methyl - isothiosemicarbazone hydroiodide, with addition of triethylamine, yielded 1 - cyclohexyl - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a pale yellow powder of melting point 111—112° C.

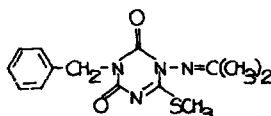
Example 10.



(10)

Analogously to Example 2, 1 - cyclohexyl - 3 - isopropylidene - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 9) yielded 1 - cyclohexyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 177—179° C.

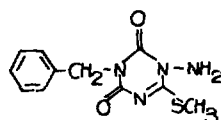
Example 11.



(11)

Analogously to Example 1, N - benzyl - bis - (chlorocarbonyl) - amine and acetone - S - methyl - isothiosemicarbazone hydroiodide, with addition of triethylamine, yielded 1 - benzyl - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a pale brown powder of melting point 148—150° C.

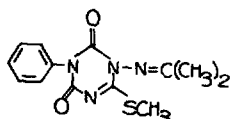
Example 12.



(12)

Analogously to Example 2, 1 - benzyl - 3 - isopropylidene - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 11) yielded 1 - benzyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 127—128° C.

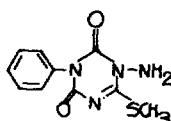
Example 13.



(13)

Analogously to Example 1, N - phenyl - bis - (chlorocarbonyl) - amine and acetone - S - methyl - isothiosemicarbazone hydroiodide, with addition of triethylamine, yielded 1 - phenyl - 3 - isopropylidene - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a pale yellow powder of melting point 206—207° C.

Example 14.



(14)

Analogously to Example 2, 1 - phenyl - 3 - isopropylidene - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 13) yielded 1 - phenyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as colourless needles of melting point 205—208° C.

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Example 15.

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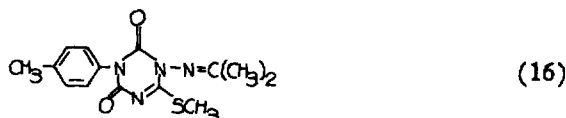


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Analogously to Example 3, 1 - phenyl - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 14) and methylamine yielded 1 - phenyl - 3 - amino - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 242—244° C.

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Example 16.



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Analogously to Example 1, N - (4 - methylphenyl) - bis - (chlorocarbonyl) - amine and acetone - S - methyl - isothiosemicarbazone hydroiodide, with addition of triethylamine, yielded 1 - (4 - methylphenyl) - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a yellow powder of melting point 170—173° C.

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Example 17.



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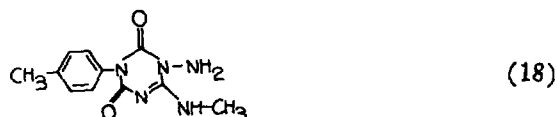
Analogously to Example 2, 1 - (4 - methylphenyl) - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 16) yielded 1 - (4 - methylphenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 196—197° C.

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Example 18.

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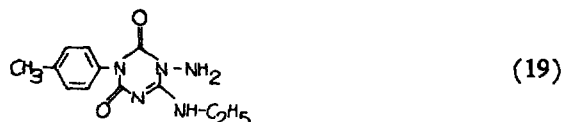


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Analogously to Example 3, 1 - (4 - methylphenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 17) and methylamine, yielded 1 - (4 - methylphenyl) - 3 - amino - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 242—243° C.

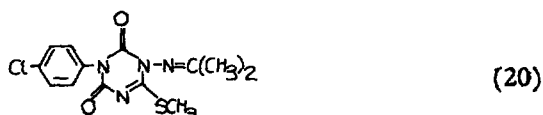
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Example 19.



Analogously to Example 3, 1 - (4 - methylphenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 17) and ethylamine, yielded 1 - (4 - methylphenyl) - 3 - amino - 4 - ethylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as colourless needles of melting point 247—248° C.

Example 20.



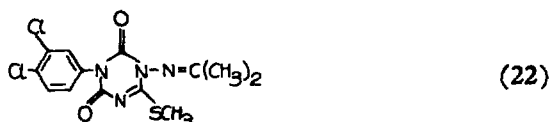
Analogously to Example 1, N - (4 - chlorophenyl) - bis - (chlorocarbonyl) - amine and acetone - S - methyl - isothiosemicarbazone hydroiodide with addition of triethylamine, yielded 1 - (4 - chlorophenyl) - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 142—144° C.

