

PATENT SPECIFICATION

(11) 1312536

1312536

NO DRAWINGS

- (21) Application No. 46509/71 (22) Filed 6 Oct. 1971
 (31) Convention Application No. 7 036 084 (32) Filed 6 Oct. 1970
 (31) Convention Application No. 7 128 896 (32) Filed 6 Aug. 1971 in
 (33) France (FR)
 (44) Complete Specification published 4 April 1973
 (51) International Classification C07D 49/32
 (52) Index at acceptance
 C2C 182—197—280 200 215 220 226 22Y 250 252 25Y
 30Y 311 313 31Y 338 342 34Y 351 352 366 368 372 378
 387 491 584 628 62X 635 65X 678 694 697 761
 764 791 79Y KS QZ RE TL
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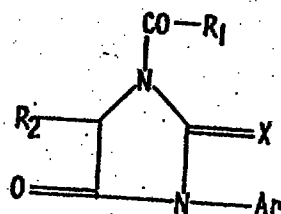


(54) HYDANTOIN DERIVATIVES

(71) We, RHONE-POULENC S.A., a French Body Corporate, of 22 Avenue Montaigne, Paris 8e, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

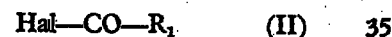
This invention relates to new hydantoin derivatives which possess fungicidal properties, to processes for their preparation and to fungicidal compositions containing them.

The hydantoin derivatives of the present invention are compounds of the general formula:

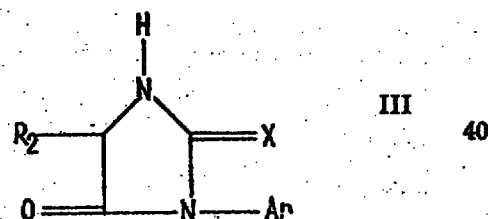


wherein Ar represents a phenyl radical or a phenyl radical carrying one to five substituents, which may be the same or different, selected from halogen atoms (preferably chlorine), alkyl and alkoxy radicals containing 1 to 4 carbon atoms and the trifluoromethyl radical, R₁ represents an alkoxy radical containing 1 to 4 carbon atoms or a grouping —NR₂R₃, in which R₂ and R₃ are the same or different and each represents a hydrogen atom, an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms, R₂ represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms, and X represents an oxygen or sulphur atom.

According to a feature of the invention, the hydantoin derivatives of general formula I are prepared by reacting a compound of the general formula:

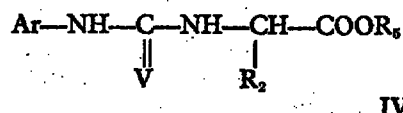


(wherein Hal represents a halogen, preferably chlorine, atom and R₁ is as hereinbefore defined) with a hydantoin compound of the general formula:



wherein Ar, R₂, and X are as hereinbefore defined. Generally the reaction can be carried out in a basic organic solvent such as pyridine or in an organic solvent such as benzene, chloroform, acetonitrile, dimethylformamide or N-methyl-pyrrolidone, in the presence of a strong base such as an alkali metal alkoxide, for example potassium ethoxide, at a temperature between 0°C and the boiling temperature of the reaction mixture.

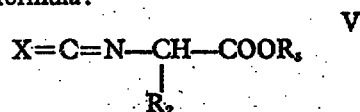
The starting materials of general Formula III can be obtained by cyclisation of an acid or ester of the general formula:



wherein R₃ represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms, and Ar, R₂, and X are as hereinbefore defined. The cyclisation can generally be effected by heating in an organic solvent in the presence of a basic condensation agent.

