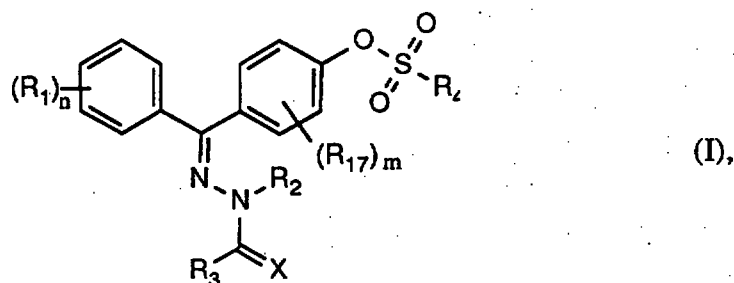


Hydrazone derivatives

The invention relates to compounds of formula



wherein

m is 0, 1, 2, 3 or 4, and, when m is greater than 1, the radicals R_{17} are identical or different;

n is 0, 1, 2, 3, 4 or 5, and, when n is greater than 1, the radicals R_1 are identical or different;

R_1 and R_{17} are each independently of the other halogen, C_1 - C_8 alkyl, halo- C_1 - C_8 alkyl, phenoxy, phenylthio, halo- C_1 - C_8 alkylthio, phenyl, C_1 - C_8 alkylthio, C_1 - C_8 alkyl-carbonyl, OSO_2R_4 , $SO_2NR_{13}R_{14}$ or $P(=Y)R_{22}R_{23}$;

either X is S, R_2 is R_{21} or H and R_3 is R_{31} , $-NR_5R_6$ or $-OR_2$,

or X is O, R_2 is R_{21} and R_3 is R_{31} ,

or X is O, R_2 is H and R_3 is $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$ or $-R_8R_{12}$,

or X and R_3 together are R_{18} ;

Y is O or S;

R_4 is C_1 - C_8 alkyl, halo- C_1 - C_8 alkyl or halo- C_1 - C_8 alkoxy;

R_{21} is C_1 - C_8 alkyl, C_3 - C_6 cycloalkyl, halo- C_1 - C_8 alkyl, C_1 - C_4 alkoxy- C_1 - C_4 alkyl, C_1 - C_4 -alkylthio- C_1 - C_4 alkyl, $R_{13}R_{14}N$ - C_1 - C_4 alkyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_1 - C_4 acyl, $CH=C(CN)_2$, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C_1 - C_4 alkyl, C_2 - C_5 -alkenyl, halo- C_1 - C_4 alkyl, C_1 - C_4 alkoxy, $SO_2NR_{13}R_{14}$, halo- C_1 - C_4 alkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 alkoxy- C_1 - C_4 alkoxy, halo- C_1 - C_4 alkylthio, $NR_{13}R_{14}$, $-NO_2$ and $-CN$;

R_{31} is H, C_1 - C_8 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl- C_1 - C_3 alkyl, halo- C_1 - C_8 alkyl, halo- C_3 - C_6 cycloalkyl- C_1 - C_3 alkyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, halo- C_2 - C_8 alkenyl, $-COOR_7$, $-SR_2$, $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$, $-R_8R_{12}$, $-R_8SR_9$, $-R_8SCSR_9$, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C_1 - C_4 alkyl, C_2 - C_5 alkenyl, halo- C_1 - C_4 alkyl, halo- C_1 - C_4 alkoxy, halo- C_1 - C_4 alkylthio, $SO_2NR_{13}R_{13}$, C_1 - C_4 alkoxy, $-NO_2$ and $-CN$;

an unsubstituted or substituted, saturated or unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group consisting of halogen, C₁-C₄alkyl, halo-C₁-C₄alkyl and C₁-C₄alkoxy;

R₅ and R₆ are each independently of the other H, C₁-C₈alkyl, halo-C₁-C₈alkyl, C₂-C₅alkenyl, C₁-C₄alkoxy, C₂-C₅alkeneoxy or -NR₁₃R₁₄;

R₇ is H, C₁-C₈alkyl, halo-C₁-C₈alkyl or C₂-C₈alkenyl;

R₈ is (CR₁₅R₁₆)_p, wherein p is 1, 2, 3 or 4;

R₉ is C₁-C₈alkyl, halo-C₁-C₁₁alkyl, C₃-C₆cycloalkyl, C₂-C₈alkenyl, halo-C₂-C₁₁alkenyl, C₂-C₈alkynyl, NR₁₀R₁₁, OR₁₀, benzyl, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₂-C₅alkenyl, halo-C₁-C₄alkyl, C₁-C₄alkoxy, -NO₂ and -CN;

R₁₀ and R₁₁ are each independently of the other C₁-C₈alkyl, C₂-C₈alkenyl or C₁-C₈alkoxy-C₁-C₈alkyl;

R₁₂ is an unsubstituted or substituted, saturated or unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group consisting of halogen, C₁-C₄alkyl, halo-C₁-C₄alkyl and C₁-C₄alkoxy;

R₁₃ and R₁₄ are each independently of the other H or C₁-C₈alkyl;

R₁₅ and R₁₆ are each independently of the other H, C₁-C₈alkyl, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₂-C₅alkenyl, halo-C₁-C₄alkyl, C₁-C₄alkoxy, -NO₂ and -CN;

R₁₈ is NC(R₁₉)=C(R₁₉)S, NC(R₁₉)=C(R₁₉)O, NC(R₁₉)₂C(R₁₉)₂S, NC(R₁₉)₂C(R₁₉)₂O, NC(R₁₉)=C(R₁₉)C(R₁₉)=N or N(R₁₉)=NC(R₁₉)=N;

R₁₉ is H, C₁-C₄alkyl, halogen or halo-C₁-C₄alkyl;

R₂₂ is C₁-C₄alkyl, C₁-C₄alkoxy or NR₁₃R₁₄; and

R₂₃ is C₁-C₄alkyl, C₁-C₄alkoxy, C₃-C₄alkylthio or NR₁₃R₁₄,

with the proviso that, in the compounds of formula I, R₂ is other than H when either m is 0, n is 1, R₁ is 4-Cl, R₃ is -N(OCH₃)CH₃, R₄ is CF₃ and X is O, or when m is 0, n is 2, R₁ is 3,4-dichloro, R₃ is -N(OCH₃)CH₃, R₄ is CF₃ and X is O, or when m is 0, n is 1, R₁ is 4-Cl, R₃ is -NHNH₂, R₄ is CF₃ and X is O, and, as the case may be, tautomers thereof, in each case in free form or in salt form;

to a process for the preparation of and to the use of those compounds and tautomers, to pesticidal compositions in which the active ingredient has been selected from those compounds and tautomers, in each case in free form or in the form of an agrochemically

acceptable salt, and to a process for the preparation of and to the use of those compositions.

Certain hydrazone derivatives are proposed in the literature as insecticidally active ingredients in pesticides. The biological properties of those known compounds are not, however, entirely satisfactory in the area of pest control and, therefore, there is a need to provide further compounds having pesticidal properties, especially for the control of insects, ectoparasites and representatives of the order Acarina. This problem is solved according to the invention by the provision of the present compounds I.

Some of the compounds I may be in the form of tautomers. If, for example, R_2 is H, corresponding compounds I, that is to say those having a $-N(H)-C(R_3)=X$ partial structure, may be in equilibrium with the respective tautomers having a $-N=C(R_3)-XH$ partial structure. Accordingly, hereinafter there is to be understood by compounds I, where appropriate, also corresponding tautomers, even if the latter are not specifically mentioned in every case.

The compounds I and, as the case may be, their tautomers may be in the form of salts. Compounds I having at least one basic centre may form, for example, acid addition salts. These are formed, for example, with strong inorganic acids, such as mineral acids, e.g. sulfuric acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted or substituted, for example halo-substituted, C_1-C_4 alkanecarboxylic acids, e.g. acetic acid, saturated or unsaturated dicarboxylic acids, e.g. oxalic, malonic, maleic, fumaric or phthalic acid, hydroxycarboxylic acids, e.g. ascorbic, lactic, malic, tartaric or citric acid, or benzoic acid, or with organic sulfonic acids, such as unsubstituted or substituted, for example halo-substituted, C_1-C_4 alkane- or aryl-sulfonic acids, e.g. methane- or p-toluene-sulfonic acid. Compounds I having at least one acid group may furthermore form salts with bases. Suitable salts with bases are, for example, metal salts, such as alkali metal salts and alkaline earth metal salts, e.g. sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine, e.g. ethylamine, diethylamine, triethylamine or dimethylpropylamine, or a mono-, di- or tri-hydroxy-lower alkylamine, e.g. mono-, di- or tri-ethanolamine. Furthermore, corresponding internal salts may also be formed. Within the scope of the invention, agrochemically advantageous salts are preferred; also included, however, are salts that have disadvantages for agrochemical applications, for example salts that are toxic to bees and to fish, which can be used, for

example, for the isolation and purification of free compounds I or their agrochemically acceptable salts. In view of the close relationship between the compounds I in free form and in the form of their salts, hereinbefore and hereinafter any reference to the free compounds I or their salts is to be understood as including also the corresponding salts or the free compounds I, respectively, where appropriate and expedient. The same applies to tautomers of compounds I and their salts.

Unless defined otherwise, the general definitions used hereinbefore and hereinafter have the meanings given below.

Halogen - as a group *per se* and as a structural unit of other groups and compounds, such as of haloalkyl, halocycloalkyl and haloalkenyl, - is fluorine, chlorine, bromine or iodine, especially fluorine, chlorine or bromine, more especially fluorine or chlorine.

Unless defined otherwise, groups and compounds containing carbon each contain from 1 up to and including 8, preferably from 1 up to and including 4, especially 1 or 2, carbon atoms.

C₃-C₆cycloalkyl is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

Alkyl - as a group *per se* and as a structural unit of other groups and compounds, such as of haloalkyl, alkoxy and alkylthio, - is, duly taking into account the number of carbon atoms contained in the group or compound in question, either straight-chained, i.e. methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, or branched, e.g. isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isooctyl.

Halo-substituted carbon-containing groups and compounds, such as haloalkyl, halocycloalkyl or haloalkenyl, may be partially halogenated or perhalogenated, and, in the case of multiple halogenation, the halogen substituents may be identical or different. Examples of haloalkyl - as a group *per se* and as a structural unit of other groups and compounds, such as of halocycloalkylalkyl and haloalkenyl, - are methyl substituted by from one to three fluorine, chlorine and/or bromine atoms, such as CHF₂ or CF₃; ethyl substituted by from one to five fluorine, chlorine and/or bromine atoms, such as CH₂CF₃, CF₂CF₃, CF₂CCl₃, CF₂CHCl₂, CF₂CHF₂, CF₂CFCI₂, CF₂CHBr₂, CF₂CHClF, CF₂CHBrF or CCIFCHClF; propyl or isopropyl substituted by from one to seven fluorine, chlorine and/or bromine atoms, such as CH₂CHBrCH₂Br, CF₂CHFCF₃, CH₂CF₂CF₃ or CH(CF₃)₂; and butyl or

one of its isomers substituted by from one to nine fluorine, chlorine and/or bromine atoms, such as $\text{CF}(\text{CF}_3)\text{CHFCF}_3$ or $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$.

Acyl groups may be formyl, acetyl, propionyl, butyryl or isobutyryl.

Examples of saturated heterocyclic rings are pyrrolidiny, piperidyl and morpholiny, and examples of unsaturated heterocyclic and heterobicyclic rings are thienyl, pyrrol, imidazolyl, pyrazolyl, triazolyl, thiazolyl, isothiazolyl, pyridyl, indolyl, benzo[b]thienyl and benzo[b]furyl.

Preferred embodiments within the scope of the invention, taking into account the proviso mentioned above, are:

(1) A compound of formula I wherein m is 0, 1 or 2, preferably 0 or 1, especially 0, and, when m is greater than 1, the radicals R_{17} are identical or different, or, as the case may be, a tautomer thereof;

(2) A compound of formula I wherein n is 1, 2 or 3, preferably 1 or 2, especially 1, and, when n is greater than 1, the radicals R_1 are identical or different, or, as the case may be, a tautomer thereof;

(3) A compound of formula I wherein R_1 is halogen, $\text{C}_1\text{-C}_4$ alkyl or halo- $\text{C}_1\text{-C}_4$ alkyl, preferably halogen, especially fluorine, chlorine or bromine, or, as the case may be, a tautomer thereof;

(4) A compound of formula I wherein either X is S, R_2 is R_{21} and R_3 is R_{31} , $-\text{NR}_5\text{R}_6$ or $-\text{OR}_2$, especially X is S, R_2 is R_{21} and R_3 is R_{31} ; or X is O, R_2 is R_{21} and R_3 is R_{31} ; or X is O, R_2 is H and R_3 is $-\text{R}_8\text{OR}_9$, $-\text{R}_8\text{OCOR}_9$, $-\text{R}_8\text{NR}_{10}\text{R}_{11}$ or $-\text{R}_8\text{R}_{12}$, especially X is O, R_2 is H and R_3 is $-\text{R}_8\text{OR}_9$;

(5) A compound of formula I wherein

R_{21} is C_1 - C_4 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, C_1 - C_2 acyl or phenyl, preferably C_1 - C_4 alkyl, C_3 - C_6 cycloalkyl, C_1 - C_4 acyl or phenyl, especially C_1 - C_4 alkyl, formyl or acetyl; or, as the case may be, a tautomer thereof;

(6) A compound of formula I wherein

R_{31} is H, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkylmethyl, halo- C_1 - C_4 alkyl, halo- C_3 - C_6 cycloalkylmethyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, halo- C_2 - C_4 alkenyl, $-COOR_7$, $-SR_2$, $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$, $-R_8R_{12}$, $-R_8SR_9$, $-R_8SCSR_9$, phenyl or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group consisting of halogen, C_1 - C_4 alkyl and C_1 - C_4 alkoxy, preferably H, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, halo- C_1 - C_3 alkyl, halo- C_3 - C_6 cycloalkylmethyl, C_2 - C_4 alkenyl, halogen, $-COOR_7$, $-SR_2$, $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$, $-R_8R_{12}$, phenyl or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group halogen; especially H, C_1 - C_4 alkyl, C_3 - C_6 cycloalkyl, halo- C_1 - C_2 alkyl, halocyclopropylmethyl, C_2 - C_4 alkenyl, fluorine, chlorine, $-SR_2$, $-R_8OCOR_9$, $-R_8R_{12}$ or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing N or S, the substituents being selected from the group fluorine and chlorine,

or, as the case may be, a tautomer thereof;