Example 21.



Analogously to Example 2, 1 - (4 - chlorophenyl) - 3 - iso - propylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 20) yielded 1 - (4 - chlorophenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 210—212° C.

Example 22.



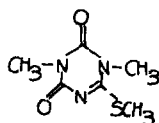
Analogously to Example 1, N - (3,4 - dichlorophenyl) - bis - (chlorocarbonyl) - amine and acetone - S - methyl - isothiosemicarbazone hydroiodide, with addition of triethylamine, yielded 1 - (3,4 - dichlorophenyl) - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 181—182° C.

Example 23.



Analogously to Example 2, 1 - (3,4 - dichlorophenyl) - 3 - isopropylideneamino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 22) yielded 1 - (3,4 - dichlorophenyl) - 3 - amino - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 247° C (decomposition).

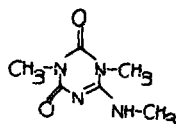
Example 24.



(24)

23.2 g (0.1 mole) of N,S - dimethyl - isothiurea hydroiodide were initially introduced into 100 ml of water and 250 ml of benzene. 15.6 g (0.1 mole) of N-methyl - bis - (chlorocarbonyl) - amine in 100 ml of dry benzene and 12 g (0.3 mole) of sodium hydroxide dissolved in 100 ml of water were simultaneously slowly added dropwise from two dropping funnels with vigorous stirring. The reaction took place strongly exothermically. The mixture was stirred for a further hour, any product which precipitated was filtered off, and the benzene phase was separated off, dried over calcium chloride and evaporated *in vacuo*. The residue, together with the filter residue, was recrystallised from isopropanol. 14 g (75%) of 1,3 - dimethyl - 4-methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione were obtained as a colourless powder of melting point 137—139° C.

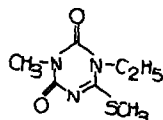
Example 25.



(25)

Analogously to Example 3, 1,3 - dimethyl - 4 - methylmercapto - tetrahydro-1,3,5 - triazine - 2,6 - dione (prepared according to Example 24) and methylamine yielded 1,3 - dimethyl - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 294—296° C.

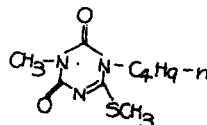
Example 26.



(26)

Analogously to Example 24, N - ethyl - S - methyl - iso - thiourea hydroiodide and N - methyl - bis - (chlorocarbonyl) - amine yielded 1 - methyl - 3 - ethyl - 4-methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 118—119° C.

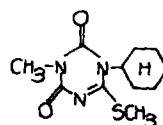
Example 27.



(27)

Analogously to Example 24, N - n - butyl - S - methyl - iso - thiourea hydroiodide and N - methyl - bis - (chlorocarbonyl) - amine yielded 1 - methyl - 3 - butyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 121—122° C.

Example 28.



(28)

Analogously to Example 24, N - cyclohexyl - S - methyl - isothiurea hydroiodide and N - methyl - bis - (chlorocarbonyl) - amine yielded 1 - methyl - 3 - cyclohexyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 121—122° C.

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Example 29.

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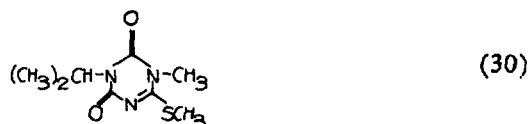


Analogously to Example 24, N - phenyl - S - methyl - iso - thiourea hydroiodide and N - methyl - bis - (chlorocarbonyl) - amine yielded 1 - methyl - 3 - phenyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as yellow needles of melting point 216—217° C.

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Example 30.



Analogously to Example 24, N,S - dimethyl - isothiurea hydroiodide and N - isopropyl - bis - (chlorocarbonyl) - amine (prepared analogously to Synthesis 1970, page 542—543; boiling point 66—67° C/12 mm Hg yielded 1 - isopropyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 73—75° C.

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Example 31.

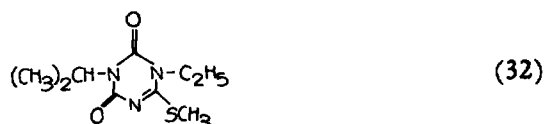


Analogously to Example 3, 1 - isopropyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 30) and methylamine yielded 1 - isopropyl - 3 - methyl - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 224—226° C.

