(12) UK Patent Application (19) GB (11) 2 164 936 A

(43) Application published 3 Apr 1986

(21) Application No 8522914

(22) Date of filing 17 Sep 1985

(30) Priority data
(31) 4479/84 (32) 19 Sep 1984 (33) CH
3526/85 15 Aug 1985

(51) INT CL⁴
C07C 119/055

(52) Domestic classification
C2C 1173 1175 1178 1200 1230 1530 215 220 221 225 226 227 22X 22Y 250 251 25Y 30Y 311 313 31Y 326 328 337 338 339 364 36Y 373 37Y 624 62Y 634 644 652 662 666 672 682 687 689 694 695 697 699 710 749 758 805 80Y AA MB MG NV RS
U1S 1308 C2C

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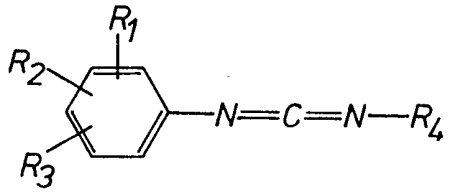
CA 94(9): 65567a
CA 90(3): 22658f
CA 83(19): 163859q
CA 83(17): 147569q
CA 100(25): 209261p
CA 94(13): 103254p

(58) Field of search
C2C

(54) Pesticidal substituted carbodiimides

(57) Substituted carbodiimides of the formula



wherein

R_1 is hydrogen, halogen, C_1-C_{10}alkyl, C_1-C_5alkoxy, C_1-C_5alkoxy which is substituted by 1 to 7 halogen atoms, or is C_1-C_5 alkylthio;

R_2 is hydrogen, halogen, C_1-C_{10}alkyl or C_1-C_5alkoxy;

R_3 is hydrogen, C_1-C_{10}alkyl, halogen, phenoxy, phenylthio, or is phenoxy or phenylthio, each mono- or disubstituted by a member selected from the group consisting of halogen, methyl, ethyl, C_1-C_3 haloalkyl containing 1 to 7 halogen atoms and cyano, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisting of halogen and C_1-C_3haloalkyl containing 1 to 7 halogen atoms;

R_4 is C_1-C_{12}alkyl, alkoxyalkyl containing a total of 2 to 10 carbon atoms, C_3-C_{10}cycloalkyl, C_3-C_{10}cycloalkylmethyl, C_3-C_{10}cycloalkyl which is substituted by 1 to 3 C_1-C_3alkyl groups, or is C_1-C_5-alkyl which is substituted to 1 or 2 C_3-C_{10}cycloalkyl groups, or is a polycyclic alkyl group containing 7 to 10 carbon atoms, phenyl(C_1-C_5)alkyl or phenyl(C_1-C_5)alkyl which is mono- or disubstituted at the phenyl nucleus by halogen, trifluoromethyl, methoxy or ethoxy, have use in pest control, especially for controlling insects and representatives of the order Acarina that attack plants and animals, in particular plant-destructive sucking insects.

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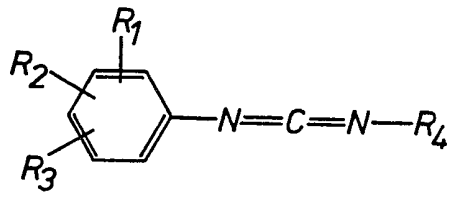
Formulae in the printed specification were reproduced from drawings submitted after the date of filing, in accordance with Rule 20(14) of the Patents Rules 1982.

SPECIFICATION

Substituted carbodiimides

The present invention relates to novel substituted N-phenyl-N'-alkylcarbodiimides, to the preparation thereof and to the use thereof in pest control.

The compounds of the invention are of formula I



(I)

wherein

R_1 is hydrogen, halogen, C_1–C_{10}alkyl, C_1–C_5alkoxy, C_1–C_5alkoxy which is substituted by 1 to 7 halogen atoms, or is C_1–C_5alkylthio;

R_2 is hydrogen, halogen, C_1–C_{10}alkyl or C_1–C_5alkoxy;

R_3 is hydrogen, C_1–C_{10}alkyl, halogen, phenoxy, phenylthio, or is phenoxy or phenylthio, each mono- or disubstituted by a member selected from the group consisting of halogen, methyl, ethyl, C_1–C_3haloalkyl containing 1 to 7 halogen atoms and cyano, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisting of halogen and C_1–C_3haloalkyl containing 1 to 7 halogen atoms;

R_4 is C_1–C_{12}alkyl, alkoxyalkyl containing a total of 2 to 10 carbon atoms, C_3–C_{10}cycloalkyl, C_3–C_{10}cycloalkylmethyl, C_3–C_{10}cycloalkyl which is substituted by 1 to 3 C_1–C_3alkyl groups, or is C_1–C_5alkyl which is substituted by 1 or 2 C_3–C_{10}cycloalkyl groups, or is a polycyclic alkyl group containing 7 to 10 carbon atoms, phenyl(C_1–C_5)alkyl or phenyl(C_1–C_5)alkyl which is mono- or disubstituted at the phenyl nucleus by halogen, trifluoromethyl, methoxy or ethoxy.

Alkyl and alkoxy groups and substituents R_1 to R_4 may be straight chain or branched. Examples of such groups are therefore methyl, methoxy, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl and the isomers thereof.

Within the scope of the present invention, halogen is preferably F, C1 and Br, most preferably F and C1.

On account of their activity as pesticides, preferred compounds of formula I are those wherein

R_1 is hydrogen, halogen, C_1–C_{10}alkyl, C_1–C_5alkoxy, C_1–C_5alkoxy which is substituted by 1 to 7 halogen atoms, or is C_1–C_5alkylthio;

R_2 is hydrogen, halogen, C_1–C_{10}alkyl or C_1–C_5alkoxy;

R_3 is hydrogen, C_1–C_{10}alkyl, halogen, phenoxy or phenoxy which is mono- or disubstituted by a member selected from the group consisting of halogen, trifluoromethyl and cyano, or is phenylthio, pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisting of halogen and trifluoromethyl; and

R_4 is C_1–C_{10}alkyl, alkoxyalkyl containing a total of 2 to 10 carbon atoms, C_3–C_{10}cycloalkyl, C_3–C_{10}cycloalkylmethyl, or C_3–C_{10}cycloalkyl which is substituted by a C_1–C_3alkyl group.

On account of their biological activity, further valuable compounds of formula I are those wherein

R_1 is hydrogen, fluorine, chlorine, C_1–C_4alkyl, methoxy, ethoxy, trifluoromethoxy or C_1–C_3alkylthio;

R_2 is hydrogen, fluorine, chlorine, C_1–C_4alkyl, methoxy or ethoxy;

R_3 is hydrogen, C_1–C_4alkyl, fluorine, chlorine, phenoxy, phenylthio, phenoxy which is mono- or disubstituted by chlorine and/or trifluoromethyl, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisiting of fluorine, chlorine and trifluoromethyl; and

R_4 is C_1–C_8alkyl, alkoxyalkyl containing a total of 2 to 7 carbon atoms, C_3–C_8cycloalkyl, C_3–C_6cycloalkylmethyl, methyl(C_3–C_6)cycloalkyl, phenyl(C_1–C_4)alkyl or phenyl(C_1–C_4)alkyl which is mono- or disubstituted at the phenyl nucleus by chlorine, trifluoromethyl or methoxy;

as well as those compounds of formula I, wherein

R_1 is hydrogen, fluorine, chlorine, C_2–C_4alkyl or methoxy;

R_2 is hydrogen, chlorine, C_3–C_4alkyl or methoxy;

R_3 is methyl, ethyl, isopropyl, chlorine, phenoxy, phenoxy which is mono- or disubstituted by chorine and/or trifluoromethyl, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by chlorine and/or trifluoromethyl; and

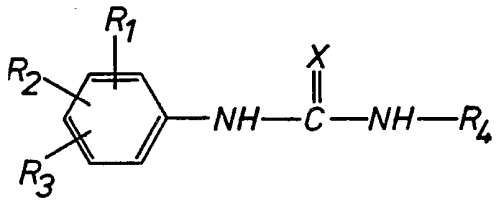
R_4 is C_3–C_8alkyl, C_1–C_4alkoxy (C_1–C_3)alkyl, C_3–C_6cycloalkyl, phenyl(C_1–C_4)alkyl or phenyl(C_1–C_4)al-

kyl which is substituted at the phenyl nucleus by a chlorine atom or a methoxy group.

Particularly preferred compounds of formula I are those wherein one of the radicals R_1, R_2 and R_3 is in the 4-position and the other two independently of each other are in the 2- and 6-positions. R_4 is preferably isopropyl and tert-butyl.

Still further preferred carbodiimides of formula I are those wherein R_1 and R_2 are attached to the phenyl radical in the 2- and 6-positions.