(7) A compound of formula I wherein

R_4 is C_1 - C_4 alkyl or halo- C_1 - C_4 alkyl, preferably halo- C_1 - C_4 alkyl, especially halo- C_1 - C_2 alkyl, most especially trifluoromethyl, or, as the case may be, a tautomer thereof;

(8) A compound of formula I wherein

R_5 and R_6 are each independently of the other H, C_1 - C_4 alkyl, halo- C_1 - C_4 alkyl,

C_2-C_4 alkenyl, C_1-C_3 alkoxy, C_2-C_3 alkeneoxy or $-NR_{13}R_{14}$,
preferably H, C_1-C_2 alkyl, halo- C_1-C_2 alkyl, C_2-C_3 alkenyl, C_1-C_2 alkoxy, C_2-C_3 alkeneoxy
or $-NR_{13}R_{14}$,
especially H, C_1-C_2 alkyl, C_2-C_3 alkenyl, C_1-C_2 alkoxy, C_2-C_3 alkeneoxy or $-NR_{13}R_{14}$,
or, as the case may be, a tautomer thereof;

(9) A compound of formula I wherein
 R_7 is C_1-C_4 alkyl, halo- C_1-C_4 alkyl or C_2-C_4 alkenyl,
preferably C_1-C_2 alkyl or halo- C_1-C_2 alkyl,
especially methyl or ethyl,
or, as the case may be, a tautomer thereof;

(10) A compound of formula I wherein
 R_8 is $(CR_{15}R_{16})_p$, wherein p is 1, 2 or 3,
preferably 1 or 2,
especially 1,
or, as the case may be, a tautomer thereof;

(11) A compound of formula I wherein
 R_9 is C_1-C_4 alkyl, halo- C_1-C_{11} alkyl, C_3-C_6 cycloalkyl, C_2-C_4 alkenyl, halo- C_2-C_{11} alkenyl, C_2-C_4 alkynyl, $NR_{10}R_{11}$, OR_{10} , benzyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of halogen, C_1-C_2 alkyl, halo- C_1-C_2 alkyl, C_1-C_3 alkoxy, $-NO_2$ and $-CN$;
preferably C_1-C_4 alkyl, halo- C_8-C_{11} alkyl, C_3-C_5 cycloalkyl, C_2-C_3 alkenyl, halo- C_8-C_{11} alkenyl, C_2-C_3 alkynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of fluorine, chlorine, methyl, C_1-C_2 alkoxy and $-NO_2$;
especially C_1-C_4 alkyl, halo- C_8-C_{11} alkyl, cyclopropyl, vinyl, halo- C_8-C_{11} alkenyl, ethynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of chlorine, methyl, methoxy and $-NO_2$;
or, as the case may be, a tautomer thereof;

(12) A compound of formula I wherein
 R_{10} and R_{11} are each independently of the other C_1-C_4 alkyl, C_2-C_4 alkenyl or C_1-C_4 alkoxy- C_1-C_4 alkyl,
preferably C_1-C_2 alkyl, C_2-C_3 alkenyl or C_1-C_2 alkoxy- C_1-C_2 alkyl,

especially methyl, allyl or methoxyethyl,
or, as the case may be, a tautomer thereof;

(13) A compound of formula I wherein

R_{12} is an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group consisting of halogen, C_1 - C_4 alkyl and C_1 - C_4 alkoxy;

preferably an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S,

especially an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S,

most especially imidazolyl, pyrazolyl or triazolyl,

or, as the case may be, a tautomer thereof;

(14) A compound of formula I wherein

R_{13} and R_{14} are each independently of the other H or C_1 - C_4 alkyl,

preferably H or C_1 - C_2 alkyl,

especially H or methyl,

or, as the case may be, a tautomer thereof;

(15) A compound of formula I wherein

R_{15} and R_{16} are each independently of the other H, C_1 - C_4 alkyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of halogen, C_1 - C_2 alkyl, C_2 - C_3 alkenyl, halo- C_1 - C_3 alkyl, C_1 - C_2 alkoxy, $-NO_2$ and $-CN$;

preferably H, C_1 - C_2 alkyl or phenyl,

especially H, methyl or phenyl,

or, as the case may be, a tautomer thereof;

(16) A compound of formula I wherein

R_{17} is halogen or C_1 - C_4 alkyl,

preferably chlorine or methyl,

or, as the case may be, a tautomer thereof;

(17) A compound of formula I wherein

R_{18} is $NC(R_{19})=C(R_{19})S$, $NC(R_{19})=C(R_{19})O$, $NC(R_{19})=C(R_{19})C(R_{19})=N$ or $N(R_{19})=NC(R_{19})=N$,

preferably $NC(R_{19})=C(R_{19})S$, $NC(R_{19})=C(R_{19})O$ or $NC(R_{19})=C(R_{19})C(R_{19})=N$, especially $NC(R_{19})=C(R_{19})S$ or $NC(R_{19})=C(R_{19})O$,

or, as the case may be, a tautomer thereof;

(18) A compound of formula I wherein

m is 0,

n is 1,

R_1 is fluorine, chlorine or bromine,

R_2 is C_1 - C_4 alkyl, C_3 - C_6 cycloalkyl, C_1 - C_4 acyl or phenyl,

R_3 is H, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, halo- C_1 - C_3 alkyl, halo- C_3 - C_6 cycloalkylmethyl, C_2 - C_4 alkenyl, $-COOR_7$, $-SR_2$, $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$, $-R_8R_{12}$, phenyl or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group halogen,

R_4 is C_1 - C_4 alkyl or halo- C_1 - C_4 alkyl,

R_7 is C_1 - C_2 alkyl or halo- C_1 - C_2 alkyl,

R_8 is $CR_{15}R_{16}$,

R_9 is C_1 - C_4 alkyl, halo- C_8 - C_{11} alkyl, C_3 - C_5 cycloalkyl, C_2 - C_3 alkenyl, halo- C_8 - C_{11} alkenyl, C_2 - C_3 alkynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of fluorine, chlorine, methyl, C_1 - C_2 alkoxy and $-NO_2$;

R_{10} and R_{11} are each independently of the other methyl, allyl or methoxyethyl,

R_{12} is an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S, and

R_{15} and R_{16} are each independently of the other H, methyl or phenyl,

or, as the case may be, a tautomer thereof;

(19) A compound of formula I wherein

m is 0,

n is 1,

R_1 is fluorine, chlorine or bromine,

R_2 is C_1 - C_4 alkyl, formyl or acetyl,

R_3 is H, C_1 - C_6 alkyl, C_3 - C_6 cycloalkyl, halo- C_1 - C_3 alkyl, halo- C_3 - C_6 cycloalkylmethyl,

C_2-C_4 alkenyl, $-COOR_7$, $-SR_2$, $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$, $-R_8R_{12}$, phenyl or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group halogen,

R_4 is halo- C_1-C_2 alkyl,

R_7 is methyl or ethyl,

R_8 is $CR_{15}R_{16}$,

R_9 is C_1-C_4 alkyl, halo- C_8-C_{11} alkyl, cyclopropyl, vinyl, halo- C_8-C_{11} alkenyl, ethynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of chlorine, methyl, methoxy and $-NO_2$;

R_{10} and R_{11} are each independently of the other methyl, allyl or methoxyethyl,

R_{12} is an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S, and

R_{15} and R_{16} are each independently of the other H, methyl or phenyl, or, as the case may be, a tautomer thereof;

(20) A compound of formula I wherein

m is 0,

n is 1,

R_1 is fluorine, chlorine or bromine,

R_2 is C_1-C_4 alkyl, formyl or acetyl,

R_3 is H, C_1-C_4 alkyl, C_3-C_6 cycloalkyl, halo- C_1-C_2 alkyl, halocyclopropylmethyl, C_2-C_4 alkenyl, $-COOR_7$, $-SR_2$, $-R_8-OCOR_9$, $-R_8-R_{12}$ or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing N or S, the substituents being selected from the group fluorine and chlorine;

R_4 is trifluoromethyl,

R_7 is methyl or ethyl,

R_8 is $CR_{15}R_{16}$,

R_9 is C_1-C_4 alkyl, halo- C_8-C_{11} alkyl, cyclopropyl, vinyl, halo- C_8-C_{11} alkenyl, ethynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of chlorine, methyl, methoxy and $-NO_2$;

R_{12} is an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S, and

R_{15} and R_{16} are each independently of the other H, methyl or phenyl, or, as the case may be, a tautomer thereof;

(21) A compound of formula I wherein

m is 0,

n is 1,

R₁ is fluorine, chlorine or bromine,

R₂ is C₁-C₄alkyl, formyl or acetyl,

R₃ is H, C₁-C₄alkyl, C₃-C₆cycloalkyl, halo-C₁-C₂alkyl, halocyclopropylmethyl, C₂-C₄alkenyl, -COOR₇, -SR₂, -R₈-OCOR₉, -R₈-R₁₂ or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing N or S, the substituents being selected from the group fluorine and chlorine;

R₄ is trifluoromethyl,

R₇ is methyl or ethyl,

R₈ is CH₂, C(methyl)₂ or CH(phenyl),

R₉ is C₁-C₄alkyl, halo-C₈-C₁₁alkyl, cyclopropyl, vinyl, halo-C₈-C₁₁alkenyl, ethynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of chlorine, methyl, methoxy and -NO₂; and

R₁₂ is an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S,

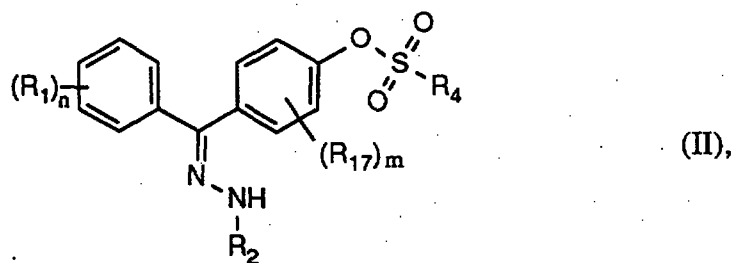
or, as the case may be, a tautomer thereof.

Especially preferred within the scope of the invention are the compounds of formula I listed in Table 1 and, as the case may be, the tautomers thereof, and, most especially, the compounds of formula I mentioned in Examples P2, P3, P5 to P13, P15, P16 and P18 and, as the case may be, the tautomers thereof.

Specifically preferred within the scope of the invention is 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-formyl-N-methylhydrazone (compound 1 in Table 1).

The invention further relates to a process for the preparation of the compounds of formula I and, as the case may be, their tautomers, taking into account the proviso mentioned above, in each case in free form or in salt form, in which process, for example,

a) a compound of formula



which is known or can be prepared analogously to corresponding known compounds and wherein m , n , R_1 , R_2 , R_4 and R_{17} are as defined for formula I, or, as the case may be, a tautomer thereof, in free form or in salt form, is reacted with phosgene or thiophosgene, preferably in the presence of a base, and the intermediate, which is optionally isolated, is reacted, if desired in the presence of a base, with a compound of formula Y_1H , wherein Y_1 is $-NR_5R_6$, $-OR_2$ or $-SR_2$ and R_2 , R_5 and R_6 are as defined for formula I, or with a salt thereof, or

b) for the preparation of a compound of formula I wherein X is O, a compound of formula II is reacted, if desired in the presence of a base, with a compound of formula R_3COY_2 , wherein R_3 is as defined for formula I with the exception of the meanings $-OR_2$ and $-SR_2$, and Y_2 is a leaving group, or

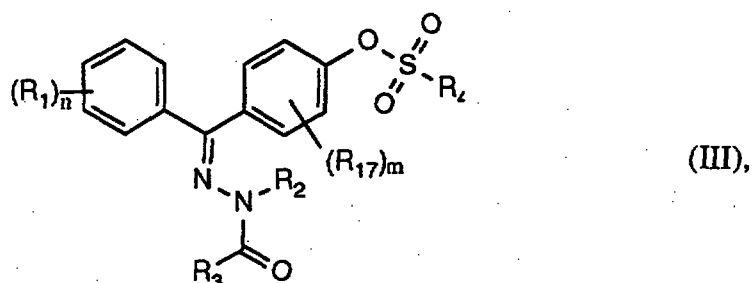
c) for the preparation of a compound of formula I wherein X is S, a compound of formula II is reacted with a compound of formula $Y_3-N=C=S$, wherein Y_3 is H, C_1-C_8 alkyl, halo- C_1-C_8 alkyl or C_2-C_5 alkenyl, preferably H or C_1-C_8 alkyl, to form compounds of formula I wherein X is S, or

d) for the preparation of a compound of formula I wherein X is S and R_3 is $-SR$, wherein R is C_1-C_8 alkyl, C_3-C_6 cycloalkyl, C_2-C_8 alkenyl or C_2-C_8 alkynyl, preferably C_1-C_8 alkyl or C_3-C_6 cycloalkyl, especially C_1-C_8 alkyl, a compound of formula II is reacted, if desired in the presence of a base, with CS_2 , and the intermediate, which is optionally isolated, is reacted, if desired in the presence of a base, with a compound of formula RY_4 , wherein R is as defined above and Y_4 is a leaving group, or

e) for the preparation of a compound of formula I wherein X is O, a compound of formula II is reacted, if desired in the presence of a base, with a compound of formula ClR_8COY_5 , wherein R_8 is as defined for formula I and Y_5 is a leaving group, and the resulting intermediate is reacted, if desired in the presence of a base, optionally in the presence of an alkali metal halide, such as in the presence of sodium iodide, with a compound of formula