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Example 32.



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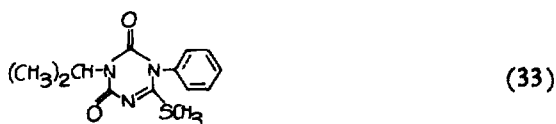
25

Analogously to Example 24, N - ethyl - S - methyl - iso - thiourea hydroiodide and N - isopropyl - bis - (chlorocarbonyl) - amine yielded 1 - isopropyl - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 198—200° C.

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Example 33.

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Analogously to Example 24, N - phenyl - S - methyl - iso - thiourea hydroiodide and N - isopropyl - bis - (chlorocarbonyl) - amine yielded 1 - isopropyl - 3 - phenyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 137—139° C.

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Example 34.

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Analogously to Example 24, N,S - dimethyl - isothiurea hydroiodide and N-cyclohexyl - bis - (chlorocarbonyl) - amine (prepared analogously to Synthesis 1970, pages 542—543; boiling point 80—82° C/0.3 mm Hg) yielded 1 - cyclohexyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 135—137° C.

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Example 35.



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Analogously to Example 24, N,S - dimethyl - isothiurea hydroiodide and N-phenyl - bis - (chlorocarbonyl) - amine yielded 1 - phenyl - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as colourless flakes of melting point 236—239° C.

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Example 36.



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Analogously to Example 3, 1 - phenyl - 3 - methyl - 4 - methylmercapto-tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 35) and methylamine yielded 1 - phenyl - 3 - methyl - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 297—299° C.

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Example 37.

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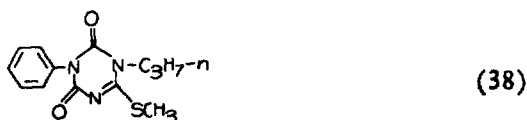
25

Analogously to Example 24, N - ethyl - S - methyl - iso - thiourea hydroiodide and N - phenyl - bis - (chlorocarbonyl) - amine yielded 1 - phenyl - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 149—150° C.

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Example 38.

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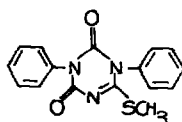
(28)

Analogously to Example 24, N - n - propyl - S - methyl - iso - thiourea hydroiodide and N - phenyl - bis - (chlorocarbonyl) - amine yielded 1 - phenyl - 3 - n - propyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 124—126° C.

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Example 39.

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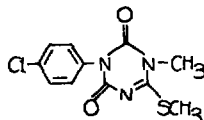
(39)

Analogously to Example 24, N - phenyl - S - methyl - iso - thiourea hydroiodide and N - phenyl - bis - (chlorocarbonyl) - amine yielded 1,3 - diphenyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as colourless needles of melting point 219—220° C.

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Example 40.

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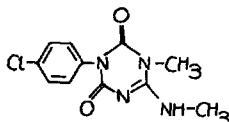
(40)

Analogously to Example 24, N,S - dimethyl - isothiurea hydroiodide and N - (4 - chlorophenyl) - bis - (chlorocarbonyl) - amine yielded 1 - (4 - chlorophenyl) - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 146—148° C.

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Example 41.

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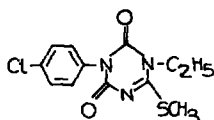
(41)

Analogously to Example 3, 1 - (4 - chlorophenyl) - 3 - methyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione (prepared according to Example 40) and methylamine yielded 1 - (4 - chlorophenyl) - 3 - methyl - 4 - methylamino - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 312—313° C.

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Example 42.

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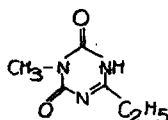
(42)

Analogously to Example 24, N - ethyl - S - methyl - isothio - urea hydroiodide and N - (4 - chlorophenyl) - bis - (chlorocarbonyl) - amine yielded 1 - (4 - chlorophenyl) - 3 - ethyl - 4 - methylmercapto - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 198—200° C.

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Example 43.