The compounds of formula I can be prepared by methods which are known per se. Thus, for example, a compound of formula I can be obtained by removing water or hydrogen sulfide from a compound of formula II

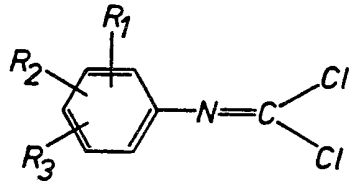


(II)

wherein R_1 to R_4 are as defined above and X is oxygen or sulfur. Such elimination reactions can be carried out in accordance with procedures known from the literature, e.g. with the aid of HgO, specific pyridinium salts, chloroacetates, cyanuric chloride, p-toluenesulfochloride or specific phosphate derivatives [T. Shibanuma, Chemistry Letters *(1977)*, pp. 575–6; S. Kim, Tetrahedron Letters *(1985)*, pp, 1661–1664; W. Weith, B.*6* (1873) 1398; G. Amiard, Bull. Soc. chim. *1956*, 1360].

The above process can preferably be carried out under normal pressure and in the presence of a preferably aprotic organic solvent or diluent. Examples of suitable solvents or diluents are: ethers and ethereal compounds such as diethyl ether, dipropyl ether, dibutyl ether, dioxane, dimethoxyethane and tetrahydrofuran; N,N-dialkylated carboxmides; aliphatic, aromatic and halogenated hydrocarbons, especially benzene, toluene, xylene, chloroform, methylene chloride, carbon tetrachloride and chlorobenzene; nitriles such as acetonitrile or propionitrile; and ketones, e.g. acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone. The process is generally carried out at a temperature in the range from −5 to +150°C, preferably from 10 to 50°C, e.g. at room temperature.

The carbodiimides of formula I can also be prepared in a manner known per se by reacting suitably substituted isocyanide dichlorides of formula III with a salt of the respective desired primary amine of formula IV (q.v. US patent specification 3 231 610):



$$+ \quad R_4NH_2 \cdot HA \longrightarrow (I) \qquad (III)$$

(IV)

in which formulae III and IV the radicals R_1 to R_4 are as defined above and A is an anion, e.g. Cl^-. Suitable primary amine salts for this reaction are e.g. the hydrohalides. The reaction is preferably carried out in the presence of an inert organic solvent with a relatively high boiling point, e.g. chlorinated benzenes, nitrobenzene, dimethylacetamide or tetramethylenesulfone. Examples of further suitable solvents are: high boiling aliphatic, cycloaliphatic and aromatic hydrocarbons such as p-chlorobromobenzene, 1-chloronaphthalene or halogenated xylenes. In general, the reaction is preferably carried out at a temperature in the range form 80 to 200°C.

The starting materials of formulae II, III and IV are known and can be obtained in accordance with known procedures (q.v. Belgian patent specification 863 078, German patent application 1 094 737 and US patent specification 3 932 507).

The use of N,N'-diphenylcarbodiimides as acaricides, in particular as ectoparasiticides, is known from German Offenlegungsschrift 2 553 270. The use of substituted N-benzyl-N'-alkylcarbodiimides as insecticides is described in Japanese patent publication 5 0069 226. US patent specification 3 231 610 also relates to substituted carbodiimides having herbicidal and insecticidal properties. In addition to N,N'-dialkylcarbodiimides and N,N'-diphenylcarbodiimides, the general formula indicated in said US patent specification also comprises specific N-phenyl-N'-alkylcarbodiimides; however, in the cited US patent specification only chlorine- or nitro-substituted N,N'-diphenylcarbodiimides are specifically disclosed, but not N-phenyl-N'-alkylcarbodiimides.

In contradistinction thereto, the substituted N-phenyl-N'-alkylcarbodiimides of the present invention are therefore novel compounds which, while being well tolerated by plants and having low mammalian toxicity to warm-blooded animals, surprisingly posses a pronounced activity for controlling insects and representatives of the order Acarina that attack plants and animals.

In particular, the compounds of formula I are suitable for controlling insects of the orders: Lepidoptera, Coleoptera, Homoptera, Heteroptera, Diptera, Thysanoptera, Orthoptera, Anoplura, Siphonaptera, Mallophaga, Thysanura, Isoptera, Psocoptera and Hymenoptera, as well as representatives of the order Acarina, in particular plant-destructive acarids, e.g. spider-mites.

The good pesticidal activity of the compounds of formula I of the invention corresponds to a mortality of at least 50–60% of the above pests.

In addition to their very effective action against flies, e.g. Musca domestica, and mosquito larvae, the compounds of formula I are particularly suitable for controlling plant-destructive feeding insects in ornamentals and crops of useful plants, especially in cotton (e.g. against Spodoptera littoralis and Heliothis virescens) and in crops of vegetables (e.g. against Leptinotarsa decemlineata and Pieris brassicae). The larvicidal and ovicidal action of the compounds of formula I is to be particularly highlighted. If compounds of formula I are ingested by adult insect stages with the feed, then a diminished oviposition and/or reduced hatching rate is observed in many insects, especially in Coleoptera, e.g. Anthonomomus grandis.

The compounds of formula I can also be used for controlling ectoparasites such as Lucili sericata, and ticks, in domestic animals and productive livestock, e.g. by treating animals, cowsheds, barns, stables etc., and pastures.

The activity of the compounds of formula I and of the compositions containing them can be substantially broadened and adapted to prevailing circumstances by addition of other insecticides and/or acaricides. Examples of suitable additives include: organophosphorus compounds, nitrophenols and derivatives thereof, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons, and Bascillus thuringiensis preparations.

The compounds of formula I are used in unmodified form, or preferably together with the adjuvants conventionally employed in the art of formulation, and are therefore formulated in known manner to emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations in e.g. 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 containing the compound (active ingredient) of formula I or combinations thereof with other insecticides or acaricides, and, where appropriate, a solid or liquid adjuvant, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with extenders, e.g. solvents, solid carriers and, in some cases, surface-active compounds (surfactants).

Suitable solvents are: aromtic hydrocarbons, preferably the fractions containing 8 to 12 carbon atoms, e.g. xylene mixtures or substituted naphthalenes, phthalates such as dibutyl phthalate or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins, alcohols and glycols and their ether and esters, such as ethanol, ethylene glycol monomethyl or monoethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethylformamide, as well as vegetable oils or epoxidised vegetable oils such as epoxidised coconut oil or soybean oil; or water.

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 acid or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, for example pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are materials such as calcite or sand. In addition, a great number of pregranulated materials of inorganic or organic nature can be used, e.g. especially dolomite or pulverised plant residues.

Depending on the nature of the compound of formula I to be formulated, or of combinations thereof with other insecticides or acaricides, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

Suitable anionic surfactants can be both water-soluble soaps and water-soluble synthetic surface-active compounds.

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 tallow oil. Further suitable surfactants are also the fatty acid methyltaurin salts as well as modified and unmodified phospholipids.

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 contain a C_8–C_{22}alkyl radical which also includes the alkyl moiety of acyl radicals, e.g. the sodium or calcium salt of lignosulfonic acid, of dodecylsulfate, or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These

compounds also comprise the salt of sulfuric acid esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing about 8 to 22 carbon atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolamine salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid, or of a naphthalenesulfonic acid/formaldehyde condensation product. Also suitable are corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 moles of ethylene oxide.

Non-ionic surfactants are preferably polyglycol ether derivatives of aliphtic or cycloaliphatic alcohols, or 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 the 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 compound usually contain 1 to 5 ethylene glycol units per propylene glycol unit.

Representative examples of non-ionic surfactants are nonylphenolpolyethoxyethanols, 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, methylsulfates, or ethylsulfates, e.g. stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants customarily employed in the art of formulation are described e.g. in "McCutcheon's Detergents and Emulsifiers Annual", MC Publishing Corp. Ridgewood, New Jersey, 1979; Dr. Helmut Stache, "Tensid Taschenbuch" (Handbook of Surfactants), Carl Hanser Verlag, Munich/Vienna, 1981.

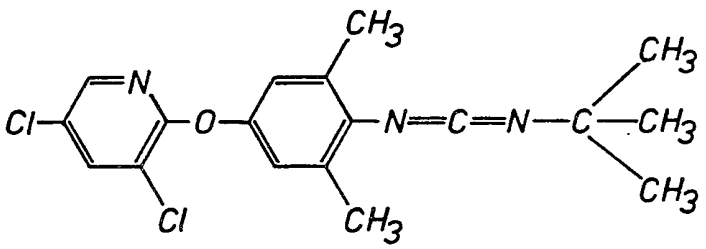
The pesticidal compositions usually contain 0.1 to 99%, preferably 0.1 to 95%, of a compound of formula I or combination thereof with other insecticides or acaricides, 1 to 99.9% of a solid or liquid adjuvant, and 0 to 25%, preferably 0.1 to 20%, of a surfactant.

Whereas commercial products are preferably formulated as concentrates, the end user will normally employ dilute formulations of substantially lower concentration.

The compositions may also contain further ingredients, such as stabilisers, antifoams, viscosity regulators, binders, tackifiers as well as fertilisers or other active ingredients in order to obtain special effects.