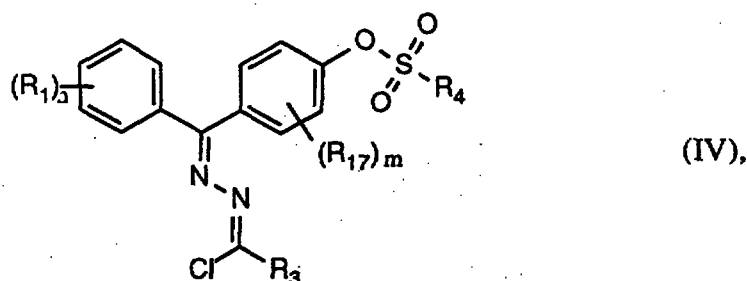
R_9COOH , $HNR_{10}R_{11}$ or R_{12} , wherein R_9 , R_{10} , R_{11} and R_{12} are as defined for formula I, or

f) for the preparation of a compound of formula I wherein X is S, a compound of formula



which is known or can be prepared analogously to corresponding known compounds, for example in accordance with Variant b), and wherein m , n , R_1 , R_2 , R_3 , R_4 and R_{17} are as defined for formula I, is reacted with P_2S_5 , or

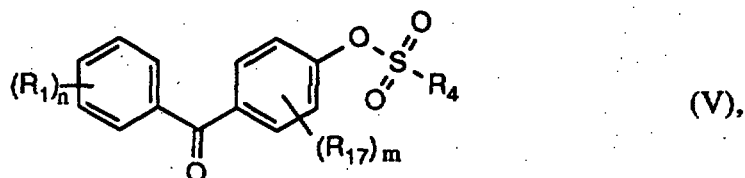
g) for the preparation of a compound of formula I wherein X is S and R_2 is H, a compound of formula



which is known or can be prepared analogously to corresponding known compounds and wherein m , n , R_1 , R_3 , R_4 and R_{17} are as defined for formula I, is reacted, if desired in the presence of a base, with H_2S , or

h) a compound of formula I wherein R_2 is H is reacted, if desired in the presence of a base, with a compound of formula R_2Y_6 , wherein R_2 is as defined for formula I with the exception of the meaning H, and Y_6 is a leaving group, or

i) a compound of formula



which is known or can be prepared analogously to corresponding known compounds and

wherein m , n , R_1 , R_4 and R_{17} are as defined for formula I, is reacted, if desired in the presence of an acid catalyst, if desired in the presence of a water-binding agent, with a compound of formula



which is known or can be prepared analogously to corresponding known compounds and wherein R_2 , R_3 and X are as defined for formula I, or with a salt thereof and/or, as the case may be, with a tautomer thereof,

and in each case, if desired, a compound of formula I or a tautomer thereof obtainable according to the process or by other means, in each case in free form or in salt form, is converted into a different compound of formula I or a tautomer thereof, a mixture of isomers obtainable according to the process is separated and the desired isomer is isolated and/or a free compound of formula I or a tautomer thereof obtainable according to the process is converted into a salt, or a salt of a compound of formula I or of a tautomer thereof obtainable according to the process is converted into the free compound of formula I or a tautomer thereof or into a different salt.

The remarks made above regarding tautomers and salts of compounds I apply analogously to starting materials mentioned hereinbefore and hereinafter with regard to their tautomers and salts.

The reactions described hereinbefore and hereinafter are carried out in a manner known *per se*, for example in the absence or, customarily, in the presence of a suitable solvent or diluent or of a mixture thereof, the reactions being performed as necessary with cooling, at room temperature or with heating, for example in a temperature range of approximately from -80°C to the boiling temperature of the reaction medium, preferably from approximately -20°C to approximately $+150^\circ\text{C}$, and, if necessary, in a closed vessel, under pressure, in an inert gas atmosphere and/or under anhydrous conditions. Especially advantageous reaction conditions are to be found in the Examples.

The starting materials mentioned hereinbefore and hereinafter which are used for the preparation of the compounds I and, as the case may be, their tautomers, in each case in free form or in salt form, are known or can be prepared by methods known *per se*, for example in accordance with the details given below.

Variant a):

Suitable bases for facilitating the reaction are, for example, alkylamines, alkylene-diamines, unsubstituted or N-alkylated, saturated or unsaturated cycloalkylamines, and basic heterocycles. There may be mentioned by way of example triethylamine, diisopropylethylamine, triethylenediamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl 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 hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of a base, bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately +100°C, preferably from approximately -20°C to approximately +20°C.

In a preferred form of Variant a), a compound II is reacted with phosgene at from -20° to 0°, preferably -10°, in an aromatic hydrocarbon, preferably in toluene, and in the presence of a sulfonic acid as catalyst, preferably in the presence of triethylamine, and the product is isolated and further reacted with Y_1H .

Variant b):

Suitable leaving groups are, for example, halogens, C_1 - C_8 alkoxy or C_1 - C_8 alkylcarboxy,

preferably halogens, especially chlorine.

Suitable bases for facilitating the reaction are, for example, alkylamines, alkylene-diamines, unsubstituted or N-alkylated, saturated or unsaturated cycloalkylamines, and basic heterocycles. There may be mentioned by way of example triethylamine, diisopropylethylamine, triethylenediamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl 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 hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of a base, bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately +100°C, preferably from approximately -10°C to approximately +20°C.

In a preferred form of Variant b), a compound II is reacted with one of the mentioned acylating agents at from -20° to 0°, preferably 0°, in an ether, preferably in diethyl ether.

Variant c):

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an

inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl ether, tetrahydrofuran or dioxane; ketones, such as acetone, methyl ethyl ketone or methyl isobutyl ketone; alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol or glycerol; amides, such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately +100°C, preferably from approximately -10°C to approximately +20°C.

Variant d):

Suitable leaving groups are, for example, halogens or C₁-C₈alkylsulfates, preferably halogens, especially bromine or iodine, most especially iodine.

Suitable bases for facilitating the reaction are, for example, alkali metal or alkaline earth metal hydroxides, hydrides, amides, alkanolates, acetates, carbonates, dialkylamides or alkylsilylamides, alkylamines, alkylenediamines, unsubstituted or N-alkylated, saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. There may be mentioned by way of example sodium hydroxide, hydride, amide, methanolate, acetate or carbonate, potassium tert-butanolate, hydroxide, carbonate or hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropylethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)-pyridine, quinuclidine, N-methylmorpholine, benzyltrimethylammonium hydroxide and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU). Especially suitable bases are alkali metal or alkaline earth metal hydrides, most especially alkali metal hydrides.

The reactants can be reacted with each other as such, that is to say without the addition of

a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl 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 hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of a base, bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately $+100^{\circ}\text{C}$, preferably from approximately -10°C to approximately $+20^{\circ}\text{C}$.

In a preferred form of Variant d), a compound II is reacted at from -20° to 0° , preferably 0° , with CS_2 in the presence of an alkali metal hydride, preferably sodium hydride, in a carboxylic acid amide, preferably in dimethylformamide, and then, without isolation of the intermediate, with one of the mentioned alkylating agents.

Variant e):

Suitable leaving groups are, for example, halogens or $\text{C}_1\text{-C}_8$ alkoxy, preferably halogens, especially chlorine.

Suitable bases for facilitating the reaction are, for example, alkylamines, alkylene-diamines, unsubstituted or N-alkylated, saturated or unsaturated cycloalkylamines, and basic heterocycles. There may be mentioned by way of example triethylamine, diisopropylethylamine, triethylenediamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl 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 hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of a base, bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately $+100^{\circ}\text{C}$, preferably from approximately 0°C to approximately $+90^{\circ}\text{C}$.

In a preferred form of Variant e), a compound II is reacted, at from -20° to 20° , preferably 20° , in the presence of a base, preferably pyridine, in a halogen-containing hydrocarbon, preferably in methylene chloride, with one of the acylating agents mentioned in Variant e) and then with one of the nucleophilic reagents mentioned in Variant d).

Variant f):

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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, dimethoxy diethyl ether, tetrahydrofuran or dioxane; and sulfoxides, such as dimethyl sulfoxide.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately +100°C, preferably from approximately -10°C to approximately +20°C.

In a preferred form of Variant f), a compound II is reacted at from -20° to 0°, preferably 0°, with CS₂ in the presence of a base, preferably sodium hydride, in a carboxylic acid amide, preferably in dimethylformamide, and then with an alkylating agent.

Variant g):

Suitable bases for facilitating the reaction are, for example, alkylamines, alkylene-diamines, unsubstituted or N-alkylated, saturated or unsaturated cycloalkylamines, and basic heterocycles. There may be mentioned by way of example triethylamine, diisopropylethylamine, triethylenediamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, quinuclidine, N-methylmorpholine and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

The reactants can be reacted with each other as such; that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl 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 hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of a base, bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately +100°C, preferably from approximately 0°C to approximately +50°C.

In a preferred form of Variant g), a compound IV is reacted with H₂S at from -20° to 20°, preferably 20°, in the presence of a base, preferably triethylamine, in an ether, preferably in tetrahydrofuran.

Variant h):

Suitable leaving groups are, for example, halogens or C₁-C₈alkylsulfates, preferably halogens, especially bromine or iodine, most especially iodine.

Suitable bases for facilitating the reaction are, for example, alkali metal or alkaline earth metal hydroxides, hydrides, amides, alkanolates, acetates, carbonates, dialkylamides or alkylsilylamides, alkylamines, alkylenediamines, unsubstituted or N-alkylated, saturated or unsaturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. There may be mentioned by way of example sodium hydroxide, hydride, amide, methanolate, acetate or carbonate, potassium tert-butanolate, hydroxide, carbonate or hydride, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, diisopropylethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)-pyridine, quinuclidine, N-methylmorpholine, benzyltrimethylammonium hydroxide and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl ether, tetrahydrofuran or dioxane; ketones, such as acetone, methyl ethyl ketone or methyl isobutyl ketone; alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol or

glycerol; amides, such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of a base, bases used in excess, such as triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately $+100^{\circ}\text{C}$, preferably from approximately 0°C to approximately $+90^{\circ}\text{C}$.

Variant i):

Suitable acid catalysts for facilitating the reaction are, for example, sulfonic acids, such as methane- or p-toluene-sulfonic acid, camphor-10-sulfonic acid, pyridinio-p-toluene-sulfonate, including the acidic ion-exchange resins with sulfo groups, Lewis acids, such as boron trifluoride diethyl ether or dimethyl ether complexes, and mineral acids, such as sulfuric acid or phosphoric acid.

Suitable water-binding agents for facilitating the removal of water are, for example, carbodiimides, such as N,N'-dicyclohexylcarbodiimide, or 1-alkyl-2-halo-pyridinium salts, such as 1-methyl-2-chloro-pyridinium iodide.

The reactants can be reacted with each other as such, that is to say without the addition of a solvent or diluent, for example in the melt. In most cases, however, the addition of an inert solvent or diluent or of a mixture thereof is advantageous. Examples of such solvents or diluents are: 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; esters, such as ethyl acetate; 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, dimethoxy diethyl ether, tetrahydrofuran or dioxane; ketones, such as acetone, methyl ethyl ketone or methyl isobutyl ketone; alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol or glycerol; amides, such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric acid triamide; nitriles,

such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide. If the reaction is carried out in the presence of an acid catalyst, acids used in excess, for example strong organic carboxylic acids, such as unsubstituted or substituted, for example halo-substituted, C₁-C₄alkanecarboxylic acids, for example formic acid, acetic acid or propionic acid, may also serve as solvents or diluents.

The reaction is advantageously carried out in a temperature range of from approximately -30°C to approximately +100°C, preferably from approximately 0°C to approximately +90°C.

Salts of compounds I can be prepared in a manner known *per se*. For example, acid addition salts of compounds I are obtained by treatment with a suitable acid or a suitable ion-exchange reagent, and salts with bases are obtained by treatment with a suitable base or a suitable ion-exchange reagent.

Salts of compounds I can be converted into free compounds I in customary manner: acid addition salts, for example, by treatment with a suitable basic agent or a suitable ion-exchange reagent, and salts with bases, for example, by treatment with a suitable acid or a suitable ion-exchange reagent.

Salts of compounds I can be converted into different salts of compounds I in a manner known *per se*: acid addition salts, for example, can be converted into different acid addition salts, for example by treatment of a salt of an inorganic acid, such as a hydrochloride, with a suitable metal salt, such as a sodium, barium or silver salt, of an acid, for example with silver acetate, in a suitable solvent in which an inorganic salt being formed, for example silver chloride, is insoluble and therefore separates from the reaction mixture.

Depending upon the procedure and the reaction conditions, compounds I having salt-forming properties can be obtained in free form or in the form of salts.

The compounds I, II, III and IV may be in the form of one of the possible isomers or in the form of a mixture thereof; for example, depending upon the number and the absolute and relative configuration of the asymmetric carbon atoms, they may be in the form of pure isomers, such as antipodes and/or diastereoisomers, or in the form of mixtures of isomers, such as mixtures of enantiomers, for example racemates, mixtures of diastereoisomers or mixtures of racemates; the invention relates both to the pure isomers and to all possible

mixtures of isomers and this is to be understood hereinbefore and hereinafter, even if stereochemical details are not specifically mentioned in every case.

Mixtures of diastereoisomers and mixtures of racemates of compounds I, II, III and IV that are obtainable in accordance with the process - depending upon the starting materials and procedures chosen, - or by other means, can be separated into the pure diastereoisomers or racemates in known manner on the basis of the physico-chemical differences between the constituents, for example by fractional crystallisation, distillation and/or chromatography.

Mixtures of enantiomers, such as racemates, accordingly obtainable can be separated into the optical antipodes by known methods, for example by recrystallisation from an optically active solvent, by chromatography on chiral adsorbents, for example high-pressure liquid chromatography (HPLC) on acetylcellulose, with the aid of suitable micro-organisms, by cleavage with specific immobilised enzymes, or *via* the formation of inclusion compounds, for example using chiral crown ethers, in which case only one enantiomer is complexed.

Apart from by the separation of corresponding mixtures of isomers, it is possible according to the invention to obtain pure diastereoisomers or enantiomers also by generally known methods of diastereoselective or enantioselective synthesis, for example by carrying out the process of the invention with starting materials having correspondingly suitable stereochemistry.