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(43)

10.9 g (0.1 mole) of propionamidinium hydrochloride were suspended in 125 ml of water and 200 ml of benzene. 15.6 g (0.1 mole) of N - methyl - bis - (chlorocarbonyl) - amine in 100 ml of dry benzene and 18 g (0.45 mole) of sodium hydroxide dissolved in 100 ml of water were simultaneously slowly added dropwise from two dropping funnels, with vigorous stirring. The reaction took place exothermically. The mixture was stirred for a further hour, the aqueous phase was separated off and acidified with glacial acetic acid and the mixture was evaporated *in vacuo*. The residue was repeatedly extracted by boiling with ethyl acetate. The solution was concentrated *in vacuo* and cooled. The precipitate was filtered off. 7.8 g (50%) of 1 - methyl - 4 - ethyl - tetrahydro - 1,3,5 - triazine - 2,6 - dione were obtained as colourless needles of melting point 202—203° C.

Example 44.



Analogously to Example 43, propionamidinium hydrochloride and N - isopropyl - bis - (chlorocarbonyl) - amine yielded 1 - isopropyl - 4 - ethyl - tetrahydro - 1,3,5 - triazine - 2,6 - dione as colourless needles of melting point 146—148° C.

Example 45.



Analogously to Example 43, acetamidinium hydrochloride and N - phenyl - bis - (chlorocarbonyl) - amine yielded 1 - phenyl - 4 - methyl - tetrahydro - 1,3,5 - triazine - 2,6 - dione as a colourless powder of melting point 245—247° C.

Example 46.



Analogously to Example 43, propionamidinium hydrochloride and N - phenyl - bis - (chlorocarbonyl) - amine yielded 1 - phenyl - 4 - ethyl - tetrahydro - 1,3,5 - triazine - 2,6 - dione as colourless needles of melting point 172—175° C.

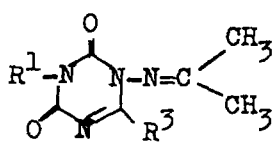
Example 47.

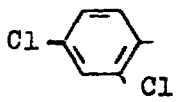
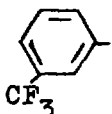
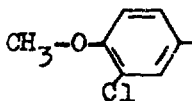


13 g (0.1 mole) of O - acetyl - propionamidoxime (melting point: 80—83° C) were initially introduced into 100 ml of benzene. 21.8 g (0.1 mole) of N - phenyl - bis - (chlorocarbonyl) - amine in 100 ml of benzene were added dropwise and this was followed by the slow dropwise addition of 20.2 g (0.2 mole) of triethylamine in 50 ml of benzene. The reaction was exothermic. The mixture was stirred for a further hour, the precipitate was filtered off and the benzene filtrate was concentrated *in vacuo*. The residue was recrystallised from isopropanol. 14 g (51%) of 1 - phenyl - 3 - acetoxy - 4 - ethyl - tetrahydro - 1,3,5 - triazine - 2,6 - dione were obtained as colourless needles of melting point 128—130° C.

The compounds listed in Table 1 below were prepared analogously to Example 1:

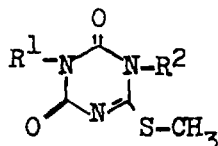
Table 1



Example No.	R ¹	R ³	Melting point, °C
48	CH ₃	-S-C ₂ H ₅	118 - 120
49	C ₄ H ₉	-S-C ₂ H ₅	81 - 83
50		-S-C ₂ H ₅	94 - 96
51	C ₂ H ₅ -	-S-CH ₃	151 - 152
52	C ₃ H ₇	-S-CH ₃	92 - 93
53	C ₄ H ₉	-S-CH ₃	red oil
54	(CH ₃) ₂ CH-CH ₂ -	-S-CH ₃	127 - 128
55	C ₂ H ₅ -CH(CH ₃)-	-S-CH ₃	74 - 76
56	C ₁₂ H ₂₅ -	-S-CH ₃	95 - 96
57		-S-CH ₃	183 - 184
58		-S-CH ₃	135 - 136
59		-S-CH ₃	155 - 156
60		-S-CH ₃	177 - 178

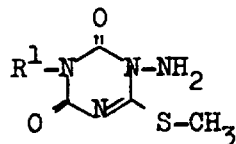
The compounds listed in Table 2 below were prepared analogously to Example 1.