Example 1: Preparation of N-[2,6-dimethyl-4-(3,5-dichloro-2-pyridyloxy)phenyl]-N'-tert-butylcarbodiimide

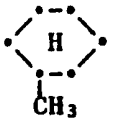
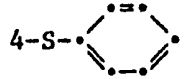
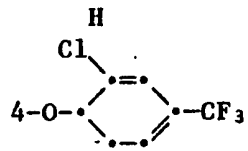
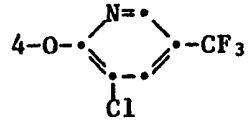
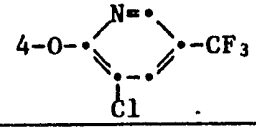
A reaction vessel is charged with 16.6 g of N-[2,6-dimethyl-4-(3,5-dichloro-2-pyridyloxy)phenyl]-N'-tert-tubylthiourea and 12.8 g of 2-chloro-1-methylpyridinium iodide in 150 ml of acetonitrile. With stirring, a solution of 8.4 g of triethylamine in 80 ml of acetonitrile is added dropwise at room temperature. The reaction mixture is subsequently stirred for 2 hours at 80°C and then concentrated by rotary evaporation at 50°C. 150 ml of hexane are added to the residue and the resultant solution is filtered. The hexane phase is washed with three 30 ml portions of cold water, dried over sodium sulfate and filtered. The filtrate is concentrated by evaporation, affording the title compound of the formula

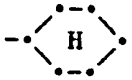
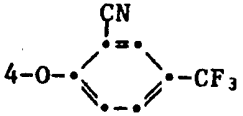
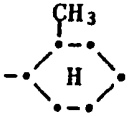
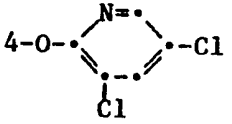
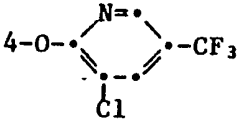
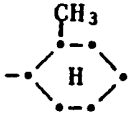


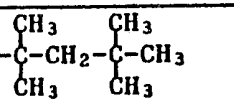
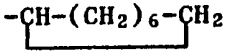
as a clear pale yellow oil which crystallises on standing and has a melting point of 69–71°C (compound 1).

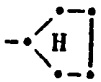
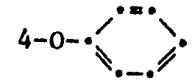
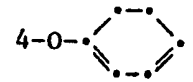
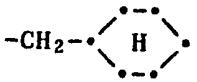
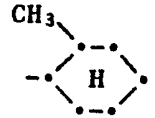
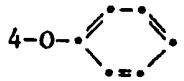
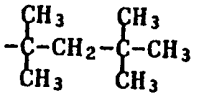
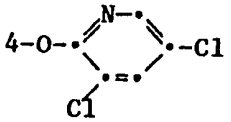
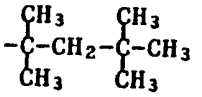
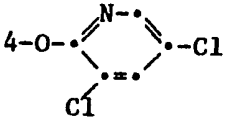
The following compounds of formula I are also obtained in accordance with the procedure described above:

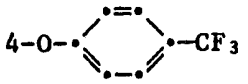
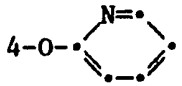
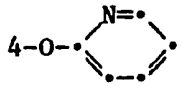
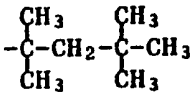
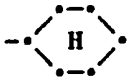
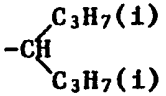
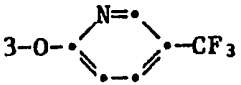
Compound	R_1	R_2	R_3	R_4	Physical data
2	2-CH_3	6-CH_3	4-O-	-C_4H_9(t)	n_{20}^{D}=1.5764
3	2-C_3H_7(i)	H	6-C_3H_7(i)	-C_4H_9(t)	white, viscous substance which liquefies at room temperature
4	2-C_3H_7(i)	6-C_3H_7(i)	4-O-	-C_4H_9(t)	m.p. 45-46°C
5	3-Cl	H	4-Cl	-C_4H_9(t)	n_{21}^{D}=1.5613
6	2-Cl	H	4-Cl	-C_4H_9(t)	n_{20}^{D}=1.5895
7	H	H	4-O-	-C_4H_9(t)	m.p. 51-53°C
8	6-C_4H_9(s)	2-C_2H_5	4-O-	-C_4H_9(t)	n_{22}^{D}=1.5575
9	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{24}^{D} = 1.5685
10	H	H	4-O-	-C_4H_9(t)	n_{24}^{D}=1.5756
11	H	H	4-O-		n_{24}^{D}=1.5952

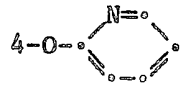
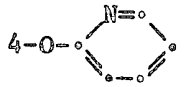
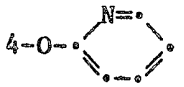
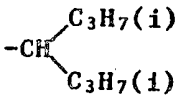
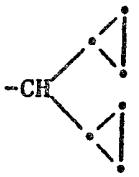
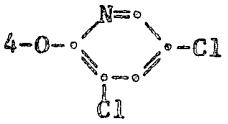
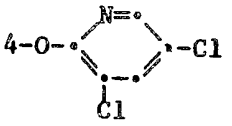
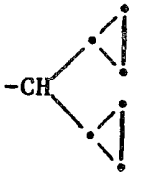
Compound	R_1	R_2	R_3	R_4	Physical data
12	2-C_3H_7(i)	H		-C_4H_9(t)	n_{20}^{D}=1.5300
13	2-CH_3	6-CH_3		-C_4H_9(t)	n_{20}^{D}=1.5815
14	2-CH_3	6-CH_3		-C_4H_9(t)	n_{20}^{D}=1.5374
15	2-CH_3	6-CH_3		-CH_2-C_4H_9(t)	n_{20}^{D}=1.5720
16	2-CH_3	6-CH_3			n_{20}^{D}=1.5505
17	H	H		-C_4H_9(t)	n_{20}^{D}=1.6142
18	2-CH_3	4-Cl		-CH_3	n_{20}^{D}=1.6230
19	2-CH_3	6-CH_3		-C_4H_9(t)	n_{20}^{D}=1.5460
20	2-CH_3	6-CH_3		-C_3H_7(i)	m.p. 50-52°C
21	2-CH_3	6-CH_3		-C_4H_9(t)	m.p. 65-68°C

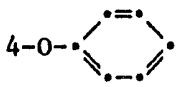
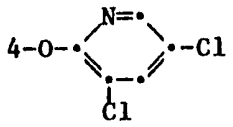
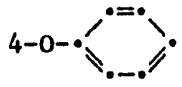
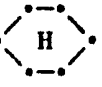
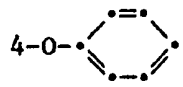
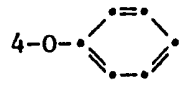
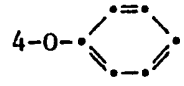
Compound	R_1	R_2	R_3	R_4	Physical data
22	6-CH_3	2-CH_3	4-O- 		n_{27}^{D}=1.5905
23	6-OCH_3	2-OCH_3	H	-C_4H_9(t)	m.p. 61-64°C
24	2-CH_3	6-CH_3		-C_4H_9(t)	m.p. 67-68°C
25	H	2-CH_3		C_4H_9(t)	n_{21}^{D}=1.5350
26	2-C_4H_9(s)	6-C_2H_5			n_{21}^{D}=1.5672
27	2-OCH_3	6-OCH_3	H		m.p. 57-60°C
28	2-CH_3	6-CH_3		-$(CH_2)_3$-O-$(CH_2)_3$-CH_3	n_{21}^{D}=1.5726
29	2-CH_3	6-CH_3		-$(CH_2)_3$-O-$(CH_2)_3$-CH_3	n_{21}^{D}=1.5355
30	2-C_3H_7(i)	H	6-C_3H_7(i)		n_{21}^{D}=1.5388
31	2-C_4H_9(s)	6-C_2H_5	4-O- 		n_{21}^{D}=1.5721

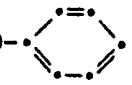
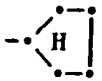
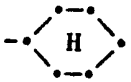
Compound	R_1	R_2	R_3	R_4	Physical data
32	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{21}^{D}=1.5177
33	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{21}^{D}=1.5473
34	4-CH_3	H	2-CH_3	-C_4H_9(t)	n_{21}^{D}=1.5340
35	2-CH_3	H	6-CH_3	-C_3H_7(i)	n_{23}^{D}=1.5459
36	2-CH_3	H	6-CH_3	-C_4H_9(t)	n_{23}^{D}=1.5354
37	2-CH_3	H	6-CH_3	-C_4H_9(s)	n_{23}^{D}=1.5424
38	2-Cl	H	4-Cl	-C_4H_9(t)	n_{22}^{D}=1.5650
39	2-Cl	H	4-Cl	-C_3H_7(i)	n_{22}^{D}=1.5826
40	2-C_2H_5	H	6-C_4H_9(s)	-C_4H_9(t)	n_{23}^{D}=1.5230
41	6-C_3H_7(i)	H	2-C_2H_5	-C_3H_7(i)	n_{25}^{D}=1.5300
42	2-C_3H_7(i)	H	6-CH_3	-C_4H_9(t)	n_{23}^{D}=1.5261
43	2-C_3H_7(i)	H	6-C_2H_5	-C_4H_9(t)	n_{23}^{D}=1.5256
44	2-C_3H_7(i)	H	6-C_3H_7(i)	-C_3H_7(i)	n_{23}^{D}=1.5293
45	2-CH_3	H	4-CH_3	-C_3H_7(i)	n_{22}^{D}=1.5450
46	2-C_2H_5	H	6-C_4H_9(s)		n_{22}^{D}=1.5498