Advantageously, the biologically more active isomer, for example enantiomer, or mixture of isomers, for example mixture of enantiomers, will be isolated or synthesised, insofar as the individual components have differing biological activity.

The compounds I, II, III and IV can also be obtained in the form of their hydrates and/or may include other solvents, for example solvents that have been used, where appropriate, for the crystallisation of compounds that are in solid form.

The invention relates to all those forms of the process according to which a compound obtainable as starting material or intermediate at any stage of the process is used as starting material and all or some of the remaining steps are carried out, or a starting material is used in the form of a derivative or a salt and/or its racemates or antipodes or, especially, is formed under the reaction conditions.

The starting materials and intermediates used in the process of the present invention are preferably those which result in the compounds I described at the beginning as being especially valuable.

The invention relates especially to the preparation processes described in Examples P1 to P17.

The invention relates also to those starting materials and intermediates used according to the invention for the preparation of the compounds I or the salts thereof, in each case in free form or in salt form, that are novel, to the use thereof and to processes for the preparation thereof.

The compounds I according to the invention are valuable active ingredients in the area of pest control while being well tolerated by warm-blooded animals, fish and plants, the above-mentioned proviso (A) not applying to these active ingredients. In particular, the compounds according to the invention are effective against insects of the type occurring on useful plants and ornamentals in agriculture and in horticulture, especially in cotton, vegetable or fruit crops, and in forestry. The compounds according to the invention are especially suitable for the control of insects in fruit and vegetable crops, especially of phytopathogenic insects, such as *Spodoptera littoralis*, *Heliothis virescens*, *Diabrotica balteata* and *Crocidolomia binotalis*. Further areas of use of the compounds according to the invention are the protection of stored goods and material stocks, and also in the hygiene sector, especially the protection of domestic animals and productive livestock. The compounds of the invention are effective against all or individual development stages of normally sensitive and also resistant types of pest. Their action may manifest itself, for example, in mortality of the pests, which occurs immediately or only at a later date, for example during moulting, or in reduced oviposition and/or a reduced hatching rate.

The above-mentioned pests include:

of the order Lepidoptera, for example

Acleris spp., *Adoxophyes* spp., *Aegeria* spp., *Agrotis* spp., *Alabama argillaceae*, *Amylois* spp., *Anticarsia gemmatilis*, *Archips* spp., *Argyrotaenia* spp., *Autographa* spp., *Busseola fusca*, *Cadra cautella*, *Carposina nipponensis*, *Chilo* spp., *Choristoneura* spp., *Clysia ambiguella*, *Cnaphalocrocis* spp., *Cnephasia* spp., *Cochylis* spp., *Coleophora* spp., *Crocidolomia binotalis*, *Cryptophlebia leucotreta*, *Cydia* spp., *Diatraea* spp., *Diparopsis*

castanea, Earias spp., Ephestia spp., Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypiella, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta spp.;

of the order Coleoptera, for example

Agriotes spp., Anthonomus spp., Atomaria linearis, Chaetocnema tibialis, Cosmopolites spp., Curculio spp., Dermestes spp., Diabrotica spp., Epilachna spp., Eremnus spp., Leptinotarsa decemlineata, Lissorhoptrus spp., Melolontha spp., Oryzaephilus spp., Otiorhynchus spp., Phlyctinus spp., Popillia spp., Psylliodes spp., Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Tenebrio spp., Tribolium spp. and Trogoderma spp.;

of the order Orthoptera, for example

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta spp. and Schistocerca spp.;

of the order Isoptera, for example

Reticulitermes spp.;

of the order Psocoptera, for example

Liposcelis spp.;

of the order Anoplura, for example

Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;

of the order Mallophaga, for example

Damalinea spp. and Trichodectes spp.;

of the order Thysanoptera, for example

Frankliniella spp., Hercinothrips spp., Taeniothrips spp., Thrips palmi, Thrips tabaci and Scirtothrips aurantii;

of the order Heteroptera, for example

Cimex spp., Distantiella theobroma, Dysdercus spp., Euchistus spp., Eurygaster spp., Leptocoris spp., Nezara spp., Piesma spp., Rhodnius spp., Sahlbergella singularis, Scotinophara spp. and Triatoma spp.;

of the order Homoptera, for example

Aleurothrixus floccosus, *Aleyrodes brassicae*, *Aonidiella* spp., *Aphididae*, *Aphis* spp., *Aspidiotus* spp., *Bemisia tabaci*, *Ceroplaster* spp., *Chrysomphalus aonidium*, *Chrysomphalus dictyospermi*, *Coccus hesperidum*, *Empoasca* spp., *Eriosoma larigerum*, *Erythroneura* spp., *Gascardia* spp., *Laodelphax* spp., *Lecanium corni*, *Lepidosaphes* spp., *Macrosiphus* spp., *Myzus* spp., *Nephotettix* spp., *Nilaparvata* spp., *Paratoria* spp., *Pemphigus* spp., *Planococcus* spp., *Pseudaulacaspis* spp., *Pseudococcus* spp., *Psylla* spp., *Pulvinaria aethiopica*, *Quadraspidotus* spp., *Rhopalosiphum* spp., *Saissetia* spp., *Scaphoideus* spp., *Schizaphis* spp., *Sitobion* spp., *Trialeurodes vaporariorum*, *Trioza erytrae* and *Unaspis citri*;

of the order Hymenoptera, for example

Acromyrmex, *Atta* spp., *Cephus* spp., *Diprion* spp., *Diprionidae*, *Gilpinia polytoma*, *Hoplocampa* spp., *Lasius* spp., *Monomorium pharaonis*, *Neodiprion* spp., *Solenopsis* spp. and *Vespa* spp.;

of the order Diptera, for example

Aedes spp., *Antherigona soccata*, *Bibio hortulanus*, *Calliphora erythrocephala*, *Ceratitis* spp., *Chrysomyia* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Drosophila melanogaster*, *Fannia* spp., *Gastrophilus* spp., *Glossina* spp., *Hypoderma* spp., *Hyppobosca* spp., *Liriomyza* spp., *Lucilia* spp., *Melanagromyza* spp., *Musca* spp., *Oestrus* spp., *Orseolia* spp., *Oscinella frit*, *Pegomyia hyoscyami*, *Phorbia* spp., *Rhagoletis pomonella*, *Sciara* spp., *Stomoxys* spp., *Tabanus* spp., *Tannia* spp. and *Tipula* spp.;

of the order Siphonaptera, for example

Ceratophyllus spp. and *Xenopsylla cheopis* and

of the order Thysanura, for example

Lepisma saccharina.

The good pesticidal activity of the compounds of the invention corresponds to a mortality of at least 50 to 60 % of the mentioned pests.

The activity of the compounds according to the invention and of the compositions comprising them can be substantially broadened and adapted to prevailing circumstances by the addition of other insecticides. Examples of suitable additives are representatives of the following classes of compounds: organophosphorus compounds, nitrophenols and derivatives thereof, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons and *Bacillus thuringiensis* preparations.

The compounds according to the invention are used in unmodified form or, preferably,

together with the adjuvants customarily employed in formulation technology and can therefore be formulated in known manner e.g. into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules, and also encapsulations in polymer substances. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or mixtures comprising the compound (active ingredient) of the invention or a combination thereof with other insecticides, and, where appropriate, solid or liquid adjuvants, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredient with the adjuvants, such as extenders, e.g. solvents or solid carriers, or surface-active compounds (surfactants).

Suitable solvents are: aromatic hydrocarbons, preferably alkylbenzene fractions containing 8 to 12 carbon atoms, such as xylene mixtures or alkylated naphthalenes, aliphatic or cycloaliphatic hydrocarbons, such as cyclohexane, paraffins or tetrahydronaphthalene, alcohols, such as ethanol, propanol or butanol, glycols and their ethers and esters, such as propylene glycol, dipropylene glycol ether, ethylene glycol, ethylene glycol monomethyl or monoethyl ether, ketones, such as cyclohexanone, isophorone or diacetanol alcohol, strongly polar solvents, such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or N,N-dimethylformamide, water and vegetable oils or epoxidised vegetable oils, such as rape oil, castor oil, coconut oil or soybean oil or epoxidised rape oil, castor oil, coconut oil or soybean oil; and, where appropriate, silicone oils.

The solid carriers used, e.g. for dusts and dispersible powders, are normally natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. In order to improve the physical properties it is also possible to add highly dispersed silicic acids or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, such as pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are calcite or sand. In addition, a great number of granulated materials of inorganic or organic nature can be used, especially dolomite or pulverised plant residues.

Depending upon the nature of the compound of the invention or of the combination of that compound with other insecticides which is to be formulated, suitable surface-active

compounds are non-ionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

Non-ionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols. Further suitable non-ionic surfactants are water-soluble adducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which adducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit. Representative examples of non-ionic surfactants are nonylphenol polyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Fatty acid esters of polyoxyethylene sorbitan, e.g. polyoxyethylene sorbitan trioleate, are also suitable non-ionic surfactants.

Cationic surfactants are preferably quaternary ammonium salts which contain, as N-substituent, at least one C_8 - C_{22} alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates. Examples are stearyltrimethylammonium chloride and benzyldi(2-chloroethyl)ethylammonium bromide.

Both so-called water-soluble soaps and water-soluble synthetic surface-active compounds are suitable anionic surfactants. Suitable soaps are the alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts of higher fatty acids (C_{10} - C_{22}), e.g. the sodium or potassium salts of oleic or stearic acid or of natural fatty acid mixtures which can be obtained e.g. from coconut oil or tall oil; mention may also be made of fatty acid methyltaurin salts. More frequently, however, so-called synthetic surfactants are used, especially fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates. The fatty sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts and generally contain a C_8 - C_{22} alkyl radical, which also includes the alkyl moiety of acyl radicals; there may be mentioned by way of example the sodium or calcium salt of ligno-

sulfonic acid, of dodecyl sulfate or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated or sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing approximately 8 to 22 carbon atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanol-ammonium salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid or of a condensate of naphthalenesulfonic acid and formaldehyde. Also suitable are corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 mol of ethylene oxide, or phospholipids.

The surfactants listed above are to be regarded merely as examples; many more surfactants customarily employed in formulation technology and suitable for use according to the invention are described in the relevant literature.

The pesticidal compositions usually comprise 0.1 to 99 %, preferably 0.1 to 95 %, of a compound of the invention or of a combination of that compound with other insecticides, and 1 to 99.9 %, preferably 5 to 99.9 %, of a solid or liquid adjuvant, it generally being possible for 0 to 25 %, preferably 0.1 to 20 %, of the composition to be surfactants (percentages are by weight in each case). Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations which have considerably lower active ingredient concentrations. Typical concentration rates are from 0.1 to 1000 ppm, preferably from 0.1 to 500 ppm, active ingredient. The application rates per hectare are generally from 1 to 1000 g of active ingredient per hectare, preferably from 25 to 500 g/ha.

Preferred formulations have especially the following composition (throughout, percentages are by weight):

Emulsifiable concentrates:

active ingredient:	1 to 90 %, preferably 5 to 20 %
surfactant:	1 to 30 %, preferably 10 to 20 %
liquid carrier:	5 to 94 %, preferably 70 to 85 %

Dusts:

active ingredient:	0.1 to 10 %, preferably 0.1 to 1 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

active ingredient:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surfactant:	1 to 40 %, preferably 2 to 30 %

Wettable powders:

active ingredient:	0.5 to 90 %, preferably 1 to 80 %
surfactant:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	5 to 95 %, preferably 15 to 90 %

Granules:

active ingredient:	0.5 to 30 %, preferably 3 to 15 %
solid carrier:	99.5 to 70 %, preferably 97 to 85 %

The compositions may also comprise other adjuvants, such as stabilisers, e.g. vegetable oils or epoxidised vegetable oils (e.g. epoxidised coconut oil, rape oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, as well as fertilisers or other active ingredients for obtaining special effects.

The following Examples serve to illustrate the invention. They do not limit the invention. Temperatures are given in degrees Celsius.

Preparation Examples

General Remarks

The compounds are obtained as isomeric mixtures usually in the form of viscous oils. They can be purified by column chromatography. NMR spectra and elemental analyses confirm the required structures.

Example P1: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methylhydrazone
180 g of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone are heated under reflux in 600 ml of absolute alcohol with 29.6 g of glacial acetic acid and 31.8 g of methylhydrazine for one day. The solution is then concentrated by evaporation *in vacuo*, and the residue is taken up in approximately 150 ml of toluene and again concentrated by evaporation. The oil which remains is taken up in hexane/ethyl acetate 9:1 and the solution is

stirred over magnesium sulfate and sodium bicarbonate for approximately 30 minutes. The salts are removed by filtration and the filtrate is concentrated by evaporation *in vacuo*. The title compound remains behind in the form of a yellow oil.

Example P2: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-formyl-N-methylhydrazone (compound 1.1 in Table 1)

With the exclusion of moisture, 150 g of sodium formate are introduced into approximately 125 ml of ether with stirring, and 147 g (1.87 mol) of acetyl chloride are added dropwise thereto at a reaction temperature of 0°C. The reaction mixture is then stirred for several hours at room temperature, sodium chloride is removed by filtration, and the residue is washed with dry ether to yield a solution of approximately 1.87 mol of formyl acetate in ether.

A portion of that solution, containing 0.49 mol of formyl acetate, is added dropwise to a solution of 184 g of the hydrazone from Example P1 in 200 ml of ether. The reaction is complete after a few hours. Ice-water is added, the organic layer is collected, washed once more with water, dried over magnesium sulfate and filtered, and the filtrate is concentrated by evaporation and purified by column chromatography on silica gel using ethyl acetate/hexane 1:9 as eluant. The product is obtained as an isomeric mixture in the form of an oily-waxy mass.

Example P3: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-acetyl-N-formylhydrazone (compound 1.2 in Table 1)

4.05 g of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-formylhydrazone are stirred in 30 ml of dry tetrahydrofuran with 0.7 ml of acetyl chloride and 1.4 ml of triethylamine and, after 20 hours, the reaction solution is concentrated by evaporation and the residue is chromatographed on a column of silica gel using ethyl acetate/hexane 1:5 as eluant. The title compound is obtained as an isomeric mixture having a melting point of 137-142°C.