Table 2



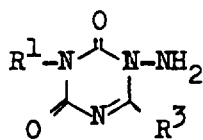
Example No.	R ¹	R ²	Melting point, °C
61	(CH ₃) ₂ CH	-N=CH-CH(CH ₃) ₂	94 - 97
62	(CH ₃) ₂ CH	-N=CH-	108 - 110
63	(CH ₃) ₂ CH	-N=CH-	151 - 153
64	(CH ₃) ₂ CH	-N=CH--NO ₂	198 - 200
65	(CH ₃) ₂ CH-CH ₂	-N=CH-CH(CH ₃) ₂	67 - 69
66	(CH ₃) ₂ CH-CH ₂	-N=CH-	140 - 143
67	C ₂ H ₅ -CH(CH ₃)-	-N=CH-	101 - 103
68	C ₂ H ₅ -CH(CH ₃)-	-N=CH--NO ₂	138 - 140
69	C ₂ H ₅ -CH(CH ₃)-	-N=CH-	134 - 136
70		-N=CH-CH(CH ₃) ₂	103 - 106
71		-NH-CH(OH)-CCl ₃	159 - 160
72		-N=CH-	138 - 141
73		-N=CH--NO ₂	208 - 209
74		-N=CH-	133 - 135

2. The compounds listed in Table 3 below were prepared analogously to Example

Table 3

Example No.	R ¹	Melting point, °C
75	C ₂ H ₅	199 - 201
76	C ₃ H ₇	131 - 132
77	C ₄ H ₉	133 - 134
78	(CH ₃) ₂ CH-CH ₂ -	166 - 168
79	C ₂ H ₅ -CH(CH ₃)-	151 - 152
80	C ₁₂ H ₂₅	116 - 118
81		237 - 238
82		195 - 198
83		220 - 223

The compounds listed in Table 4 below were prepared analogously to Example 3.

Table 4

Example No.	R ¹	R ³	Melting point, °C
84	C ₂ H ₅	NH-CH ₃	162-164
85	C ₂ H ₅	NH-C ₂ H ₅	194 - 195
86	C ₂ H ₅	NH-CH(CH ₃) ₂	147 - 150

Table 4 (continued)

Example No.	R ¹	R ³	Melting point, °C
87	C ₃ H ₇	NH-CH ₃	144 - 145
88	C ₃ H ₇	NH-C ₂ H ₅	130 - 133
89	C ₃ H ₇	NH-CH(CH ₃) ₂	123 - 124
90	C ₃ H ₇	N(CH ₃) ₂	104 - 105
91	(CH ₃) ₂ CH	NH-CH(CH ₃) ₂	158 - 160
92	(CH ₃) ₂ CH	NH-CH ₂ -CH(CH ₃) ₂	154 - 156
93	(CH ₃) ₂ CH-CH ₂	NH-CH ₃	160 - 161
94	(CH ₃) ₂ CH-CH ₂	NH-C ₂ H ₅	142 - 144
95	(CH ₃) ₂ CH-CH ₂	NH-CH(CH ₃) ₂	136 - 138
96	C ₂ H ₅ -CH(CH ₃)-	NH-CH ₃	150 - 151
97	C ₂ H ₅ -CH(CH ₃)-	NH-C ₂ H ₅	104 - 106
98	C ₂ H ₅ -CH(CH ₃)-	NH-CH(CH ₃) ₂	145 - 146
99	C ₂ H ₅ -CH(CH ₃)-	NH-C ₄ H ₉	120 - 121
100	C ₁₂ H ₂₅	NH-CH ₃	148 - 149
101		NH-CH ₃	169 - 171
102		NH-C ₂ H ₅	178 - 179
103		NH-CH(CH ₃) ₂	169 - 172
104		N(CH ₃) ₂	207 - 210
105		NH-C ₂ H ₅	234 - 235
106		N(CH ₃) ₂	172 - 173
107	(CH ₃) ₂ CH	NH ₂	246 - 248
108	C ₂ H ₅ -CH(CH ₃)-	NH ₂	188 - 190

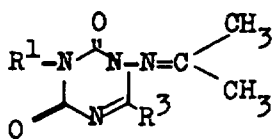
Table 4 (continued)

Example No.	R ¹	R ³	Melting point, °C
109		NH ₂	263 - 265
110	C ₃ H ₇	NH-NH ₂	234 (decomp.)
111	(CH ₃) ₂ CH	NH-NH ₂	224 (decomp.)
112	(CH ₃) ₂ CH-CH ₂	NH-NH ₂	229 - 230
113	C ₂ H ₅ -CH(CH ₃)-	NH-NH ₂	179-181
114		NH-NH ₂	273 (decomp.)
115	(CH ₃) ₂ CH-CH ₂	NH-OH	260 (decomp.)
116		NH-OH	225 (decomp.)
117		NH-OH	208 (decomp.)