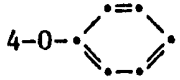
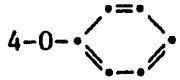
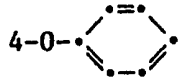
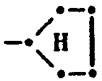
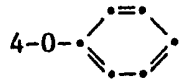
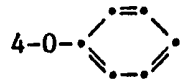
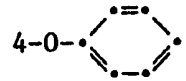
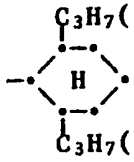
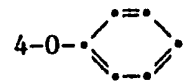
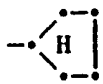
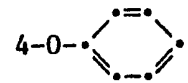
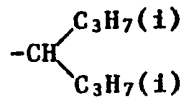
Compound	R_1	R_2	R_3	R_4	Physical data
47	$2\text{-}C_2H_5$	H	$6\text{-}C_4H_9(s)$		$n_{22}^{D}=1.5464$
48	$2\text{-}S\text{-}C_3H_7(i)$	H	6-Cl	$-C_4H_9(t)$	$n_{21}^{D}=1.5805$
49	$4\text{-}OCF_3$	H	H	$-C_4H_9(t)$	$n_{22}^{D}=1.4780$
50	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$		$-(CH_2)_3\text{-}O\text{-}(CH_2)_3\text{-}CH_3$	$n_{23}^{D}=1.5452$
51	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$		$-(CH_2)_3\text{-}OCH_3$	$n_{23}^{D}=1.5589$
52	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$	H		$n_{21}^{D}=1.5408$
53	$2\text{-}C_2H_5$	$6\text{-}C_4H_9(s)$	H		$n_{21}^{D}=1.5402$
54	$2\text{-}C_2H_5$	$6\text{-}C_4H_9(s)$			$n_{21}^{D}=1.5482$
55	$2\text{-}CH_3$	$6\text{-}CH_3$			$n_{21}^{D}=1.5730$
56	$2\text{-}CH_3$	$6\text{-}CH_3$			m.p. 41-44°C

Compound	R_1	R_2	R_3	R_4	Physical data
57	H	2-CH_3		-C_4H_9(t)	m.p. 37-38°C
58	2-C_3H_7(i)	H		-$CH(CH_3)-CH_2-OCH_3$	n_{21}^D = 1.5329
59	H	2-C_3H_7(i)		-$CH_2-CH_2-CH_2-O-C_4H_9$(n)	n_{21}^D = 1.5548
60	H	2-C_3H_7(i)		-C_4H_9(t)	m.p.33-35°C
61	4-C_4H_9(t)	H	H	-C_4H_9(t)	n_{21}^D=1.1538
62	4-C_4H_9(t)	H	H		n_{21}^D=1.5212
63	4-C_4H_9(t)	H	H		n_{21}^D=1.5485
64	H	2-C_3H_7(i)			n_{21}^D=1.5249
65	4-CH_3	2-CH_3		-C_4H_9(t)	n_{21}^D =1.5217

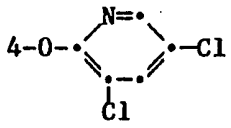
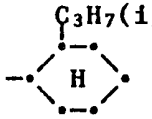
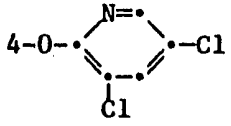
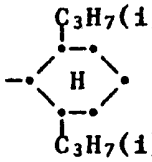
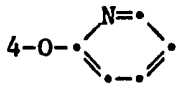
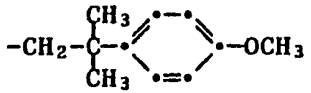
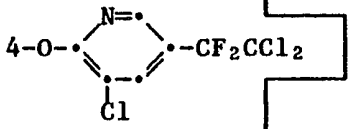
Compound	R_1	R_2	R_3	R_4	Physical data
66	2-CH_3	6-CH_3		-C_4H_9(t)	n_{21}^{D}=1.5768
67	2-CH_3	6-CH_3		-$CH(CH_3)-CH_2-OCH_3$	n_{21}^{D}=1.5792
68	2-CH_3	6-CH_3			n_{21}^{D}=1.5989
69	H	2-C_3H_7(i)	6-C_3H_7(i)		n_{21}^{D}=1.5200
70	H	2-C_3H_7(i)	6-C_3H_7(i)		n_{21}^{D}=1.5409
71	2-CH_3	6-CH_3		-$C(CH_3)_2-C_2H_5$	n_{21}^{D}=1.5852
72	2-CH_3	6-CH_3			n_{21}^{D}=1.6000

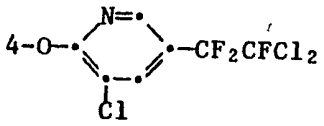
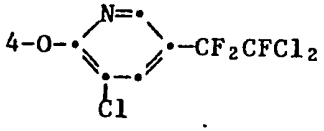
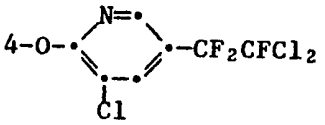
Compound	R_1	R_2	R_3	R_4	Physical data
73	2-CH_3	6-CH_3	4-O- 	-CH(C_3H_7(i))(C_3H_7(i))	n_{21}^{D}=1.5662
74	2-CH_3	6-CH_3	4-O- 	-CH_2- 	n_{21}^{D}=1.5950
75	2-CH_3	6-CH_3	4-O- 	-CH(CH_3)- 	n_{21}^{D}=1.5820
76	2-C_3H_7(i)	H	H	-C_4H_9(i)	n_{23}^{D}=1.5359
77	2-CH_3	H	6-C_2H_5	-C_3H_7(i)	n_{23}^{D}=1.5396
78	H	6-C_2H_5	2-CH_3	-C_4H_9(t)	n_{23}^{D}=1.5296
79	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	-$(CH_2)_3$-O-C_2H_5	n_{23}^{D}=1.5527
80	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	-$(CH_2)_3$-O-C_3H_7(i)	n_{23}^{D}=1.5473
81	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	-$C(CH_3)_2$-CH_2-$C(CH_3)_2$-CH_3	n_{23}^{D}=1.5466

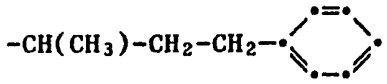
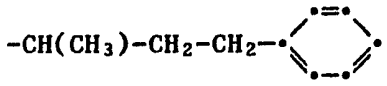
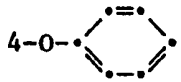
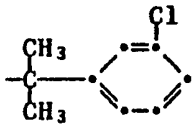
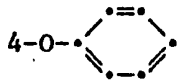
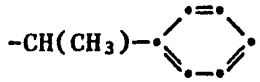
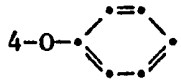
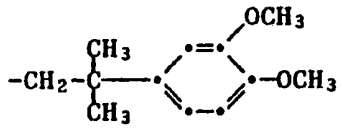
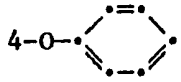
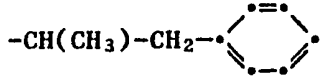
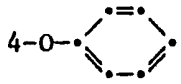
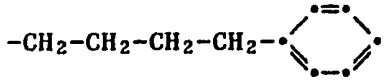
Compound	R_1	R_2	R_3	R_4	Physical data
82	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	- 	n_{23}^{D}=1.5680
83	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	- 	n_{23}^{D}=1.5702
84	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	-CH_2- 	n_{23}^{D}=1.5740
85	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	-CH_2- 	n_{23}^{D}=1.5663
86	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	-CH_2-CH-$(CH_2)_6$-CH_2	n_{23}^{D}=1.5657
87	2-C_3H_7(i)	6-C_3H_7(i)	H	-CH_2-CH-$(CH_2)_6$-CH_2	n_{23}^{D}=1.5440
88	2-C_2H_5	6-C_2H_5	H	-C_3H_6(i)	n_{23}^{D}=1.5358
89	2-C_2H_5	6-C_2H_5	H	-C_4H_9(t)	n_{23}^{D}=1.5294
90	2-C_2H_5	6-C_2H_5	4-O- 	-C_3H_7(i)	n_{25}^{D}=1.572

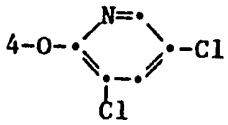
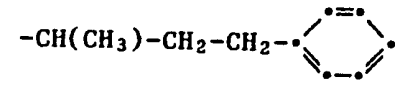
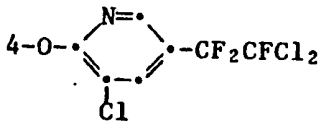
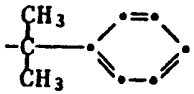
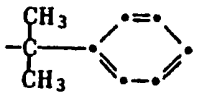
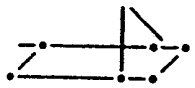
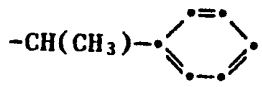
Compound	R_1	R_2	R_3	R_4	Physical data
91	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$	4-O- 	$-C_4H_9(t)$	$n_{23}^{D}=1.5670$
92	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$	4-O- 	$-C(CH_3)_2\text{-}C_2H_5$	$n_{23}^{D}=1.5550$
93	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$	4-O- 		$n_{23}^{D}=1.5844$
94	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$	4-O- 	$-C_4H_9(s)$	$n_{23}^{D}=1.5703$
95	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$	4-O- 	$-C(CH_3)_2\text{-}C_2H_5$	$n_{23}^{D}=1.5650$
96	$2\text{-}CH_3$	$6\text{-}CH_3$	4-O- 		$n_{21}^{D}=1.5643$
97	$2\text{-}CH_3$	$6\text{-}CH_3$	4-O- 		$n_{21}^{D}=1.5951$
98	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$	4-O- 		$n_{21}^{D}=1.5510$