The compound of general formula IV can be obtained either:

(a) by the action of an acid or ester of the general formula:

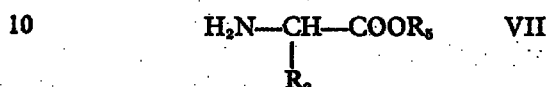


(wherein R_2 , X and R_s are as hereinbefore defined) on an aniline of the general formula:



(wherein Ar is as hereinbefore defined), or

(b) by the action of an amino-acid or ester of the general formula:

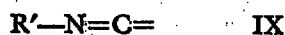


(wherein R_2 and R_s are as hereinbefore defined) on a phenyl isocyanate or isothiocyanate of the general formula



15 (wherein Ar and X are as hereinbefore defined) according to known methods for the preparation of ureas and thioureas.

According to another feature of the invention the hydantoin derivatives of general formula I, wherein R_1 represents a grouping $-\text{NR}_2\text{R}_3$ in which R_2 represents a hydrogen atom and R_3 represents an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms, are prepared by reacting an isocyanate of the general formula:



(wherein R' represents an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms with a hydantoin compound of the general formula III by known methods for the preparation of ureas, for example by heating the reactants in an organic solvent such as benzene or acetone in the presence of a basic condensation agent such as triethylamine. By the term "known methods" is meant methods heretofore used or described in the literature.

40 The hydantoin derivatives of general formula I obtained by the aforementioned processes may optionally be purified by physical methods such as crystallisation, distillation or chromatography.

45 The hydantoin derivatives of general formula I possess valuable fungicidal properties; they are particularly active against grey moulds (*Botrytis cinerea*), bean anthracnose (*Colletotrichum lindemuthianum*) and sclerotinia rot (*Sclerotinia sclerotiorum*) when used in quantities of between 25 and 100 g. per hectolitre

of, for example, water. They are particularly interesting for the treatment of vines, strawberry plants, fruit trees (e.g. peach, apricot and cherry trees) and market gardening produce (e.g. vegetables for salads) to control fungal infections. Preferred compounds are those in which Ar represents the phenyl radical or a phenyl radical carrying one or two substituents selected from chlorine and fluorine atoms, alkyl radicals containing 1 to 4 carbon atoms (preferably methyl) and the trifluoromethyl radical, and more particularly those compounds wherein Ar represents the 3,5-dichlorophenyl radical, R_1 represents a grouping $-\text{NR}_2\text{R}_3$ in which R_2 represents a hydrogen atom and R_3 represents an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms (preferably allyl), and R_2 and X are as hereinbefore defined. Of outstanding importance are 1 - propylcarbamoyl-5 - (3,5 - dichlorophenyl)hydantoin, 1 - allylcarbamoyl - 3 - (3,5 - dichlorophenyl)hydantoin, 1 - isopropylcarbamoyl - 3(3,5 - dichlorophenyl)hydantoin, 1 - methylcarbamoyl - 3-3,5 - dichlorophenyl)hydantoin, 1 - ethylcarbamoyl - 3 - (3,5 - dichlorophenyl) hydantoin, 1 - methylcarbamoyl - 3 - (3,5 - dichlorophenyl) - 2 - thiohydantoin and 1 - ethylcarbamoyl - 3 - (3,5 - dichlorophenyl) - 2-thiohydantoin.

The present invention also includes within its scope fungicidal compositions which comprise, as the active ingredient, at least one hydantoin derivative of general formula I in association with one or more diluents or adjuvants compatible with the hydantoin derivative(s). These compositions can optionally contain other compatible pesticides, such as insecticides or fungicides (e.g. maneb). Preferably the compositions contain between 0.005% and 80% by weight of the hydantoin derivative.

The compositions may be solid if there is employed a powdered solid compatible diluent such as talc, calcined magnesite, kieselguhr, tricalcium phosphate, powdered cork, adsorbent charcoal, or a clay such as kaolin or bentonite. These solid compositions are preferably prepared by grinding the hydantoin derivative with the solid diluent, or by impregnating the solid diluent with a solution of the hydantoin derivative in a volatile solvent, evaporating the solvent, and if necessary grinding the product so as to obtain a powder.