Example P4: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-chlorocarbonyl-N-methylhydrazone

At -10°C, a solution of 40.5 g of the hydrazone from Example P1 and 10.1 g of triethylamine in 100 ml of ethyl acetate are added dropwise to 57 ml of 0.11M phosgene solution in toluene. After approximately 1 hour, the reaction solution is filtered and washed with a small amount of ethyl acetate, the filtrate is concentrated by evaporation *in vacuo*, and the

residue is purified on a column of silica gel using ethyl acetate/hexane 1:9 as eluant. The product is obtained in the form of a sticky crystalline mass.

Example P5: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methyl-N-methylaminocarbonylhydrazone (compound 1.3 in Table 1)

0.025 mol of methylamine (33 % in absolute alcohol) is added all at once to 0.01 mol of the carbamoyl chloride from Example P4 in the form of a crude solution in ethyl acetate. After 15 minutes, the reaction mixture is poured onto ice-water, and the organic layer is separated off and, after being dried over magnesium sulfate, is concentrated by evaporation *in vacuo*. Purification by column chromatography on silica gel using ethyl acetate/hexane (1:2) as eluant yields the title compound having a melting point of 112-116°C.

Example P6: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methyl-N-thiomethylcarbonylhydrazone (compound 1.4 in Table 1)

0.02 mol of the carbamoyl chloride from Example P4 in ethyl acetate solution is stirred overnight with 1.5 g of sodium methylmercaptide; working-up yields the title compound in the form of a viscous yellowish oil.

Example P7: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methylthiomethylcarbonylhydrazone (compound 1.126 in Table 1)

0.065 mol of a solution of triethylammonium hydrogen sulfide in tetrahydrofuran (prepared beforehand by passing 34 g of hydrogen sulfide into a solution of 101 g of triethylamine in tetrahydrofuran) is added to 2.55 g of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-(1-chloro)-ethylidenehydrazone in 20 ml of tetrahydrofuran. The reaction mixture is then stirred for a few hours and is concentrated by evaporation, and the residue is chromatographed on silica gel using ethyl acetate/hexane 1:9 as eluant, to yield an isomeric mixture of the title compound in the form of a thick yellowish oil.

Example P8: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N,N-dimethylaminothiocarbonyl-N-methylhydrazone (compound 1.127 in Table 1)

Analogously to Example P4, but using thiophosgene instead of phosgene, a yellow solution of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methyl-N-chlorothiocarbamoylhydrazone in ethyl acetate is prepared. To an aliquot of that solution, containing 0.023 mol of the thiocarbamoyl chloride, there are added 6.5 g of 33 % dimethylamine solution in absolute alcohol. After three hours, ice-water is added and the organic layer is separated off, dried and concentrated by evaporation. The residue is

purified on a column of silica gel using ethyl acetate/hexane 1:9 as eluant. The title compound is obtained in the form of a viscous yellow oil.

Example P9: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methyl-N-thioformylhydrazone (compound 1.128 in Table 1)

3.6 g of the compound from Example P2 are stirred with 1.9 of phosphorus pentasulfide in 30 ml of toluene for 20 hours. For working up, ice-water and sodium bicarbonate are added, extraction is carried out with ethyl acetate, the organic phase is dried and concentrated by evaporation *in vacuo* and the residue is chromatographed using ethyl acetate/hexane 1:9. The title compound is obtained in the form of an orange-coloured oil.

Example P10: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methyl-N-methylthiothiocarbonylhydrazone (compound 1.129 in Table 1)

7.1 g of the compound from Example P1 are introduced into a mixture of 25 ml of dry dimethylformamide and 1.3 ml of carbon disulfide. At 0°C, 0.6 g of sodium hydride (80 % dispersion in oil) is added. After approximately 30 minutes, 1.3 ml of methyl iodide are added. After two hours, ice-water is added and extraction is carried out with ether. The organic phases are combined, dried and concentrated by evaporation, to yield a viscous oil which is purified on a column of silica gel using ethyl acetate/hexane 1:9. The title compound is obtained as an isomeric mixture having a melting point of 94-99°C.

Example P11: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-aminothiocarbonylhydrazone (compound 1.130 in Table 1)

15 g of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenonehydrazone are stirred with 3.5 g of ammonium rhodamide in 100 ml of alcohol, and added dropwise to 4.5 g of methanesulfonic acid. The reaction mixture is then stirred for several hours until the starting material can no longer be detected in a thin-layer chromatogram. The product is precipitated by the addition of water. It is isolated by filtration, dried and recrystallised from ethyl acetate/hexane to yield the title compound having a melting point of 94-96°C.

Example P12: 4-fluoro-4'-trifluoromethanesulfonyloxybenzophenone-N-isobutylidene-carbonyl-N-methylbenzophenone (compound 1.12 in Table 1)

1.28 g of N-ethyl-diisopropylamine and 1.47 g of 3,3-dimethylacrylic acid chloride are added in succession to a solution of 3.38 g of 4-fluoro-4'-trifluoromethanesulfonyloxybenzophenone-N-methylhydrazone (prepared analogously to the method described in Example P1) in 50 ml of tetrahydrofuran, and the reaction mixture is stirred at room

temperature for 15 hours. It is then concentrated by evaporation *in vacuo*. The residue is partitioned between dichloromethane and water. The organic phase is dried over sodium sulfate, filtered and concentrated by evaporation. The crude product is chromatographed on silica gel using hexane/ethyl acetate 10:1 to yield the title compound in the form of a yellow oil.

Example P13: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methyl-N-(N'-methoxy-N'-methyl)aminocarbonylhydrazone (compound 1.5 in Table 1)

0.91 g of triethylamine and 1.1 g of N-methyl-N-methoxycarbonyl chloride are added in succession to a solution of 3.2 g of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-methylhydrazone in 50 ml of toluene. After refluxing for 2 hours, the reaction mixture is cooled and concentrated by evaporation *in vacuo*. The residue is partitioned between ethyl acetate and water. The organic phase is dried over sodium sulfate, filtered and concentrated by evaporation. The crude product is chromatographed on silica gel using ethyl acetate/hexane 1:5 to yield the title compound in the form of a brownish oil.

Example P14: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-chloromethyl-carbonylhydrazone

7.2 g of chloroacetyl chloride are added dropwise over a period of 30 minutes to a solution of 22 g of 4-chloro-4'-trifluoromethanesulfonyloxybenzophenonehydrazone and 5.5 g of pyridine in 100 ml of methylene chloride. The reaction mixture is stirred at room temperature for 16 hours, then poured onto 100 ml of water and extracted with 200 ml of methylene chloride. The organic phase is washed with saturated sodium chloride solution, dried with magnesium sulfate and concentrated by evaporation. The resulting crude product is purified by chromatography on silica gel using hexane/ethyl acetate 3:1 to yield the title compound in the form of a solid having a melting point of 123-125°C.

Example P15: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-(6-chloro-6,6-difluoro-2-oxa-3-oxohexanecarbonyl)hydrazone (compound 1.78 in Table 1)

A mixture of 3 g of the product from Example P14, 0.1 g of sodium iodide, 1.0 g of 4-chloro-4,4-difluorobutyric acid and 0.67 g of triethylamine in 10 ml of DMF is heated at 90°C for 16 hours. The reaction mixture is then poured onto water and extracted with 100 ml of ethyl acetate. The organic phase is washed with saturated sodium chloride solution, dried with magnesium sulfate and concentrated by evaporation. The resulting crude product is purified by chromatography on silica gel using methylene chloride/2 % methanol to yield the title compound in the form of an amorphous solid.

Example P16: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-(acetoxy-methylenecarbonyl)hydrazone (compound 1.77 in Table 1)

A mixture of 4 g of the product from Example P14, 0.13 g of sodium iodide and 0.72 g of sodium acetate in 10 ml of DMF is heated at 50°C for 5 hours. The reaction mixture is then poured onto water and extracted with 100 ml of ethyl acetate. The organic phase is washed with saturated sodium chloride solution, dried with magnesium sulfate and concentrated by evaporation. The resulting residue is purified by chromatography on silica gel using hexane/ethyl acetate 1:1 to yield the title compound in the form of an amorphous solid.

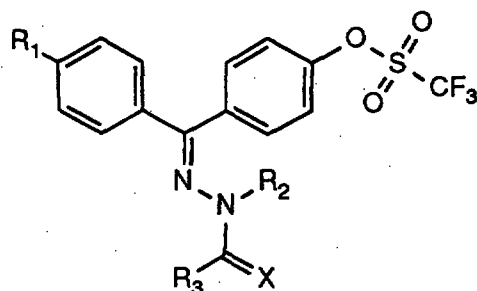
Example P17: 4-chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-(1-imidazolyl)-methylenecarbonylhydrazone (compound 1.80 in Table 1).

A mixture of 3 g of the product from Example P14, 0.1 g of sodium iodide, 0.45 g of imidazole and 0.66 g of triethylamine in 10 ml of DMF is heated at 50°C for 10 hours. The reaction mixture is then poured onto water and extracted with 100 ml of ethyl acetate. The organic phase is washed with saturated sodium chloride solution, dried with magnesium sulfate and concentrated by evaporation. The resulting crude product is purified by chromatography on silica gel using methylene chloride/methanol (1 %) to yield the title compound in the form of an amorphous solid.

Example P18:

In a manner analogous to that described in Examples P2, P3, P5 to P13 and P15 to P17, it is also possible to prepare the other compounds listed in Tables 1 to 4. In the column "physic. data" of those Tables, the numbers indicate the melting point.

Table 1



comp. no.	X	R ₁	R ₂	R ₃	physic. data
1.1	O	Cl	CH ₃	H	oil/wax
1.2	O	Cl	CHO	CH ₃	137-142°
1.3	O	Cl	CH ₃	NHCH ₃	112-116°
1.4	O	Cl	CH ₃	SCH ₃	oil
1.5	O	Cl	CH ₃	N(OCH ₃)CH ₃	resin
1.6	O	F	CH ₃	N(OCH ₃)CH ₃	resin
1.7	O	Cl	CH ₃	N(OC ₂ H ₅)CH ₃	resin
1.8	O	Cl	CH ₃	N(OC ₂ H ₅)C ₂ H ₅	oil
1.9	O	F	CH ₃	CH ₃	resin
1.10	O	F	CH ₃	C ₂ H ₅	88-91°
1.11	O	F	CH ₃	i-C ₃ H ₇	resin
1.12	O	F	CH ₃	CH=C(CH ₃) ₂	resin
1.13	O	F	CH ₃	cyclo-C ₃ H ₅	72-76°
1.14	O	Cl	CH ₃	cyclo-C ₃ H ₅	80-82°
1.15	O	Cl	CH ₃	NHOC ₂ H ₅	oil
1.16	O	Cl	CH ₃	NHOCH ₂ CH=CH ₂	oil
1.17	O	Cl	CH ₃	NHOCH ₂ C(CH ₃)=CH ₂	oil
1.18	O	Cl	CH ₃	CH ₂ -cyclo-C ₃ H ₃ F ₂ (2,2)	resin
1.19	O	Cl	CHO	CF ₃	108-110°
1.20	O	F	CH ₃	CH ₂ -cyclo-C ₃ H ₃ F ₂ (2,2)	resin
1.21	O	Cl	CH ₃	NH ₂	118-126°
1.22	O	Cl	CH ₃	CH ₃	80-82
1.23	O	Cl	CH ₃	Cl	oil
1.24	O	Br	CH ₃	C ₂ H ₅	
1.25	O	Br	CH ₃	CH ₃	94-105°

1.26	O	Br	CH ₃	n-C ₃ H ₇	113-115°
1.27	O	Br	CH ₃	i-C ₃ H ₇	honey
1.28	O	Br	CH ₃	CH(CH ₃)C ₂ H ₅	oil
1.29	O	Br	CH ₃	cyclohexyl	resin
1.30	O	Br	CH ₃	t-C ₄ H ₉	resin
1.31	O	Br	CH ₃	n-C ₃ H ₇	resin
1.32	O	Br	CH ₃	cyclo-C ₃ H ₅	92-103°
1.33	O	Cl	CH ₃	thien-2-yl	amorphous
1.34	O	Cl	CH ₃	thien-3-yl	resin
1.35	O	Cl	CH ₃	5-chlorothien-2-yl	resin
1.36	O	Cl	CH ₃	3-chlorothien-2-yl	
1.37	O	Cl	CH ₃	benzo[b]thien-2-yl	
1.38	O	Cl	CH ₃	5-chlorobenzo[b]thien-2-yl	
1.39	O	Cl	CH ₃	3-chlorobenzo[b]thien-2-yl	amorphous
1.40	O	Cl	CH ₃	pyrid-2-yl	
1.41	O	Cl	CH ₃	pyrid-3-yl	
1.42	O	Cl	CH ₃	pyrid-4-yl	
1.43	O	Cl	CH ₃	6-chloropyrid-3-yl	
1.44	O	Br	CH ₃	thien-2-yl	amorphous
1.45	O	Br	CH ₃	thien-3-yl	resin
1.46	O	Br	CH ₃	5-chlorothien-2-yl	amorphous
1.47	O	Br	CH ₃	3-chlorothien-2-yl	amorphous
1.48	O	Br	CH ₃	benzo[b]thien-2-yl	amorphous
1.49	O	Br	CH ₃	5-chlorobenzo[b]thien-2-yl	
1.50	O	Br	CH ₃	3-chlorobenzo[b]thien-2-yl	amorphous
1.51	O	Br	CH ₃	pyrid-2-yl	
1.52	O	Br	CH ₃	pyrid-3-yl	
1.53	O	Br	CH ₃	pyrid-4-yl	
1.54	O	Br	CH ₃	6-chloropyrid-3-yl	
1.55	O	Cl	CH ₃	CF ₃	
1.56	O	Cl	CH ₃	SC ₂ H ₅	
1.57	O	Cl	CH ₃	N(CH ₃) ₂	
1.58	O	Cl	CH ₃	NHNH ₂	
1.59	O	Cl	CH ₃	N(CH ₃)NH ₂	
1.60	O	Cl	CH ₃	NHN(CH ₃) ₂	
1.61	O	Cl	C ₂ H ₅	H	oil