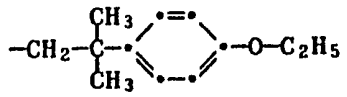
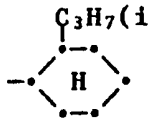
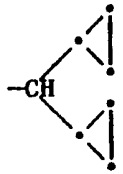
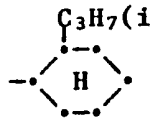
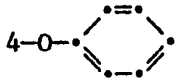
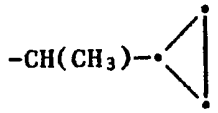
Compound	R_1	R_2	R_3	R_4	Physical data
99	2-C_3H_7(i)	6-C_3H_7(i)	4-O-	-CH	n_{21}^D=1.5531
100	2-C_3H_7(i)	6-C_3H_7(i)	4-O-	C_3H_7(i), H, C_3H_7(i)	n_{21}^D=1.5531
101	2-C_3H_7(i)	6-C_3H_7(i)	4-O-	-CH(CH_3)- H	n_{21}^D=1.5640
102	2-C_2H_5	6-C_4H_9(s)	4-O-	-CH	n_{21}^D=1.5698
103	2-CH_3	6-CH_3	4-O- N= -Cl, Cl	-CH(CH_3)- H	n_{21}^D=1.5938

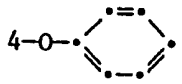
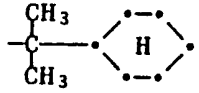
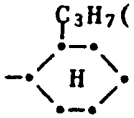
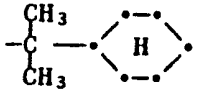
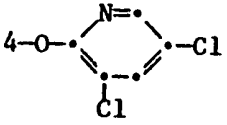
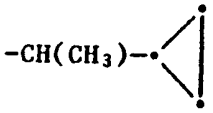
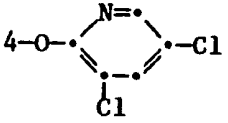
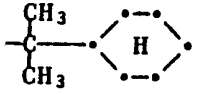
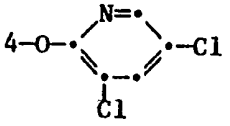
Compound	R_1	R_2	R_3	R_4	Physical data
104	2-CH_3	6-CH_3			n_{21}^{D}=1.5879
105	2-CH_3	6-CH_3			n_{21}^{D}=1.5742
106	2-CH_3	4-O-CF_2CHF_2	6-CH_3	-C_4H_9(t)	n_{21}^{D}=1.4820
107	2-CH_3	6-CH_3		-C_4H_9(t)	n_{24}^{D}=1.5618
108	2-CH_3	6-CH_3			n_{21}^{D}=1.6119
109	2-C_3H_7(i)	6-C_3H_7()	H		n_{21}^{D}=1.5570
110	2-C_3H_7(i)	6-C_3H_7()	H		n_{21}^{D}=1.5532
111	2-CH_3	6-CH_3		-C_4H_9(t)	n_{21}^{D}=1.5515

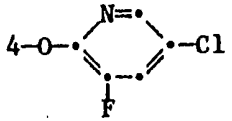
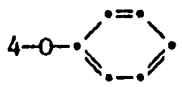
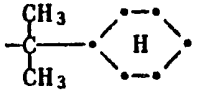
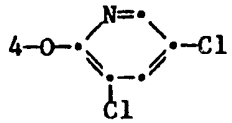
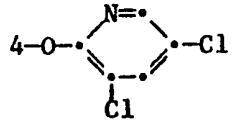
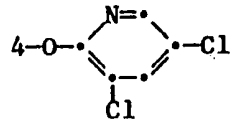
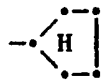
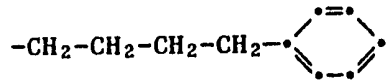
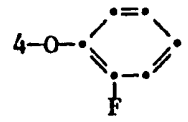
Compound	R_1	R_2	R_3	R_4	Physical data
112	$2\text{-}CH_3$	$6\text{-}CH_3$		$-C_3H_7(i)$	$n_{22}^{D}=1.5592$
113	H	$2\text{-}C_3H_7(i)$			$n_{21}^{D}=1.5550$
114	$2\text{-}CH_3$	$6\text{-}CH_3$		$-C(CH_3)_2\text{-}_2H_5$	$n_{21}^{D}=1.5538$
115	$2\text{-}CH_3$	$6\text{-}CH_3$			$n_{21}^{D}=1.5739$
116	H	$4\text{-}O\text{-}CF_2CHF_2$	$2\text{-}C_3H_7(i)$	$-CH(CH_3)\text{-}CH_2\text{-}CH_2-$ 	$n_{21}^{D}=1.5177$
117	$2\text{-}C_3H_7(i)$	$4\text{-}O\text{-}CF_2CHF_2$	H		$n_{21}^{D}=1.5100$

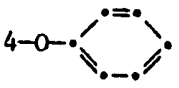
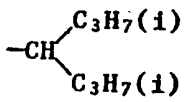
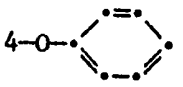
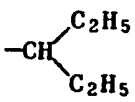
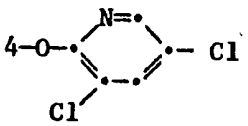
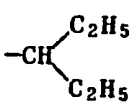
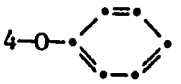
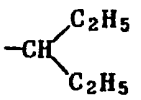
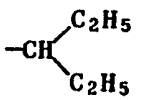
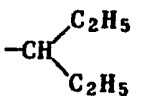
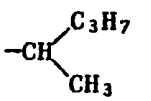
Compound	R_1	R_2	R_3	R_4	Physical data
118	2-C_3H_7(i)	H			n_{21}^{D}=1.5572
119	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{21}^{D}=1.5561
120	2-CH_3	6-CH_3			n_{21}^{D}=1.6096
121	2-CH_3	6-CH_3			n_{21}^{D}=1.6217
122	2-CH_3	6-CH_3			n_{21}^{D}=1.5982
123	2-CH_3	6-CH_3			n_{21}^{D}=1.6026
124	2-CH_3	6-CH_3			n_{21}^{D}=1.5999

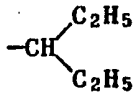
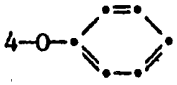
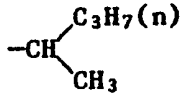
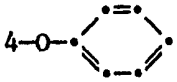
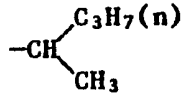
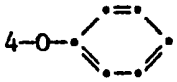
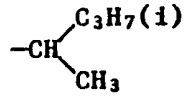
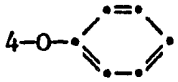
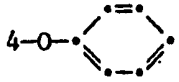
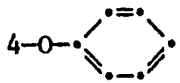
Compound	R_1	R_2	R_3	R_4	Physical data
125	2-CH_3	6-CH_3			n_{21}^{D}=1.6094
126	2-C_2H_5	6-CH_3		-C_4H_9(t)	n_{21}^{D}=1.5520
127	2-C_3H_7(i)	6-C_3H_7(i)	H	1-adamantyl	m.p. 93-95°C
128	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{21}^{D}=1.5639
129	2-C_2H_5	6-C_2H_5	H		n_{24}^{D}=1.5715
130	2-C_2H_5	6-C_4H_9(s)	H		n_{21}^{D}=1.5518
131	2-C_2H_5	6-C_4H_9(s)	H	1-adamantyl	n_{24}^{D}=1.5618
132	2-C_2H_5	6-C_4H_9(s)	H		n_{24}^{D}=1.5662

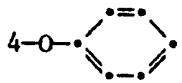
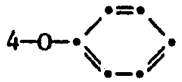
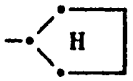
Compound	R_1	R_2	R_3	R_4	Physical data
133	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{24}^{D}=1.5550
134	2-C_2H_5	6-C_2H_5	H	1-adamantyl	n_{24}^{D}=1.5724
135	2-CH_3	6-C_3H_7(i)	H	1-adamantyl	-
136	2-CH_3	6-CH_3		1-adamantyl	-
137	2-C_3H_7(i)	H			n_{24}^{D}=1.5382
138	2-C_2H_5	6-C_4H_9(s)	H		n_{24}^{D}=1.5409
139	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{24}^{D}=1.5351
140	2-CH_3	6-CH_3			n_{24}^{D}=1.5808