Using the 3 - isopropylideneamino compounds (obtained according to Example 1) and heating the mixture under anhydrous conditions, the compounds listed in Table 5 below were obtained analogously to Example 3:

Table 5

Example No.	R ¹	R ³	Melting point, °C
118	(CH ₃) ₂ CH-CH ₂	N(CH ₃) ₂	60 - 61
119		N(CH ₃) ₂	156 - 158
120		N(CH ₃) ₂	168 - 172



WHAT WE CLAIM IS:—

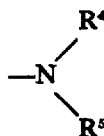
1. Tetrahydro - 1,3,5 - triazine - 2,6 - diones of the general formula



in which

R¹ is a saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbon radical, an araliphatic hydrocarbon radical or an aryl radical, each of which can carry one or more substituents selected from halogen, nitro, alkyl, alkoxy, alkylmercapto, aryl, aryloxy, halogenomethyl or arylmercapto,

R² is hydrogen, alkyl, cycloalkyl, aralkyl, aryl (which may be optionally substituted by chlorine), hydroxyl, alkoxy, acyloxy or an



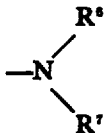
radical

wherein

R⁴ and R⁵, which may be identical or different, are each hydrogen, alkyl or acyl (both of which are optionally substituted by nitrile and/or hydroxyl and/or halogen), or

R⁴ and R⁵ conjointly form alkylidene (which can carry one or more substituents selected from aryl, halogenoaryl, alkoxyaryl, nitroaryl and heterocyclic radicals), or cycloalkylidene and

R³ is hydrogen, alkyl, halogenoalkyl, halogen, aryloxy or an



radical

wherein

R⁶ and R⁷, which may be identical or different, are each hydrogen, alkyl, cycloalkyl, aralkyl, aryl, hydroxyl, amino or alkoxy,

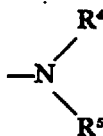
or

R⁶ and R⁷ conjointly with the nitrogen atom form a heterocyclic radical,

or

R³ is alkoxy or alkylmercapto, provided that R² is not hydrogen.

2. Compounds according to claim 1, in which R¹ is a straight-chain or branched C₁—C₁₂ alkyl, which may be substituted by halogen, or C₅—C₇ cycloalkyl, aralkyl or aryl radical which may be substituted by halogen, alkyl or trifluoromethyl; R² is hydrogen, C₁—C₄ alkyl, C₅—C₇ cycloalkyl, aralkyl, aryl or an



radical, wherein R⁴ and R⁵ are each hydrogen, alkyl or acyl or R⁴ and R⁵ conjointly form alkylidene (which may optionally carry one or more substituents selected from aryl, halogenoaryl, alkoxyaryl, nitroaryl and heterocyclic radicals) or cycloalkylidene; and R³ is straight-chain or branched C₁—C₄ alkyl, alkoxy, alkylmercapto or an —NR⁶R⁷ radical, wherein R⁶ and R⁷ are hydrogen, alkyl, hydroxyl, amino or alkoxy.

3. Compounds according to claim 1, in which R¹ is a saturated or unsaturated, aliphatic or cycloaliphatic hydrocarbon radical, an araliphatic hydrocarbon radical or an aryl radical, each of which can carry one or more substituents selected from halogen, nitro, alkyl, alkoxy, alkylmercapto, aryl, aryloxy or arylmercapto, R² is as defined



* C L M S *

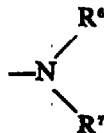
1,397,888



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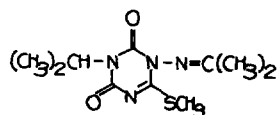
in claim 1 and R^3 is hydrogen alkyl, halogenoalkyl, halogen, aryloxy or an



radical, R^6 and R^7 being as defined in claim 1.