Instead of a solid diluent, there may be used a liquid in which the hydantoin derivative is dissolved or dispersed. The compositions may thus take the form of suspensions, emulsions or solutions in organic or aqueous-organic media, for example aromatic hydrocarbons such as toluene or xylene, mineral, animal or vegetable oils, anisole, cyclohexanone or acetophenone, or mixtures of these diluents. The compositions in the form of suspensions, emulsions or solutions may contain wetting, dispersing or emulsifying agents of the ionic or non-ionic type,

for example sulphuricinoles, quaternary ammonium derivatives or products based on condensates of ethylene oxide, such as the condensates of ethylene oxide with octylphenol, or fatty acid esters of anhydro-sorbitols which have been rendered soluble by etherification of the free hydroxy groups by condensation with ethylene oxide. It is preferable to use agents of the non-ionic type because they are not sensitive to electrolytes. When emulsions are required, the hydantoin derivatives may be used in the form of self-emulsifying concentrates containing the active substance dissolved in the emulsifying agent(s) or in a solvent containing the emulsifying agent(s) compatible with the hydantoin derivative and solvent, a simple addition of water to such concentrates producing compositions ready for use.

The hydantoin derivatives of general formula I are preferably employed as fungicides in quantities of 20 to 200 g. per hectolitre of water, and in the field at the rate of about 1,000 litres of solution per hectare under cultivation.

The following Examples illustrate the invention.

Example 1

A 22.5% (w/v) ethanolic solution of potassium ethoxide (32 cc.) is added to a suspension of 3-phenylhydantoin (12.3 g.) in benzene (150 cc.). After azeotropic distillation of the ethanol, methyl chloroformate (6.6 g.) is added and the reaction mixture heated for 10 minutes under reflux. The benzene is then evaporated under reduced pressure and the residue is recrystallised from ethanol to yield 1-methoxycarbonyl-3-phenylhydantoin (11 g.) melting at 154°C.

3-Phenylhydantoin, m.p. 156°C., employed as starting material can be prepared according to the method described by Dains, J. Amer. Chem. Soc., 44, 2312 (1922).

By proceeding as described above but starting with appropriate compounds of general formulae II and III there are obtained the following products:—

Example No.	Product	Melting Point (°C.)
2	1-Methoxycarbonyl-3-(3-chlorophenyl)-hydantoin	140
3	1-Ethoxycarbonyl-3-(3-chlorophenyl)-hydantoin	128
4	1-Methoxycarbonyl-3-(3,5-dichlorophenyl)-hydantoin	200
5	1-Ethoxycarbonyl-3-(3,5-dichlorophenyl)hydantoin	156
6	1-Ethoxycarbonyl-3-(3-fluorophenyl)hydantoin	126
7	1-Ethoxycarbonyl-3-(2,4-dichlorophenyl)-5-methylhydantoin	100
8	1-Methoxycarbonyl-3-(2,4-dichlorophenyl)-5-methylhydantoin	105
9	1-Methoxycarbonyl-3-(2,4-dichlorophenyl)-hydantoin	162
10	1-Methoxycarbonyl-3-(3,5-dimethylphenyl)-hydantoin	136

Example 11

A 22.5% (w/v) ethanolic solution of potassium ethoxide (26 cc.) is added to a suspension of 3 - (3 - chlorophenyl)hydantoin (14 g.) in benzene (200 cc.). After azeotropic distillation of the ethanol, dimethylcarbamoyl chloride (7.2 g.) is added and the reaction mixture is heated for 10 minutes under reflux. The precipitate which forms is filtered off and the benzene is evaporated under reduced pressure. The residue obtained is washed successively with anaesthetic grade diethyl ether (50 cc.) and petroleum ether (b.p. 50—70°C.; 50 cc.) to yield 1 - dimethylcarbamoyl - 3 - (3-chlorophenyl)hydantoin (7.8 g.) melting at 152°C.