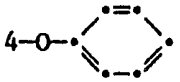
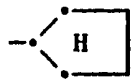
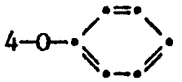
Compound	R_1	R_2	R_3	R_4	Physical data
141	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$			$n_{24}^{D}=1.5615$
142	$2\text{-}C_2H_5$	$6\text{-}C_4H_9(s)$			$n_{24}^{D}=1.5614$
143	$2\text{-}C_2H_5$	$6\text{-}C_4H_9(s)$			$n_{24}^{D}=1.5635$
144	$2\text{-}CH_3$	$6\text{-}CH_3$			$n_{24}^{D}=1.5970$
145	$2\text{-}CH_3$	$6\text{-}CH_3$			$n_{24}^{D}=1.5892$
146	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$		$-C_4H_9(t)$	$n_{24}^{D}=1.5770$

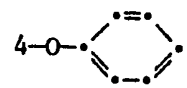
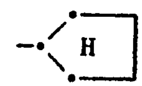
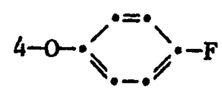
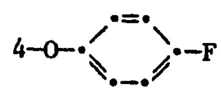
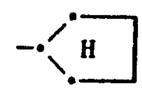
Compound	R_1	R_2	R_3	R_4	Physical data
147	2-CH_3	6-CH_3		-C_4H_9(t)	n_{24}^{D}=1.5720
148	2-CH_3	6-CH_3			n_{24}^{D}=1.5790
149	2-CH_3	6-C_2H_5		-C_4H_9(t)	n_{24}^{D}=1.5820
150	2-CH_3	6-CH_3		-C_3H_7(i)	n_{24}^{D}=1.5983
151	2-CH_3	6-CH_3			m.p. 65-68°C
152	2-C_3H_7(i)	6-C_3H_7(i)	H		n_{21}^{D}=1.5581
153	2-CH_3	6-CH_3		-C_4H_9(t)	n_{24}^{D}=1.5640

Compound	R_1	R_2	R_3	R_4
154	$2-C_2H_5$	$6-C_4H_9(s)$		
155	$2-CH_3$	$6-CH_3$		
156	$2-CH_3$	$6-CH_3$		
157	$2-C_3H_7(i)$	$6-C_3H_7(i)$		
158	$2-C_2H_5$	$6-C_4H_9(s)$		
159	$2-CH_3$	$6-CH_3$		
160	$2-C_3H_7(i)$	$6-C_3H_7(i)$		

Compound	R_1	R_2	R_3	R_4
161	2-C_3H_7(i)	6-C_3H_7(i)	H	
162	2-CH_3	6-CH_3	4-O- 	
163	2-C_3H_7(i)	6-C_3H_7(i)	4-O- 	
164	2-CH_3	6-CH_3	4-O- 	
165	2-CH_3	6-CH_3	4-O- 	-$(CH_2)_5CH_3$
166	2-CH_3	6-CH_3	4-O- 	-$(CH_2)_{11}CH_3$
167	2-C_2H_5	6-C_2H_5	H	-C_3H_7(i)
168	2-C_2H_5	6-C_2H_5	4-O- 	-C_3H_7(i)

Compound	R_1	R_2	R_3	R_4
169	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$		$-C_4H_9(t)$
170	$2\text{-}C_3H_7(i)$	$6\text{-}C_3H_7(i)$		$-C(CH_3)_2\text{-}C_2H_5$
171	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$		
172	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$		$-C_4H_9(s)$
173	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$		$-C(CH_3)_2\text{-}C_2H_5$
174	$2\text{-}C_2H_5$	$6\text{-}C_2H_5$		$-CH(CH_3)\text{-}CH_2\text{-}O\text{-}CH_3$
175	$2\text{-}C_2H_5$	$6\text{-}C_4H_9(s)$		$-C_4H_9(s)$

Compound	R_1	R_2	R_3	R_4
176	2-C_4H_9(s)	6-C_2H_5	4-O- 	-$CH(CH_3)-CH_2-O-CH_3$
177	2-C_2H_5	6-C_4H_9(s)	4-O- 	
178	2-C_2H_5	6-C_4H_9(s)	4-O- 	-$C(CH_3)_2-C_2H_5$
179	2-C_2H_5	6-C_3H_7(i)	4-O- 	-C_4H_9(s)
180	2-C_2H_5	6-C_3H_7(i)	4-O- 	-$C(CH_3)_2-C_2H_5$
181	2-C_2H_5	6-C_3H_7(i)	4-O- 	-$CH(CH_3)-CH_2-O-CH_3$

Compound	R_1	R_2	R_3	R_4
182	2-C_2H_5	6-C_3H_7(i)		
183	2-C_3H_7(i)	6-C_3H_7(i)		-C_4H_9(t)
184	2-C_3H_7(i)	6-C_3H_7(i)		

Example 2:
Formulations for liquid active ingredients of formula I according to Example 1 or combinations thereof with other insecticides or acaricides (throughout, percentages are by weight)

1. Emulsifiable concentrates	a)	b)	c)
active ingredient or active ingredient combination	25 %	40 %	50 %
calcium dodecylbenzenesulfonate	5 %	8 %	6 %
castor oil polyethylene glycol ether (36 moles of ethylene oxide)	5 %	-	-
tributylphenol polyethylene glycol ether (30 moles of ethylene oxide)	-	12 %	4 %
cyclohexane	-	15 %	20 %
xylene mixture	65 %	25 %	20 %

Emulsion of any required concentration can be produced from such concentrates by dilution with water.

2. Solutions	a)	b)	c)	d)
active ingredient or active ingredient combination	80 %	10 %	5 %	95 %
ethylene glycol monomethyl ether	20 %	-	-	-
polyethylene glycol 400	-	70 %	-	-
N-methyl-2-pyrrolidone	-	20 %	-	-
expoxidised coconut oil	-	-	1 %	5 %
ligroin (boiling range 160-190°)	-	-	94 %	-

These solutions are suitable for application in the form of micro-drops.

3. Granulates	a)	b)
active ingredient or active ingredient combination	5 %	10 %
kaolin	94 %	-
highly dispersed silicic acid	1 %	-
attapulgite	-	90 %

The active ingredient or active ingredient combination is dissolved in methylene chloride, the solution is sprayed onto the carrier, and the solvent is subsequently evaporated off in vacuo.

4. Dusts	a)	b)
active ingredient or active ingredient combination	2 %	5 %
highly dispersed silicic acid	1 %	5 %
talcum	97 %	-
kaolin	-	90 %

Ready for use dusts are obtained by intimately mixing the carriers with the active ingredient or active ingredient combination.

Formulations for solid active ingredients of formula I according to Example 1 or combinations thereof with other insecticides or acaricides (throughout, percentages are by weight)

5. Wettable powders

	a)	b)	c)
active ingredient or active ingredient combination	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium laurylsulfate	3 %	-	5 %
sodium diisobutylnaphthalenesulfonate	-	6 %	10 %
octylphenol polyethylene glycol ether (7-8 moles of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
kaolin	62 %	27 %	-

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

6. Emulsifiable concentrate

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

Emulsions of any required concentration can be obtained from this concentrate by dilution with water.

7. Dusts

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

Ready for use dusts are obtained by mixing the active ingredient or active ingredient combination with the carrier, and grinding the mixture in a suitable mill.

8. Extruder granulate

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

The active ingredient or active ingredient combination is mixed and ground with the adjuvants, and the mixture is subsequently moistened with water. The mixture is extruded, granulated and dried in a stream of air.

9. Coated granulate

active ingredient or active ingredient combination	3 %
polyethylene glycol 200	3 %
kaolin	94 %

The finely ground active ingredient or active ingredient combination is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

10. Suspension concentrate

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

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

Example 3: Action against Musca domestica

50 g of freshly prepared nutrient substrate for maggots are charged into each of a number of beakers. A specific amount of a 1% acetonic solution of the respective test compound is pipetted onto the nutrient substrate present in the beakers to give an active ingredient concentration of 400 ppm. The substrate is then thoroughly mixed and the acetone subsequently allowed to evaporate over a period of at least 20 hours.

Then 25 one-day-old maggots of Musca domestica are put into each of the beakers containing the treated nutrient substrate for testing with each active ingredient at the given concentration. After the maggots have pupated, the pupae are separated from the substrate by flushing them out with water and then deposited in containers closed with a perforated top.

Each batch of flushed out pupae is counted to determine the toxic effect of the test compound on the maggot development. A count is then made after 10 days of the number of flies which have hatched out of the pupae.

The compounds of formula I according to Example I have good activity in this test.

Example 4: Action against Lucilia sericata

1 ml of an aqueous solution containing 0.5% of test compound is added to 9 ml of a culture medium. Then about 30 freshly hatched Lucilia sericata larvae are added to the culture medium, and the insecticidal action is determined after 48 and 96 hours by evaluating the mortality rate.

The compounds of formula I according to Example 1 exhibit good activity against in this test.

Example 5: Action against Aëdes aegypti

A concentration of 400 ppm is obtained by pipetting a specific amount of a 0.1% solution of the test compound in acetone onto the surface of 150 ml of water in a breaker. After the acetone has evaporated, 30 to 40 two-day-old larvae of Aëdes aegypti are put into the beaker containing the test compound. Mortality counts are made after 2 and 7 days.