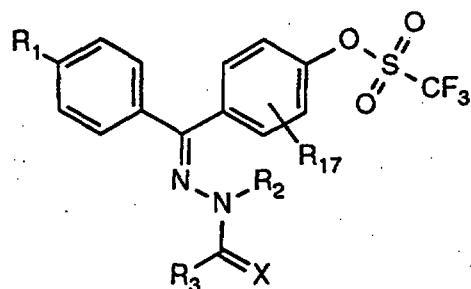
1.62	O	Cl	C ₂ H ₅	CH ₃	50-60°
1.63	O	Cl	C ₂ H ₅	C ₂ H ₅	
1.64	O	Cl	C ₂ H ₅	NH ₂	
1.65	O	Cl	C ₂ H ₅	SCH ₃	
1.66	O	Cl	C ₂ H ₅	SC ₂ H ₅	
1.67	O	Cl	C ₂ H ₅	NHNH ₂	
1.68	O	Cl	C ₂ H ₅	N(CH ₃) ₂	
1.69	O	Cl	C ₂ H ₅	NHCH ₃	
1.70	O	Cl	n-C ₄ H ₉	H	
1.71	O	Cl	n-C ₄ H ₉	CH ₃	
1.72	O	Cl	n-C ₄ H ₉	SCH ₃	
1.73	O	Cl	n-C ₄ H ₉	NH ₂	
1.74	O	Cl	CHO	C ₂ H ₅	
1.75	O	Cl	CHO	n-C ₃ H ₇	
1.76	O	Cl	CHO	i-C ₃ H ₇	
1.77	O	Cl	H	CH ₂ OCOCH ₃	50-60°
1.78	O	Cl	H	CH ₂ OCOCH ₂ CH ₂ CF ₂ Cl	amorphous
1.79	O	Cl	H	CH ₂ OCO(CH ₂) ₁₀ CF ₂ Cl	resin
1.80	O	Cl	H	CH ₂ -1-imidazolyl	75-85°
1.81	O	Cl	H	CH(C ₆ H ₅)OCOCH ₃	
1.82	O	Cl	H	C(CH ₃) ₂ OCOCH ₃	
1.83	O	Cl	H	CH ₂ OCOC ₆ H ₅	
1.84	O	Cl	H	CH ₂ OCOCH ₂ C ₆ H ₅	
1.85	O	Cl	H	CH ₂ OCOC ₆ H ₄ Cl(4)	
1.86	O	Cl	H	CH ₂ OCOC ₆ H ₄ OCH ₃ (4)	
1.87	O	Cl	H	CH ₂ OCOC ₆ H ₄ NO ₂ (4)	
1.88	O	Cl	H	CH ₂ OCO(CH ₂) ₈ CH=CHCF ₂ Cl	resin
1.89	O	Cl	H	CH ₂ OCO(CH ₂) ₃ CH=CF ₂	
1.90	O	Cl	H	CH ₂ OCO(CH ₂) ₉ CH=CF ₂	
1.91	O	Cl	H	CH ₂ OCO-t-C ₄ H ₉	
1.92	O	Cl	H	CH ₂ OCO-cyclo-C ₃ H ₅	
1.93	O	Cl	H	CH ₂ OCOCH=CH ₂	
1.94	O	Cl	H	CH ₂ OCOC≡CH	
1.95	O	Cl	H	CH ₂ -1-pyrazolyl	
1.96	O	Cl	H	CH ₂ -1-(1,2,4)triazolyl	64-68°
1.97	O	Cl	CH ₃	CH ₂ OCOCH ₃	

1.98	O	Cl	CH ₃	CH ₂ OCOCH ₂ CH ₂ CF ₂ Cl	
1.99	O	Cl	CH ₃	CH ₂ OCO(CH ₂) ₁₀ CF ₂ Cl	
1.100	O	Cl	CH ₃	CH ₂ -1-imidazolyl	123-125°
1.101	O	Cl	CH ₃	CH ₂ OCOC ₆ H ₅	145-147°
1.102	O	Cl	CH ₃	CH ₂ OCOCH ₂ C ₆ H ₅	resin
1.103	O	Cl	CH ₃	CH ₂ OCO(CH ₂) ₈ CH=CHCF ₂ Cl	
1.104	O	Cl	CH ₃	CH ₂ OCO(CH ₂) ₃ CH=CF ₂	
1.105	O	Cl	CH ₃	CH ₂ OCO(CH ₂) ₉ CH=CF ₂	
1.106	O	Cl	CH ₃	CH ₂ OCO-t-C ₄ H ₉	
1.107	O	Cl	CH ₃	CH ₂ OCO-cyclo-C ₃ H ₅	
1.108	O	Cl	CH ₃	CH ₂ OCOCH=CH ₂	
1.109	O	Cl	CH ₃	CH ₂ OCOC≡CH	
1.110	O	F	H	CH ₂ OCOCH ₃	
1.111	O	F	CH ₃	CH ₂ OCOCH ₃	
1.112	O	F	H	CH ₂ OCOCH ₂ CH ₂ CF ₂ Cl	
1.113	O	F	CH ₃	CH ₂ OCOCH ₂ CH ₂ CF ₂ Cl	
1.114	O	F	H	CH ₂ OCOC ₆ H ₅	
1.115	O	F	CH ₃	CH ₂ OCOC ₆ H ₅	
1.116	O	F	H	CH ₂ OCO(CH ₂) ₃ CH=CF ₂	
1.117	O	F	CH ₃	CH ₂ OCO(CH ₂) ₃ CH=CF ₂	
1.118	O	F	H	CH ₂ OCO-cyclo-C ₃ H ₅	
1.119	O	F	CH ₃	CH ₂ OCO-cyclo-C ₃ H ₅	
1.120	O	F	H	CH ₂ OCOCH=CH ₂	
1.121	O	F	CH ₃	CH ₂ OCOCH=CH ₂	
1.122	O	F	H	CH ₂ OCOC≡CH	
1.123	O	F	CH ₃	CH ₂ OCOC≡CH	
1.124	O	Br	H	CH ₂ OCOCH ₃	
1.125	O	Br	CH ₃	CH ₂ OCOCH ₃	
1.126	S	Cl	H	CH ₃	oil/resin
1.127	S	Cl	CH ₃	N(CH ₃) ₂	oil
1.128	S	Cl	CH ₃	H	oil
1.129	S	Cl	CH ₃	SCH ₃	94-99°
1.130	S	Cl	H	NH ₂	94-96°
1.131	S	Cl	H	N(CH ₃) ₂	154-157°
1.132	S	Cl	H	H	110-112°
1.133	S	Cl	CH ₃	NHCH ₃	201-203°

1.134	S	Cl	H	SCH ₃	oil
1.135	S	Cl	CH ₃	N(OCH ₃)CH ₃	
1.136	S	Cl	CH ₃	OCH ₃	
1.137	S	Cl	CH ₃	OC ₂ H ₅	
1.138	S	Cl	CH ₃	CH ₃	
1.139	S	Cl	C ₂ H ₅	SCH ₃	
1.140	S	Cl	C ₂ H ₅	NHCH ₃	
1.141	S	Cl	C ₂ H ₅	NH ₂	
1.142	S	Cl	C ₂ H ₅	N(CH ₃) ₂	
1.143	S	Cl	C ₂ H ₅	OCH ₃	
1.144	S	Cl	n-C ₃ H ₇	NHCH ₃	
1.145	S	Cl	n-C ₃ H ₇	NH ₂	
1.146	S	Cl	n-C ₃ H ₇	OCH ₃	
1.147	S	Cl	COCH ₃	CH ₃	
1.148	S	Cl	COCH ₃	C ₂ H ₅	
1.149	S	Cl	COCH ₃	CF ₃	
1.150	S	Cl	COCH ₃	COOCH ₃	
1.151	S	Cl	H	NHCH ₃	165-170°
1.152	S	Br	H	H	
1.153	S	Br	H	CH ₃	
1.154	S	Br	H	SCH ₃	
1.155	S	Br	H	NHCH ₃	
1.156	S	Br	H	N(OCH ₃)CH ₃	
1.157	S	Br	CH ₃	H	
1.158	S	Br	CH ₃	CH ₃	
1.159	S	Br	CH ₃	SCH ₃	
1.160	S	Br	CH ₃	NHCH ₃	
1.161	S	Br	CH ₃	N(OCH ₃)CH ₃	
1.162	S	Br	COCH ₃	CH ₃	
1.163	S	Br	COCH ₃	COOCH ₃	
1.164	O	Br	i-C ₃ H ₇	CH ₃	resin
1.165	O	Cl	C ₂ H ₅	CF ₃	oil
1.166	O	Cl	CH ₃	CH ₂ Cl	59-61°
1.167	O	Cl	n-C ₃ H ₇	H	oil
1.168	O	Cl	n-C ₃ H ₇	CH ₃	oil
1.169	O	Cl	CH ₃	CH ₂ OCOC ₆ H ₄ NO ₂ (p)	64-70°

1.170	O	Cl	CH ₃	CH ₂ OCOC ₆ H ₄ Cl(p)	resin
1.171	O	Cl	CH ₃	CH ₂ OCOC ₆ H ₄ OCH ₃ (p)	59-63°
1.172	O	Cl	CH ₃	CH ₂ -morpholine	resin
1.173	O	Cl	H	CH ₂ OCO(CH ₂) ₅ CH=CH ₂	resin
1.174	S	Cl	CH ₃	NH ₂	118-125°
1.175	O	Cl	CH ₃	CH ₂ COOCH ₃	resin
1.176	O	Cl	CH ₃	COOCH ₃	resin
1.177	O	Cl	CH ₃	C(CH ₃) ₂ OCOCH ₃	135-137°
1.178	O	Cl	CH ₃	CH ₂ OCH ₂ C ₆ H ₅	resin
1.179	O	Cl	CH ₃	(CH ₂) ₃ COOC ₂ H ₅	resin
1.180	O	Cl	CH ₃	CH ₂ -cyclo-C ₆ H ₁₁	resin
1.181	O	Cl	CH ₃	CH ₂ -cyclo-C ₅ H ₉	resin
1.182	O	Cl	CH ₃	CH(C ₆ H ₅)OCOCH ₃	resin
1.183	O	Cl	COCH ₃	CH ₃	resin
1.184	O	Cl	COCH ₃	CF ₃	resin
1.185	O	Cl	COCH ₃	cyclo-C ₃ H ₇	resin
1.186	O	Cl	i-C ₃ H ₇	H	resin
1.187	O	Cl	COCF ₃	CF ₃	resin
1.188	O	Cl	H	CH(C ₂ H ₅)SC ₆ H ₅	133-135°
1.189	O	Cl	H	CH ₂ SCSN(CH ₃) ₂	amorphous
1.190	O	Cl	H	CH ₂ SCSO-i-C ₃ H ₇	amorphous
1.191	O	Cl	COC ₂ H ₅	CH ₃	resin
1.192	O	Cl	H	CH ₂ SCSOC ₂ H ₅	resin
1.193	O	Cl	H	CH ₂ SCSN(CH ₃)OCH ₃	resin
1.194	O	Br	CH ₃	H	85-91°
1.195	O	Cl	CH ₃	OCH ₃	oil
1.196	O	Cl	CH ₃	OC ₂ H ₅	oil
1.197	O	Cl	CH ₃	O-t-C ₄ H ₉	oil
1.198	O	Cl	C ₂ H ₅	OC ₂ H ₅	oil
1.199	S	Cl	CH ₃	CH ₂ SC(=S)N(CH ₃) ₂	106-110°
1.200	S	Cl	CH ₃	CH ₂ SC(=S)-1-morpholinyl	amorphous
1.201	S	Cl	CH ₃	CH ₂ SC(=S)-1-pyrrol	amorphous
1.202	O	Cl	CH ₃	CH ₂ SC(=S)OCH ₃	amorphous
1.203	O	Cl	CH ₃	CH ₂ SC(=S)-i-OC ₃ H ₇	resin

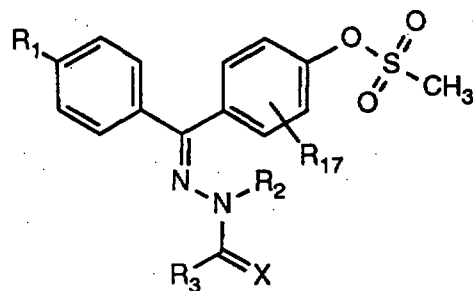
Table 2



comp. no.	X	R ₁	R ₂	R ₃	R ₁₇	physic. data
2.01	O	Cl	CH ₃	H	3-Br	oil
2.02	O	Cl	CH ₃	CH ₃	3-Br	97-99°
2.03	O	Cl	CH ₃	c-C ₃ H ₅	3-Br	oil
2.04	O	Cl	CH ₃	CF ₃	3-Br	107-109°
2.05	O	Cl	C ₂ H ₅	H	3-Br	65-68°
2.06	O	Cl	C ₂ H ₅	CF ₃	3-Br	oil
2.07	O	Cl	C ₂ H ₅	CH ₃	3-Br	oil
2.08A ¹	O	Cl	CH ₃	C ₆ H ₄ Cl(4)	3-Cl	83-85°
2.09B ¹	O	Cl	CH ₃	C ₆ H ₄ Cl(4)	3-Cl	130-133°
2.10	O	Cl	CH ₃	CF ₃	3-Cl	96-98°
2.11	O	Cl	i-C ₃ H ₇	CH ₃	3-Br	oil
2.12	O	Cl	CH ₃	H	3-Cl	resin