3 - (3 - Chlorophenyl hydantoin, m.p. 143°C., employed as starting material can be prepared according to the method described by Dains, J. Amer. Chem. Soc., 44, 2312 (1922).

Example 12

Allyl isocyanate (4.5 g.) and triethylamine (5.5 g.) are added to a solution of 3 - (3,5-dichlorophenyl)hydantoin (11 g.) in acetone (150 cc.). After 30 minutes heating under reflux followed by cooling, the acetone is evap-

orated under reduced pressure. The residue obtained is washed with petroleum ether (b.p. 50—70°C.; 250 cc.) and recrystallised from ethanol to yield 1 - allylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin (11 g.) melting at 116°C.

3 - (3,5 - Dichlorophenyl)hydantoin, m.p. 199°C., employed as starting material can be prepared according to the method described by Dhar, J. Soc. Ind. Research, 20c, 145 (1961).

Example 13

Propyl isocyanate (4.6 g.) and triethylamine (5.5 g.) are added to a solution of 3 - (3,5-dichlorophenyl)hydantoin (11 g.) in acetone (150 cc.). After 30 minutes heating under reflux followed by cooling, the acetone is evaporated under reduced pressure. The residue obtained is washed with petroleum ether (b.p. 50—70°C.; 250 cc.) and recrystallised from diisopropyl ether to yield 1 - propyl - carbamoyl - 3 - (3,5 - dichlorophenyl)hydantoin (11 g.) melting at 92°C.

By proceeding as described above but starting with appropriate compounds of general formulae III and IX there are obtained the following products:—

Example No.	Product	Melting Point (°C.)
14	1-Isopropylcarbamoyl-3-(3-chlorophenyl)hydantoin	109
15	1-Propylcarbamoyl-3-(3-chlorophenyl)hydantoin	90
16	1-Methylcarbamoyl-3-(3,5-dichlorophenyl)-hydantoin	163
17	1-Ethylcarbamoyl-3-(3,5-dichlorophenyl)-hydantoin	152
18	1-Methylcarbamoyl-3-(3-chlorophenyl)-5-methylhydantoin	130
19	1-Isopropylcarbamoyl-3-(3,5-dichlorophenyl)-hydantoin	136
20	1-Butylcarbamoyl-3-(3,5-dichlorophenyl)hydantoin	112
21	1-Isopropylcarbamoyl-3-(3,5-dichlorophenyl)-5-methylhydantoin	125
22	1-Ethylcarbamoyl-3-(3-fluorophenyl)hydantoin	140
23	1-Propylcarbamoyl-3-(3-fluorophenyl)hydantoin	93
24	1-Methylcarbamoyl-3-(3-trifluoromethylphenyl)-hydantoin	120
25	1-Methylcarbamoyl-3-(3-fluorophenyl)hydantoin	207

Example 26

Methyl isocyanate (3.4 g.) and triethylamine (4 g.) are added to a suspension of 3 - (3,5-dichlorophenyl) - 5 - methylhydantoin (10.4 g.) in benzene (150 cc.). After heating for 1 hour under reflux followed by cooling, the benzene is evaporated under reduced pressure. The residue obtained is washed with anaesthetic grade diethyl ether (30 cc.) and petroleum ether (b.p. 50—70°C.; 200 cc.) and recrystallised from ethanol to yield 1-methyl-

carbamoyl - 3 - (3,5 - dichlorophenyl) - 5-methylhydantoin (9 g.) melting at 137°C.

3 - (3,5 - Dichlorophenyl) - 5 - methylhydantoin, m.p. 156°C., employed as starting material can be prepared according to the method described by Dhar, J. Soc. Ind. Research, 20c, 145 (1961).