The compounds of formula I according to Example 1 exhibit good activity in this test.

Example 6: Insecticidal action against feeding insects

Cotton plants (about 20 cm high) are sprayed with aqueous emulsions (obtained from a 10%

emulsifiable concentrate) containing the respective test compound in concentrations of 100 to 400 ppm. After the spray coating has dried, the cotton plants are populated with Spodoptera littoralis and Heliothis virescens larvae in the L_3-stage. The test is carried out at 24°C and 60% relative humidity. At 24 hour intervals, a mortality count is made and the larvae are also examined for inhibition of development and shedding.

80 to 100% mortality against Heliothis larvae is effected with compound 31 at 100 ppm and with compound 32 at 400 ppm.

At the following concentrations, the compounds of Example 1 effect 80 to 100% mortality against larvae of Spodoptera littoralis:

Compound	Concentration
32	200 ppm
30,79,80,81,82, 84, 85 and 86	400 ppm

Example 7:

Action against Spodoptera littoralis and Heliothis virescens (larvae and eggs):

Three cotton plants each having a height of about 15–20 cm and grown in pots are treated with a sprayable liquid preparation of the test compound in a concentration of 800 ppm. After the spray coating has dried, the potted plants are placed in a metal container having a capacity of about 20 litres and covered with a glass plate. The humidity in the interior of the covered container is regulated such that no water of condensation forms. Direct light falling on the plants is avoided. The three plants are then infested altogether with:

a) 50 larvae of Spodoptera littoralis or Heliothis virescens in the L_1-stage;
b) 20 larvae of Spodoptera littoralis or Heliothis virescens in the L_3-stage;
c) 2 egg deposits of Spodoptera littoralis or Heliothis virescens.

(The procedure is that two leaves of each plant are put into a plexiglass cylinder sealed at both ends with muslin. Two egg deposits of Spodoptera, or a part of a cotton leaf with eggs of Heliothis deposited thereon, are added to the leaves sealed in the cylinder.)

Evaluation in comparison with untreated controls is made after 4 and 5 days, taking into account the following criteria:

a) the number of still living larvae,
b) inhibition of larval development and shedding,
c) feeding damage (shredding and perforation damage),
d) hatching rate (number of larvae hatched from the eggs).

In this test, the compounds of formula I according to Example 1 exhibit good overall activity.

Example 8: Ovicidal action against Spodoptera littoralis

Eggs of Spodoptera littoralis deposited on filter paper are cut out of the paper and immersed in a solution of 400 ppm of test compound in a 1:1 mixture of acetone-water. The treated deposits are then removed from this mixture and kept in plastic dishes at 28°C and 60% humidity. The hatching rate, i.e. the number of larvae which have developed from the treated eggs, is determined after 5 days.

Compounds 77, 78, 80, 81 and 88 according to Example 1 effect 80 to 100% mortality in this test.

Example 9: Ovicidal action against Laspeyresia pomonella (eggs):

Egg deposits of Laspeyrasia pomonella not more than 24 hours old are immersed on filter paper for 1 minute in an aqueous acetonic solution containing 400 ppm of the test compound. After the solution has dried, the eggs are placed in petri dishes and kept at a temperature of 28°C. The percentage of larvae hatched from the treated eggs is evaluated after 6 days.

In this test, compound 6 according to Example 1 effects 100% mortality even at 200 ppm.

Example 10: Action against Anthonomus grandis (adults)

Two cotton plants in the 6-leaf stage, in pots, are each sprayed with a wettable aqueous emulsion formulation containing 400 ppm of the test compound. After the spray coating has dried (about $1\frac{1}{2}$ hours), each plant is populated with 10 adult beetles (Anthonomus grandis). Plastic cylinders, covered at the top with gauze, are then slipped over the treated plants populated with the test insects to prevent the beetles from migrating from the plants. The

treated plants are then kept at 25°C and about 60% relative humidity. Evaluation is made after 2, 3, 4 and 5 days to determine the percentage mortality of the beetles (percentage in dorsal position) as well as the anti-feeding action as compared with untreated controls.

In this test, compounds 14, 77, 78 and 87 effect 80 to 100% mortality.

Example 11:

Action against plant-destructive acarids: Tetranychus urticae (OP-sensitive) and Tetranychus cinnabarinus (OP-tolerant)

16 hours before the test for acaricidal action, the primary leaves of Phaseolus vulgaris plants are infected with an infested piece of leaf from a mass culture of Tetranychus urticae (OP-sensitive) and Tetranychus cinnabarinus (OP-tolerant). (The tolerance refers to diazinone). The treated infested plants are sprayed to drip point with a test solution containing the respective test compound in concentrations of 0.75 to 400 ppm. A count of the number of living and dead imagines and larvae (all mobile stages) is made under a stereoscopic microscope after 24 hours and again after 7 days. One plant is used for each test compound at its given concentration and for each test species. During the test run, the plants are kept in greenhouse compartments at 25°C.

In this test, the compounds of formula I according to Example 1 show good activity against Tetranychus urticae.

At the following concentrations, the compounds of the invention effect 80 to 100% mortality against Tetranychus cinnabarinus:

Compound	Concentration
1 and 50	0.75 ppm
26,80,82 and 83	12.5 ppm
86	400 ppm

Example 12: Insecticidal contact action against Myzus persicae

Pea plants which have been reared in water to a height of about 4 cm are each populated with about 200 individuals of the species Myzus persicae before the start of the test. The treated plants are then sprayed to drip point with an aqueous suspension containing the test compound in a concentration of 12.5, 50, 200 and 400 ppm. Two plants are used for each compound at its given concentration. A mortality count is made 48 hours after application. The test is carried out at 20–22°C and 60% relative humidity.

In this test, compound 8 effects 80 to 100% mortality even at a concentration of 12.5 ppm. 80 to 100% mortality is effected by compounds 32 and 33 at 50 ppm, by compunds 30, 31 and 61 at 200 ppm and by compound 89 at 400 ppm.

Example 13: Insecticidal contact action against Aphis craccivora

Before the start of the test, bean plants (Vicia faba) reared in pots are each populated with about 200 individuals of the species Aphis craccivora. The treated plants are sprayed 24 hours later to drip point with an aqueous formulation containing the test compound in a concentration of 12.5, 50, 100, 200 and 400 ppm. Two plants are used for each test compound at its given concentration and a mortality count is made after a further 24 hours.

In this test, the compounds of the invention effect 80 to 100% mortality at the concentrations listed in the following table:

Compound	Concentration
8, 43, 47 and 61	12.5 ppm
30, 32, 33, 40, 42 and 44	50 ppm
10, 12, 14, 82, 83, 87, 89	100 ppm
31, 46, 52 and 53	200 ppm
76, 77, 79, 84 and 85	400 ppm

Example 14: Action against Laodelphax striatellus and Nilaparvata lugens (nymphs)

The test is carried out with growing plants. The procedure is that 4 rice plants (thickness of stem 8 mm) about 20 cm in height are planted into each of a number of pots (diameter 8 cm). The plants in each pot are sprayed on a rotary table with 100 ml of acetonic solutions containing the test compound in concentrations of 50 ppm to 400 ppm. After the spray coating was dried, each plant is populated with 20 nymphs of the test organisms in the third stage. To prevent the cicadas from escaping, a glass cylinder which is open at both ends is slipped over each of the plants and sealed with a gauze top. The nymphs are kept for 10 days on the treated plant until the next development stage has been reached. Evaluation of percentage mortality is made 1, 4 and 8 days after treatment.

When used at the given concentrations, the following compounds of the invention effect 80 to 100% mortality after 8 days against nymphs of Nilaparvata lugens:

Compound	Concentration
43	12.5 ppm
12, 14, 40 and 41	50 ppm
8, 19, 82 and 87	100 ppm
30, 33 and 53	200 ppm
31, 32, 44, 54, 55, 65, 80, 81, 83, 84, 85 and 89	400 ppm

Good activity against nymphs of Laodelpax striatellus can also be achieved with the compounds of formula I according to Example 1.

Example 15: Action against soil insects (Diabrotica balteata)

350 ml of soil (consisting of 95 vol.% of sand and 5 vol.% of peat) are mixed with 150 ml of each of a number of aqueous emulsion formulations which contain the test compound in increasing conentrations of 3 ppm to 200 ppm. Plastic beakers with a diameter of about 10 cm at the top are then partly filled with the treated soil. Ten L_3 larvae of Diabrotica balteata are put into each beakers, then 4 maize seedlings are planted and the beaker is filled up with soil. The beakers are sealed with plastic sheeting and kept at about 22°C. Ten days later the soil in the beakers is sieved and a mortality count of the remaining larvae is made.