¹ A and B denote isomers

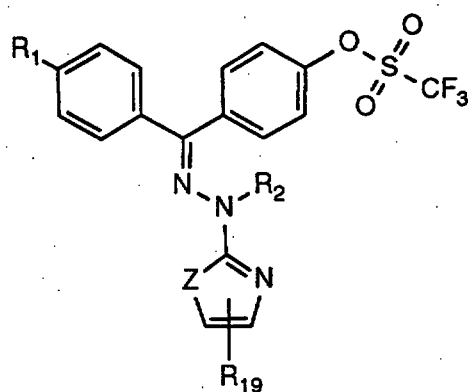
Table 3



comp. no.	X	R ₁	R ₂	R ₃	R ₁₇	physic. data
3.01	O	Cl	CH ₃	H	H	116-117°
3.02	O	Cl	CH ₃	CH ₃	H	resin
3.03	O	F	CH ₃	N(OCH ₃)CH ₃	H	resin
3.04	O	Br	CH ₃	CH ₃	H	wax
3.05A ¹	O	Br	CH ₃	i-C ₃ H ₇	H	wax
3.05B ¹	O	Br	CH ₃	i-C ₃ H ₇	H	wax
3.06	O	F	CH ₃	H	H	129-130°
3.07	O	F	CH ₃	CH ₃	H	resin
3.08	O	Cl	CH ₃	CH ₃	3-Cl	resin
3.09	O	Cl	CH ₃	H	3-Cl	118-120°
3.10	O	F	CH ₃	H	3-Cl	129-131°
3.11A ¹	O	Cl	CH ₃	(CH ₃) ₃ CH=CF ₂	3-CH ₂ CH=CH ₂	resin
3.11B ¹	O	Cl	CH ₃	(CH ₃) ₃ CH=CF ₂	3-CH ₂ CH=CH ₂	resin
3.12	O	Cl	CH ₃	CH ₃	3-CH ₂ CH=CH ₂	glass-like
3.13	O	Cl	CH ₃	CH ₂ -t-C ₄ H ₉	3-CH ₂ CH=CH ₂	resin
3.14	O	Br	CH ₃	n-C ₃ H ₇	H	101-107°
3.15	O	Br	CH ₃	c-C ₃ H ₅	H	83-91°
3.16	O	Br	CH ₃	C ₂ H ₅	H	resin
3.17	O	Br	CH ₃	CH ₂ Cl	H	resin
3.18	O	Br	CH ₃	i-C ₄ H ₉	H	97-103°

¹ A and B denote isomers

Table 4



comp. no.	Z	R ₁	R ₂	R ₁₉	physic. data
4.01	S	Cl	CH ₃	3-CH ₃	resin
4.02	S	Cl	CH ₃	2-CH ₃	
4.03	S	Cl	CH ₃	3-Cl	
4.04	S	Cl	CH ₃	2-Cl	
4.05	S	Cl	CH ₃	3-CF ₃	
4.06	S	Cl	CH ₃	2-CF ₃	
4.07	S	Cl	H	3-Cl	
4.08	S	Cl	H	3-CF ₃	
4.09	O	Cl	CH ₃	3-CH ₃	
4.10	O	Cl	CH ₃	2-Cl	
4.11	O	Cl	CH ₃	3-CF ₃	
4.12	O	Cl	H	3-CF ₃	
4.13	S	Br	CH ₃	3-CH ₃	
4.14	S	Br	CH ₃	2-CH ₃	
4.15	S	Br	CH ₃	3-Cl	
4.16	S	Br	CH ₃	2-Cl	
4.17	S	Br	CH ₃	3-CF ₃	
4.18	S	Br	CH ₃	2-CF ₃	
4.19	S	Br	H	3-Cl	
4.20	S	Br	H	3-CF ₃	
4.21	O	Br	CH ₃	3-CH ₃	
4.22	O	Br	CH ₃	2-Cl	
4.23	O	Br	CH ₃	3-CF ₃	

4.24	O	Br	H	3-CF ₃
4.25	S	F	CH ₃	3-CH ₃
4.26	S	F	CH ₃	2-CH ₃
4.27	S	F	CH ₃	3-Cl
4.28	S	F	CH ₃	2-Cl
4.29	S	F	CH ₃	3-CF ₃
4.30	S	F	CH ₃	2-CF ₃
4.31	S	F	H	3-Cl
4.32	S	F	H	3-CF ₃
4.33	O	F	CH ₃	3-CH ₃
4.34	O	F	CH ₃	2-Cl
4.35	O	F	CH ₃	3-CF ₃
4.36	O	F	H	3-CF ₃

Formulation Examples (throughout, percentages are by weight)

Example F1: Emulsifiable concentrates

	a)	b)	c)
active ingredient	25%	40%	50%
calcium dodecylbenzenesulfonate	5%	8%	6%
castor oil polyethylene glycol ether (36 mol of ethylene oxide)	5%	-	-
tributylphenol polyethylene glycol ether (30 mol of ethylene oxide)	-	12%	4%
cyclohexanone	-	15%	20%
xylene mixture	65%	25%	20%

The finely ground active ingredient is mixed with the adjuvants, giving an emulsifiable concentrate from which emulsions of any desired concentration can be prepared by dilution with water.

Example F2: Solutions

	a)	b)	c)	d)
active ingredient	80%	10%	5%	95%
ethylene glycol monomethyl ether	20%	-	-	-
polyethylene glycol (mol. wt. 400)	-	70%	-	-
N-methylpyrrolid-2-one	-	20%	-	-
epoxidised coconut oil	-	-	1%	5%
petroleum fraction (boiling range: 160-190°)	-	-	94%	-

The finely ground active ingredient is mixed with the adjuvants, giving a solution that is suitable for application in the form of microdrops.

Example F3: Granules

	a)	b)	c)	d)
active ingredient	5%	10%	8%	21%
kaolin	94%	-	79%	54%
highly dispersed silicic acid	1%	-	13%	7%
attapulgate	-	90%	-	18%

The active ingredient is dissolved in dichloromethane, the solution is sprayed onto the carrier mixture, and the solvent is evaporated off *in vacuo*.

Example F4: Dusts

	a)	b)
active ingredient	2%	5%
highly dispersed silicic acid 1%		5%
talcum	97%	-
kaolin	-	90%

Ready-for-use dusts are obtained by mixing the active ingredient with the carriers.

Example F5: Wettable powders

	a)	b)	c)
active ingredient	25%	50%	75%
sodium lignosulfonate	5%	5%	-
sodium lauryl sulfate	3%	-	5%
sodium diisobutyl-naphthalenesulfonate	-	6%	10%

octylphenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2%	-
highly dispersed silicic acid	5%	10%	10%
kaolin	62%	27%	-

The active ingredient is mixed with the adjuvants and the mixture is ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of any desired concentration.

Example F6: Emulsifiable concentrate

active ingredient	10%
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3%
calcium dodecylbenzenesulfonate	3%
castor oil polyethylene glycol ether (36 mol of ethylene oxide)	4%
cyclohexanone	30%
xylene mixture	50%

The finely ground active ingredient is mixed with the adjuvants, giving an emulsifiable concentrate from which emulsions of any desired concentration can be prepared by dilution with water.

Example F7: Dusts

	a)	b)
active ingredient	5%	8%
talcum	95%	-
kaolin	-	92%

Ready-for-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

Example F8: Extruder granules

active ingredient	10%
sodium lignosulfonate	2%
carboxymethylcellulose	1%
kaolin	87%

The active ingredient is mixed with the adjuvants, and the mixture is ground, moistened with water, extruded and granulated, and the granules are then dried in a stream of air.

Example F9: Coated granules

active ingredient	3%
polyethylene glycol (mol. wt. 200)	3%
kaolin	94%

The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol, affording non-dusty coated granules.

Example F10: Suspension concentrate

active ingredient	40%
ethylene glycol	10%
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6%
sodium lignosulfonate	10%
carboxymethylcellulose	1%
aqueous formaldehyde solution (37%)	0.2%
aqueous silicone oil emulsion (75%)	0.8%
water	32%

The finely ground active ingredient is mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

Biological Examples

Example B1: Action against *Diabrotica balteata*

Maize seedlings are sprayed with an aqueous emulsion comprising 400 ppm of test compound. After the spray coating has dried, the maize seedlings are populated with 10 *Diabrotica balteata* larvae in the second stage and then placed in a plastics container. 6 days later, the percentage reduction in the population (% activity) is determined by comparing the number of dead larvae on the treated plants with that on untreated plants.

Compounds of Tables 1 to 4 exhibit good activity in this test. In particular, compounds 1.174 to 1.177, 1.179, 1.183 to 1.189, 1.191, 1.193 to 1.196, 1.198, 2.01, 2.04 to 2.07, 2.11, 2.12, 3.01 to 3.08, 3.10, 3.15, 3.16 and 4.01 are more than 80 % effective.

Example B2: Action against *Heliothis virescens*

Young soybean plants are sprayed with an aqueous emulsion comprising 400 ppm of test compound. After the spray coating has dried, the soybean plants are populated with 10 *Heliothis virescens* caterpillars in the first stage and then placed in a plastics container. 6 days later, the percentage reduction in the population and the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

Compounds of Tables 1 to 4 exhibit good activity in this test. In particular, compounds 1.176 to 1.178, 1.183, 1.195, 1.196, 1.198, 2.11, 3.01, 3.02, 3.04 to 3.07, 3.15, 3.16 and 4.01 are more than 80 % effective.

Example B3: Action against *Heliothis virescens* (ovicidal)

Egg deposits of *Heliothis virescens* on filter paper are immersed for a short time in an aqueous acetone solution comprising 400 ppm of test compound. After the test solution has dried, the eggs are incubated in petri dishes. After 6 days, the percentage of eggs that have hatched is evaluated in comparison with untreated controls (% reduction in the hatching rate).

Compounds of Tables 1 to 4 exhibit good activity in this test. In particular, compounds 1.176 to 1.178, 1.183, 1.195 to 1.198, 2.01, 2.04 to 2.06, 2.09, 2.11, 2.12, 3.01, 3.02, 3.04, 3.06, 3.07, 3.15, 3.16 and 4.01 are more than 80 % effective.

Example B4: Action against *Plutella xylostella*

Young cabbage plants are sprayed with an aqueous emulsion comprising 400 ppm of test compound. After the spray coating has dried, the cabbage plants are populated with 10 *Plutella xylostella* caterpillars in the third stage and then placed in a plastics container. 3 days later, the percentage reduction in the population and the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

Compounds of Tables 1 to 4 exhibit good activity in this test. In particular, compounds

1.175 to 1.178, 1.183, 1.195, 1.196, 1.198, 2.11, 3.01, 3.02, 3.04 to 3.06, 3.14 to 3.16 and 4.01 are more than 80 % effective.

Example B5: Action against *Spodoptera littoralis*

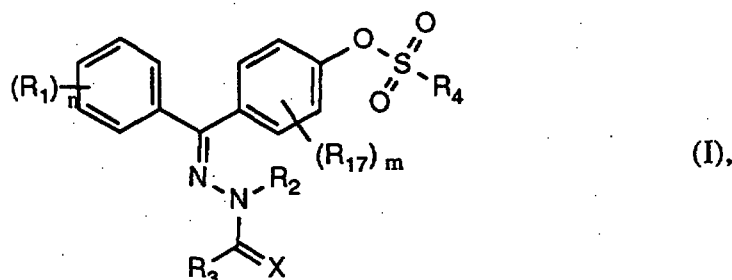
Young soybean plants are sprayed with an aqueous emulsion comprising 400 ppm of test compound. After the spray coating has dried, the soybean plants are populated with 10 *Spodoptera littoralis* caterpillars in the third stage and then placed in a plastics container. 3 days later, the percentage reduction in the population and the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

Compounds of Tables 1 to 4 exhibit good activity in this test. In particular, compounds 1.175 to 1.178, 1.183, 1.195 to 1.198, 2.11, 3.01, 3.02, 3.04 to 3.07, 3.14 to 3.16 and 4.01 are more than 80 % effective.



What is claimed is:

1. A compound of formula



wherein

m is 0, 1, 2, 3 or 4, and, when m is greater than 1, the radicals R_{17} are identical or different;

n is 0, 1, 2, 3, 4 or 5, and, when n is greater than 1, the radicals R_1 are identical or different;

R_1 and R_{17} are each independently of the other halogen, C_1 - C_8 alkyl, halo- C_1 - C_8 alkyl, phenoxy, phenylthio, halo- C_1 - C_8 alkylthio, phenyl, C_1 - C_8 alkylthio, C_1 - C_8 alkyl-carbonyl, OSO_2R_4 , $SO_2NR_{13}R_{14}$ or $P(=Y)R_{22}R_{23}$;

either X is S, R_2 is R_{21} or H and R_3 is R_{31} , $-NR_5R_6$ or $-OR_2$,

or X is O, R_2 is R_{21} and R_3 is R_{31} ,

or X is O, R_2 is H and R_3 is $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$ or $-R_8R_{12}$,

or X and R_3 together are R_{18} ;

Y is O or S;

R_4 is C_1 - C_8 alkyl, halo- C_1 - C_8 alkyl or halo- C_1 - C_8 alkoxy;

R_{21} is C_1 - C_8 alkyl, C_3 - C_6 cycloalkyl, halo- C_1 - C_8 alkyl, C_1 - C_4 alkoxy- C_1 - C_4 alkyl, C_1 - C_4 -alkylthio- C_1 - C_4 alkyl, $R_{13}R_{14}N$ - C_1 - C_4 alkyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_1 - C_4 acyl, $CH=C(CN)_2$, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C_1 - C_4 alkyl, C_2 - C_5 -alkenyl, halo- C_1 - C_4 alkyl, C_1 - C_4 alkoxy, $SO_2NR_{13}R_{14}$, halo- C_1 - C_4 alkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 alkoxy- C_1 - C_4 alkoxy, halo- C_1 - C_4 alkylthio, $NR_{13}R_{14}$, $-NO_2$ and $-CN$;

R_{31} is H, C_1 - C_8 alkyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl- C_1 - C_3 alkyl, halo- C_1 - C_8 alkyl, halo- C_3 - C_6 cycloalkyl- C_1 - C_3 alkyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, halo- C_2 - C_8 alkenyl, $-COOR_7$, $-SR_2$, $-R_8OR_9$, $-R_8OCOR_9$, $-R_8NR_{10}R_{11}$, $-R_8R_{12}$, $-R_8SR_9$, $-R_8SCSR_9$, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C_1 - C_4 alkyl, C_2 - C_5 alkenyl, halo- C_1 - C_4 alkyl, halo- C_1 - C_4 alkoxy, halo- C_1 - C_4 alkylthio, $SO_2NR_{13}R_{13}$, C_1 - C_4 alkoxy, $-NO_2$ and $-CN$;