4. The compound of the formula

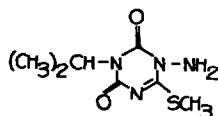
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(4)

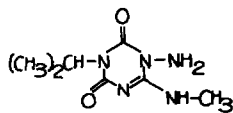
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5. The compound of the formula



(5)

6. The compound of the formula

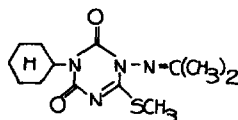


(6)

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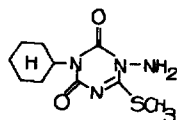
7. The compound of the formula

10



(9)

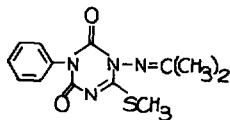
8. The compound of the formula



(10)

9. The compound of the formula

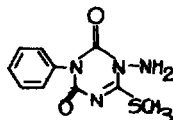
15



(13)

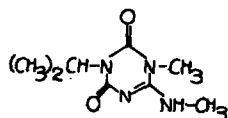
15

10. The compound of the formula



(14)

11. The compound of the formula



(31)

12. The compound of the formula



13. The compound of the formula

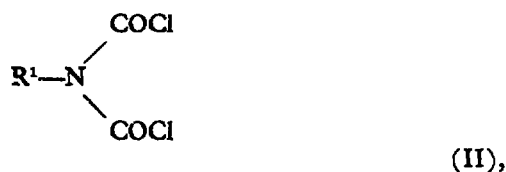


14. The compounds according to claim 1 that are hereinbefore specifically described in Examples 1—3, 7, 8, 11, 12, 15—30, 32, 33, 35—43 and 45—47.

15. The compounds according to claim 1 that are hereinbefore specifically disclosed in Examples 48—120.

16. A process for the preparation of a tetrahydro - 1,3,5 - triazine - 2,6 - dione according to any of claims 1 to 15, in which

(a) a bis - (chlorocarbonyl) - amine of the general formula



in which

R¹ has the meaning stated in claim 1,
is reacted with a compound of the general formula



in which

R² and R³ have the meanings stated in claim 1,
or a salt thereof with an organic or inorganic acid, in the presence of an acid-binding agent, it being possible, when R² is hydroxyl or amino, to protect this group by acylation or hydrazone formation and to liberate it again after the reaction,
or (b) a compound of the general formula



in which

R¹ and R² have the meanings stated in claim 1 and
R is an alkyl radical which is optionally substituted,
is reacted with a compound of the general formula





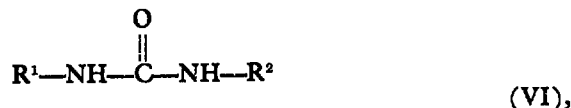
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in which

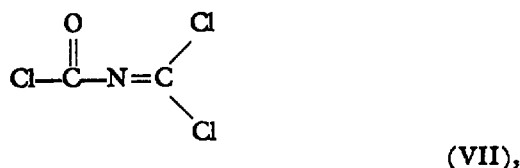
R^6 and R^7 have the meanings stated in claim 1,
or (c) a compound of the general formula



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in which

R^1 and R^2 have the meanings stated in claim 1,
is reacted with chlorocarbonylisocyanide dichloride of the formula



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optionally in the presence of an acid-binding agent, to give a compound of the formula

10



in which

15

R^1 and R^2 have the meanings stated in claim 1,
and this is optionally reacted with a compound of the general formula R^3-H , in the presence of an acid-binding agent, or with a compound of the general formula R^3-M , in which

15

M is an alkali metal atom or a magnesium halide moiety, and

R^3 in either case has the meaning stated in claim 1
or (d) a compound of the general formula

20



20

in which

25

R^1 and R^2 have the meanings stated in claim 1,
is reacted with an inorganic acid halide to give a compound of the formula (VIII) above, which is then optionally reacted with a compound of the formula R^3-H , in the presence of an acid-binding agent, or with a compound of the formula R^3-M , the radical R and M being as defined in process variant (c).

25

17. A process according to claim 16(a), in which the reaction is effected in the presence of an inert organic solvent.

30

18. A process according to claim 16(a) or 17, in which the acid-binding agent is an alkali metal hydroxide or carbonate, an alcoholate or a tertiary amine.

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19. A process according to any of claims 16(a), 17 and 18, in which the reaction is effected at between 0° and 50° C.

20. A process according to claim 19, in which the reaction is effected at between 20° to 40° C.

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21. A process according to any of claims 16(a) and 17 to 20, in which 1 mole of the compound (III) and 2—4 moles of the acid-binding agent are employed per mole of the amine (II).