In this test, the following compounds of the invention effect 80 to 100 % mortality at the concentrations listed in the following table:

Compound	Concentration
30 and 43	3 ppm
32, 42, 44 and 53	12.5 ppm
33, 36, 41, 52 and 61	50 ppm
66, 78, 87, 88 and 106	100 ppm
14	200 ppm
77, 80, 84 and 89	400 ppm

Example 16: Action against Panonychus ulmi (OP an carbamate resistant)

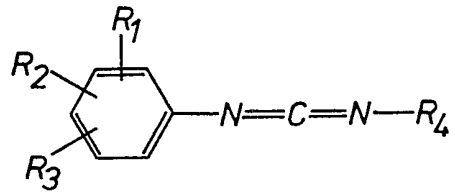
Potted apple seedlings with about 20 to 30 leaves are each populated with 60 adult females of Panonychus ulmi. The infested plants are sprayed 7 days after to drip point with an aqueous emulsion containing 0.75 ppm of the test compound. The treated plants are then stood in a greenhouse for a further 14 days at 25°C and about 50% relative humidity.

After this period, evaluation is made by taking 20 leaves from each plant, removing the mite population from these leaves by means of a brushing device and counting the number of eggs, postembryonic stages and adults under a stereoscopic microscope. An assessment is made of the percentage reduction of the mite population as compared with untreated controls.

In this test, compounds 1 and 26 according to Example 1 effect 80 to 100 % mortality

CLAIMS

1. A compound of formula I



(I),

wherein

R_1 is hydrogen, halogen, C_1–C_{10}alkyl, C_1–C_5alkoxy, C_1–C_5alkoxy which is sustituted by 1 to 7 halogen atoms, or is C_1–C_5alkylthio;

R_2 is hydrogen, halogen, C_1–C_{10}alkyl or C_1–C_5alkoxy;

R_3 is hydrogen, C_1–C_{10}alkyl, halogen, phenoxy, phenylthio, or is phenoxy or phenylthio, each mono- or disubstituted by a member selected from the group consisting of halogen, methyl, ethyl, C_1–C_3haloalkyl containing 1 to 7 halogen atoms and cyano, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisting of halogen and C_1–C_3haloalkyl containing 1 to 7 halogen atoms;

R_4 is C_1–C_{12}alkyl, alkoxyalkyl containing a total of 2 to 10 carbon atoms, C_3–C_{10}cycloalkyl, C_3–C_{10}cycloalkylmethyl, C_3–C_{10}cycloalkyl which is substituted by 1 to 3 C_1–C_3alkyl groups, or is C_1–C_5alkyl which is substituted by 1 or 2 C_3–C_{10}cycloalkyl groups, or is a polycyclic alkyl group containing 7 to 10 carbon atoms, phenyl(C_1–C_5)alkyl or phenyl(C_1–C_5)alkyl which is mono- or disubstituted at the phenyl nucleus by halogen, trifluoromethyl, methoxy or ethoxy.

2. A compound according to claim 1, wherein

R_1 is hydrogen, halogen, C_1–C_{10}alkyl, C_1–C_5alkoxy, C_1–C_5alkoxy which is substituted by 1 to 7 halogen atoms, or is C_1–C_5alkylthio;

R_2 is hydrogen, halogen, C_1–C_{10}alkyl or C_1–C_5alkoxy;

R_3 is hydrogen, C_1–C_{10}alkyl, halogen, phenoxy or phenoxy which is mono- or disubstituted by a member selected from the group consisting of halogen, trifluoromethyl and cyano, or is phenylthio, pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisting of halogen and trifluoromethyl; and

R_4 is C_1–C_{10}alkyl, alkoxyalkyl containing a total of 2 to 10 carbon atoms, C_3–C_{10}cycloalkyl, C_3–C_{10}cycloalkylmethyl, or C_3–C_{10}cycloalkyl which is substituted by a C_1–C_3alkyl group.

3. A compound according to claim 1, wherein

R_1 is hydrogen, fluorine, chlorine, C_1–C_4alkyl, methoxy, ethoxy, trifluoromethoxy or C_1–C_3alkylthio;

R_2 is hydrogen, fluorine, chlorine, C_1–C_4alkyl, methoxy or ethoxy;

R_3 is hydrogen, C_1–C_4alkyl, fluorine, chlorine, phenoxy, phenylthio, phenoxy which is mono- or disubstituted by chlorine and/or trifluoromethyl, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by a member selected from the group consisting of fluorine, chlorine and trifluoromethyl; and

R_4 is C_1–C_8alkyl, alkoxyalkyl containing a total of 2 to 7 carbon atoms, C_3–C_8cycloalkyl, C_3–C_6cycloalkylmethyl, methyl(C_3–C_6)cycloalkyl, phenyl(C_1–C_4)alkyl or phenyl(C_1–C_4)alkyl which is mono- or disubstituted at the phenyl nucleus by chlorine, trifluoromethyl or methoxy.

4. A compound according to claim 3, wherein

R_1 is hydrogen, fluorine, chlorine, C_2–C_4alkyl or methoxy;

R_2 is hydrogen, chlorine, C_3–C_4alkyl or methoxy;

R_3 is methyl, ethyl, isopropyl, chlorine, phenoxy, phenoxy which is mono- or disubstituted by chlorine and/or trifluoromethyl, or is pyridyloxy or pyridyloxy which is mono- or disubstituted by chlorine and/or trifluoromethyl; and

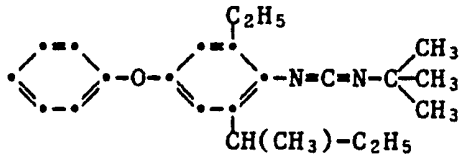
R_4 is C_3–C_8alkyl, C_1–C_4alkoxy(C_1–C_3)alkyl, C_3–C_6cycloalkyl, phenyl(C_1–C_4)alkyl or phenyl(C_1–C_4)alkyl which is substituted at the phenyl nucleus by a chlorine atom or a methoxy group.

5. A compound according to any one of claims 1 to 4, wherein one of the radicals R_1, R_2 and R_3 is in the 4-position and the other two independently of each other are in the 2- and 6-positions.

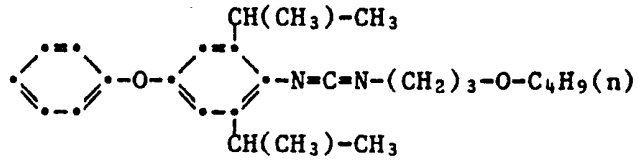
6. A compound according to any one of claims 1 to 5, wherein R_4 is isopropyl or tert-butyl.

7. A compound according to any one of claims 1 to 6, wherein R_1 and R_2 are in the 2- and 6-positions.

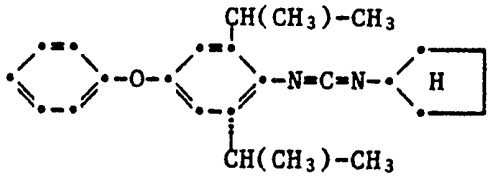
8. A compound according to claim 4 of the formula



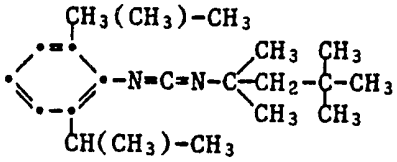
9. A compound according to claim 4 of the formula



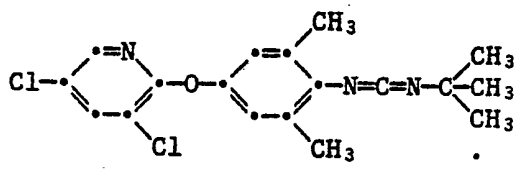
10. A compound according to claim 4 of the formula



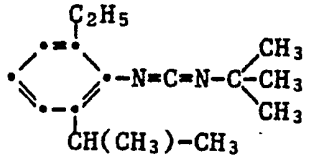
11. A compound according to claim 4 of the formula



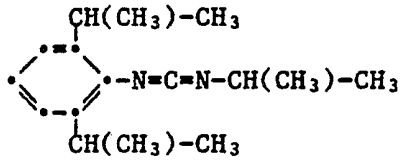
12. A compound according to claim 4 of the formula



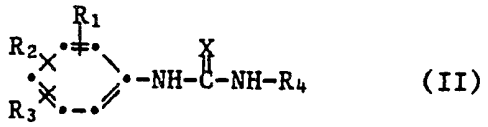
13. A compound according to claim 3 of the formula



14. A compound according to claim 4 of the formula



15. A process for the preparation of a compound of formula I according to any one of claims 1 to 14, which process comprises removing water or hydrogen sulfide respectively from a compound of formula II



(II)

wherein R_1 to R_4 are as defined in any one of claims 1 to 7 and X is oxygen or sulfur.

16. A pesticidal composition which contains as active ingredient a compound according to any one of claims 1 to 14, together with suitable carriers and/or other adjuvants.

17. Use of a compound according to any one of claims 1 to 14 for controlling insects and representatives of the order Acarina on animals and plants.

18. Use according to claim 17 for controlling plant-destructive insects.

19. A method of controlling insects and representatives of the order Acarina, which process comprises contacting or treating said pests, their various development stages or the locus thereof with a pesticidally effective amount of a compound of formula I according to any one of claims 1 to 14, or with a composition which contains a pesticidally effective amount of such a compound, together with adjuvants and carriers.

20. A compound according to claim 1 substantially as hereinbefore described with reference to Example 1.

21. A pesticidal composition according to claim 16 substantially as hereinbefore described with reference to Example 2.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.