- an unsubstituted or substituted, saturated or unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group consisting of halogen, C₁-C₄alkyl, halo-C₁-C₄alkyl and C₁-C₄alkoxy;
- R₅ and R₆ are each independently of the other H, C₁-C₈alkyl, halo-C₁-C₈alkyl, C₂-C₅-alkenyl, C₁-C₄alkoxy, C₂-C₅alkeneoxy or -NR₁₃R₁₄;
- R₇ is H, C₁-C₈alkyl, halo-C₁-C₈alkyl or C₂-C₈alkenyl;
- R₈ is (CR₁₅R₁₆)_p, wherein p is 1, 2, 3 or 4;
- R₉ is C₁-C₈alkyl, halo-C₁-C₁₁alkyl, C₃-C₆cycloalkyl, C₂-C₈alkenyl, halo-C₂-C₁₁alkenyl, C₂-C₈alkynyl, NR₁₀R₁₁, OR₁₀, benzyl, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₂-C₅alkenyl, halo-C₁-C₄alkyl, C₁-C₄alkoxy, -NO₂ and -CN;
- R₁₀ and R₁₁ are each independently of the other C₁-C₈alkyl, C₂-C₈alkenyl or C₁-C₈alkoxy-C₁-C₈alkyl;
- R₁₂ is an unsubstituted or substituted, saturated or unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing from one to three hetero atoms selected from the group O, N and S, the substituents being selected from the group consisting of halogen, C₁-C₄alkyl, halo-C₁-C₄alkyl and C₁-C₄alkoxy;
- R₁₃ and R₁₄ are each independently of the other H or C₁-C₈alkyl;
- R₁₅ and R₁₆ are each independently of the other H, C₁-C₈alkyl, or phenyl which is unsubstituted or substituted by from one to five substituents selected from the group consisting of halogen, C₁-C₄alkyl, C₂-C₅alkenyl, halo-C₁-C₄alkyl, C₁-C₄alkoxy, -NO₂ and -CN;
- R₁₈ is NC(R₁₉)=C(R₁₉)S, NC(R₁₉)=C(R₁₉)O, NC(R₁₉)₂C(R₁₉)₂S, NC(R₁₉)₂C(R₁₉)₂O, NC(R₁₉)=C(R₁₉)C(R₁₉)=N or N(R₁₉)=NC(R₁₉)=N;
- R₁₉ is H, C₁-C₄alkyl, halogen or halo-C₁-C₄alkyl;
- R₂₂ is C₁-C₄alkyl, C₁-C₄alkoxy or NR₁₃R₁₄; and
- R₂₃ is C₁-C₄alkyl, C₁-C₄alkoxy, C₃-C₄alkylthio or NR₁₃R₁₄,
- with the proviso that, in the compounds of formula I, R₂ is other than H when either m is 0, n is 1, R₁ is 4-Cl, R₃ is -N(OCH₃)CH₃, R₄ is CF₃ and X is O, or when m is 0, n is 2, R₁ is 3,4-dichloro, R₃ is -N(OCH₃)CH₃, R₄ is CF₃ and X is O, or when m is 0, n is 1, R₁ is 4-Cl, R₃ is -NHNH₂, R₄ is CF₃ and X is O, or, as the case may be, a tautomer thereof, in each case in free form or in salt form.

2. A compound according to claim 1 of formula I, wherein



m is 0 or 1,
or, as the case may be, a tautomer thereof.

3. A compound according to claim 1 of formula I, wherein

m is 0;
n is 1;
R₁ is fluorine, chlorine or bromine;
R₂ is C₁-C₄alkyl, formyl or acetyl;
R₃ is H, C₁-C₄alkyl, C₃-C₆cycloalkyl, halo-C₁-C₂alkyl, halocyclopropylmethyl, C₂-C₄-alkenyl, -COOR₇, -SR₂, -R₈-OCOR₉, -R₈-R₁₂ or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing N or S, the substituents being selected from the group fluorine and chlorine;
R₄ is trifluoromethyl;
R₇ is methyl or ethyl;
R₈ is CR₁₅R₁₆;
R₉ is C₁-C₄alkyl, halo-C₈-C₁₁alkyl, cyclopropyl, vinyl, halo-C₈-C₁₁alkenyl, ethynyl or unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of chlorine, methyl, methoxy and -NO₂;
R₁₂ is an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S; and
R₁₅ and R₁₆ are each independently of the other H, methyl or phenyl, or, as the case may be, a tautomer thereof.

4. A compound according to claim 1 of formula I, wherein

m is 0;
n is 1;
R₁ is fluorine, chlorine or bromine;
R₂ is C₁-C₄alkyl, formyl or acetyl;
R₃ is H, C₁-C₄alkyl, C₃-C₆cycloalkyl, halo-C₁-C₂alkyl, halocyclopropylmethyl, C₂-C₄-alkenyl, -COOR₇, -SR₂, -R₈-OCOR₉, -R₈-R₁₂ or an unsubstituted or substituted, unsaturated, five- or six-membered heterocyclic or heterobicyclic ring containing N or S, the substituents being selected from the group fluorine and chlorine;
R₄ is trifluoromethyl;
R₇ is methyl or ethyl;
R₈ is CH₂, C(methyl)₂ or CH(phenyl);
R₉ is C₁-C₄alkyl, halo-C₈-C₁₁alkyl, cyclopropyl, vinyl, halo-C₈-C₁₁alkenyl, ethynyl or

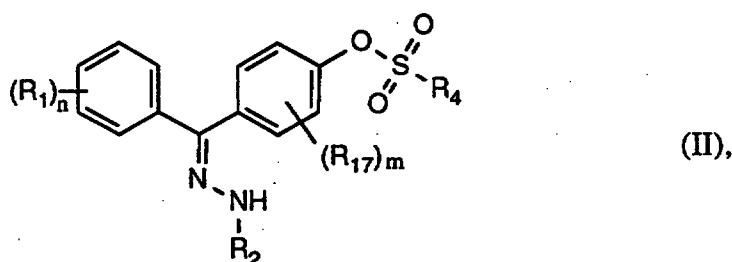


unsubstituted or mono-substituted phenyl, the substituents being selected from the group consisting of chlorine, methyl, methoxy and $-\text{NO}_2$; and R_{12} is an unsubstituted, unsaturated, five-membered heterocyclic ring containing from one to three hetero atoms selected from the group N and S, or, as the case may be, a tautomer thereof.

5. 4-Chloro-4'-trifluoromethanesulfonyloxybenzophenone-N-formyl-N-methylhydrazone according to claim 1.

6. A process for the preparation of a compound according to claim 1 of formula I or, as the case may be, a tautomer thereof, in each case in free form or in salt form, taking into account the proviso mentioned above, in which process

a) a compound of formula



which is known or can be prepared analogously to corresponding known compounds and wherein m , n , R_1 , R_2 , R_4 and R_{17} are as defined for formula I, or, as the case may be, a tautomer thereof, in free form or in salt form, is reacted with phosgene or thiophosgene, preferably in the presence of a base, and the intermediate, which is optionally isolated, is reacted, if desired in the presence of a base, with a compound of formula Y_1H , wherein Y_1 is $-\text{NR}_5\text{R}_6$, $-\text{OR}_2$ or $-\text{SR}_2$ and R_2 , R_5 and R_6 are as defined for formula I, or with a salt thereof, or

b) for the preparation of a compound of formula I wherein X is O, a compound of formula II is reacted, if desired in the presence of a base, with a compound of formula R_3COY_2 , wherein R_3 is as defined for formula I with the exception of the meanings $-\text{OR}_2$ and $-\text{SR}_2$, and Y_2 is a leaving group, or

c) for the preparation of a compound of formula I wherein X is S, a compound of formula II is reacted with a compound of formula $\text{Y}_3\text{-N=C=S}$, wherein Y_3 is H, $\text{C}_1\text{-C}_8$ alkyl, halo- $\text{C}_1\text{-C}_8$ alkyl or $\text{C}_2\text{-C}_5$ alkenyl, preferably H or $\text{C}_1\text{-C}_8$ alkyl, to form compounds of

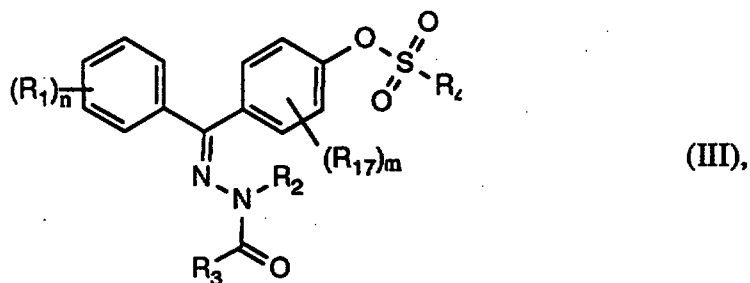


formula I wherein X is S, or

d) for the preparation of a compound of formula I wherein X is S and R_3 is -SR, wherein R is C_1 - C_8 alkyl, C_3 - C_6 cycloalkyl, C_2 - C_8 alkenyl or C_2 - C_8 alkynyl, preferably C_1 - C_8 alkyl or C_3 - C_6 cycloalkyl, especially C_1 - C_8 alkyl, a compound of formula II is reacted, if desired in the presence of a base, with CS_2 , and the intermediate, which is optionally isolated, is reacted, if desired in the presence of a base, with a compound of formula RY_4 , wherein R is as defined above and Y_4 is a leaving group, or

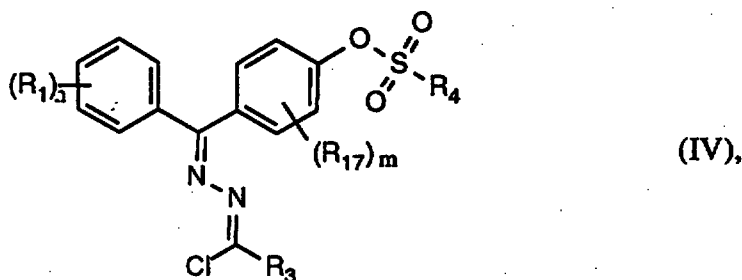
e) for the preparation of a compound of formula I wherein X is O, a compound of formula II is reacted, if desired in the presence of a base, with a compound of formula ClR_8COY_5 , wherein R_8 is as defined for formula I and Y_5 is a leaving group, and the resulting intermediate is reacted, if desired in the presence of a base, optionally in the presence of an alkali metal halide, such as in the presence of sodium iodide, with a compound of formula R_9COOH , $HNR_{10}R_{11}$ or R_{12} , wherein R_9 , R_{10} , R_{11} and R_{12} are as defined for formula I, or

f) for the preparation of a compound of formula I wherein X is S, a compound of formula



which is known or can be prepared analogously to corresponding known compounds, for example in accordance with Variant b), and wherein m, n, R_1 , R_2 , R_3 , R_4 and R_{17} are as defined for formula I, is reacted with P_2S_5 , or

g) for the preparation of a compound of formula I wherein X is S and R_2 is H, a compound of formula

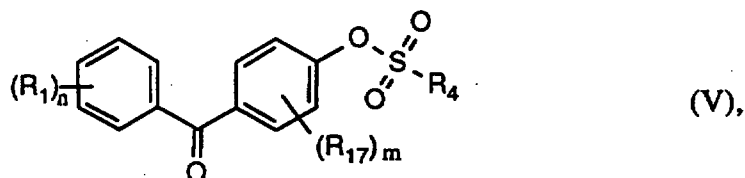




which is known or can be prepared analogously to corresponding known compounds and wherein m , n , R_1 , R_3 , R_4 and R_{17} are as defined for formula I, is reacted, if desired in the presence of a base, with H_2S , or

h) a compound of formula I wherein R_2 is H is reacted, if desired in the presence of a base, with a compound of formula R_2Y_6 , wherein R_2 is as defined for formula I with the exception of the meaning H, and Y_6 is a leaving group, or

i) a compound of formula



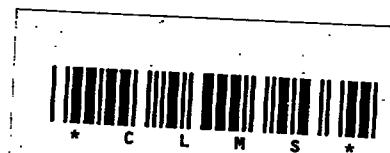
which is known or can be prepared analogously to corresponding known compounds and wherein m , n , R_1 , R_4 and R_{17} are as defined for formula I, is reacted, if desired in the presence of an acid catalyst, if desired in the presence of a water-binding agent, with a compound of formula



which is known or can be prepared analogously to corresponding known compounds and wherein R_2 , R_3 and X are as defined for formula I, or with a salt thereof and/or, as the case may be, with a tautomer thereof,

and in each case, if desired, a compound of formula I obtainable according to the process or by other means, or a tautomer thereof, in each case in free form or in salt form, is converted into a different compound of formula I or a tautomer thereof, a mixture of isomers obtainable according to the process is separated and the desired isomer is isolated and/or a free compound of formula I obtainable according to the process, or a tautomer thereof, is converted into a salt, or a salt of a compound of formula I or of a tautomer thereof obtainable according to the process is converted into the free compound of formula I or a tautomer thereof or into a different salt.

7. A pesticidal composition which comprises at least one compound according to claim 1 of formula I or, as the case may be, a tautomer thereof, in each case in free form or in the form of an agrochemically acceptable salt, as active ingredient and, where appropriate, at least one adjuvant.



8. A process for the preparation of a composition according to claim 7 comprising at least one adjuvant, which process comprises homogeneously mixing and/or grinding the active ingredient with the adjuvant(s).

9. The use of a compound according to claim 1 of formula I or, as the case may be, a tautomer thereof, in each case in free form or in the form of an agrochemically acceptable salt, in the preparation of a composition according to claim 7.

10. The use of a composition according to claim 7 in the control of pests.

11. The use according to claim 10 in the protection of plant propagation material.

12. A method of controlling pests, which comprises applying to the pests or their habitat a composition according to claim 7.

13. A method according to claim 12 for the protection of plant propagation material, which comprises treating the propagation material or the planting site of the propagation material.

14. Plant propagation material treated in accordance with the method described in claim 13.