35

22. A process according to claim 16(b), in which R is an alkyl or carboxy-alkyl radical.

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23. A process according to claim 16(b) or 22, in which the reaction is effected in the presence of an organic solvent.

40



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24. A process according to any of claims 16(b), 22 and 23, in which the reaction is effected in the presence, as a catalyst, of an acid.

25. A process according to claim 24, in which the acid is phosphoric acid, acetic acid, trichloroacetic acid, benzenesulphonic acid or *p* - toluenesulphonic acid.

5 26. A process according to any of claims 16(b) and 22 to 25, in which the reaction is effected at between 0° and 50° C. 5

27. A process according to claim 26, in which the reaction is effected at between 20° and 30° C.

10 28. A process according to any of claims 16(b) and 22 to 27, in which an excess of 5 to 10 moles of the compound (V) and, if required, 0.1—1 mole of acid catalyst are employed per mole of the compound (IV). 10

29. A process according to claim 16(c), in which the reaction is effected in the presence of an inert organic solvent.

15 30. A process according to claim 16(c) or 29, in which the reaction is effected at between -20° and +40° C. 15

31. A process according to claim 30, in which the reaction is effected at between 0° and 30° C.

20 32. A process according to any of claims 16(c) and 29 to 31, in which 1 mole of the compound (VII) and, if required, 2 moles of acid-binding agent are employed per mole of the compound (VI). 20

33. A process according to claim 16(d), in which the reaction is effected in the presence of an inert organic solvent.

34. A process according to claim 16(d) or 33, in which the reaction is effected at between 20° and 120° C.

25 35. A process according to claim 34, in which the reaction is effected at between 40° and 80° C. 25

36. A process according to any of claims 16(d) and 33 to 35, in which 1—10 moles of inorganic acid halide are used per mole of the compound (IX).

30 37. A process according to any of claims 16(d) and 33 to 36, in which the inorganic acid halide is thionyl chloride, phosgene, phosphorus oxychloride or phosphorus pentachloride. 30

38. A process according to any of claims 16(c), 16(d) and 29 to 37, in which the compound (VIII) is reacted with a compound R³—H in the presence, as an acid-binding agent, of a tertiary amine.

35 39. A process according to any of claims 16(c), 16(d) and 29 to 37, in which the compound (VIII) is reacted with a compound R³—M, wherein M is Li, Na, K, MgCl, MgBr or MgI. 35

40. A process for the preparation of a compound according to claim 1, substantially as hereinbefore described in any of Examples 1 to 47.

40 41. A process according to any of claims 16 to 39 whenever directed to the preparation of a compound according to any of claims 3 to 14. 40

42. A compound according to claim 1, whenever prepared by a process according to any of claims 16 to 39.

45 43. A compound according to claim 1, whenever prepared by a process according to claim 40 or 41. 45

44. A herbicidal composition containing as active ingredient a compound according to any of claims 1 to 15, 42 and 43 in admixture with a solid or liquified gaseous diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

50 45. A composition according to claim 44 containing from 0.1 to 95% of the active compound, by weight. 50

46. A composition according to claim 45 containing from 0.5 to 90% of the active compound, by weight.

55 47. A composition according to any of claims 44 to 46, in which the active compound is according to any of claims 3 to 14 and 43. 55

48. A method of combating weeds which comprises applying to the weeds or a weed habitat a compound according to any of claims 1 to 15, 42 and 43, alone or in the form of a composition containing as active ingredient a compound according to any of claims 1 to 15, 42 and 43 in admixture with a diluent or carrier.

60 49. A method according to claim 48, in which the active compound is applied to an area of agriculture in an amount of 0.1 to 20 kg per hectare. 60

50. A method according to claim 49, in which the active compound is applied to an area of agriculture in an amount of 0.5 to 15 kg per hectare.



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51. A method according to any of claims 48 to 50, in which the active compound is one of those hereinbefore mentioned in Example A or B.

52. A method according to any of claims 48 to 50, in which the active compound is according to any of claims 3 to 14 and 43.

53. Crops protected from damage by weeds by being grown in areas in which immediately prior to and/or during the time of the growing a compound according to any of claims 1 to 15, 42 and 43 was applied alone or in admixture with a diluent or carrier.

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