By proceeding as described above but starting with appropriate compounds of general formulae III and IX there are obtained the following products:—

Example No.	Product	Melting Point (°C.)
27	1-Butylcarbamoyl-3-(3,5-dichlorophenyl)-5-methylhydantoin	95
28	1-t-Butylcarbamoyl-3-(3,5-dichlorophenyl)-hydantoin	181

Example 29

Methyl isocyanate (3.4 g.) and triethylamine (5 g.) are added to a solution of 3 - (3,5-dimethylphenyl)hydantoin (10.2 g.) in acetone (120 cc.). After leaving the reaction mixture to stand for 24 hours at a temperature of about 20°C., the precipitate which forms is filtered off and dried *in vacuo* over sulphuric acid. There is thus obtained 1 - methylcarbamoyl - (3,5 - dimethylphenyl)hydantoin (11 g.) melting at 204°C.

3 - (3,5 - Dimethylphenyl)hydantoin, m.p. 128°C., employed as starting material can be prepared according to the method described by Dhar, J. Soc. Ind. Research, 20c, 145 (1961).

of 3 - phenyl - 2 - thiohydantoin (6.8 g.) in N - methylpyrrolid - 2 - one (150 cc.). After distillation of the ethanol under reduced pressure, ethyl chloroformate (3.8 g.) is added and the reaction mixture stirred for 5 hours at about 25°C. A small amount of insoluble material is separated by filtration and the filtrate poured into ice-water (500 cc.). The precipitate which forms is filtered off and recrystallised from ethanol to yield 1 - ethoxycarbonyl - 3 - phenyl - 2 - thiohydantoin (4.2 g.) melting at 142°C.

3 - Phenyl - 2 - thiohydantoin, m.p. 242°C., employed as starting material can be prepared according to the method described by Aschan, Ber., 17, 424 (1884).

By proceeding as described above but starting with appropriate compounds of general formulae II and III there are obtained the following products:—

Example No.	Product	Melting Point (°C.)
31	1-Methoxycarbonyl-3-phenyl-2-thiohydantoin	180
32	1-Methoxycarbonyl-3-(3,5-dichlorophenyl)-2-thiohydantoin	174

Example 33

Methyl isocyanate (3.2 g.) and triethylamine (0.5 cc.) are added to a suspension of 3 - (3-chlorophenyl) - 2 - thiohydantoin (7 g.) in benzene (100 cc.). After heating for 2 hours under reflux followed by cooling, the precipitate which forms is filtered off, washed with diisopropyl ether (2 x 50 cc.) and dried *in vacuo* over sulphuric acid. There is thus obtained 1 - methylcarbamoyl - 3 - (3-chloro-

phenyl) - 2 - thiohydantoin (6.7 g.) melting at 170°C.

3 - (3 - Chlorophenyl) - 2 - thiohydantoin, m.p. 216°C., employed as starting material can be prepared according to the method described by Dains, J. Amer. Chem. Soc., 44, 2312 (1922).

By proceeding as described above but starting with appropriate compounds of general formulae III and IX there are obtained the following products:—

Example No.	Product	Melting Point (°C.)
34	1-Methylcarbamoyl-3-(dichlorophenyl)-2-thiohydantoin	210
35	1-Ethylcarbamoyl-3-(3,5-dichlorophenyl)-2-thiohydantoin	216

Example 36

A 22.5% (w/v) ethanolic solution of potassium ethoxide (15.4 cc.) is added to a solution of 3 - (3,5 - dichlorophenyl) - 2 - thiohydantoin (10.4 g.) in dimethylformamide (150 cc.). After removal of the ethanol by distillation, dimethylcarbamoyl chloride (4.3 g.) is added. After leaving the reaction mixture overnight at a temperature of about 20°C., the reaction mixture is poured into water (1,500 cc.) and the precipitate which forms is extracted with methylene chloride (1,000 cc.). After chromatography through a column of "Florisil" (an activated magnesium silicate) and recrystallisation from toluene, there is obtained 1 - dimethylcarbamoyl - 3 - (3,5 - dichlorophenyl) - 2 - thiohydantoin (1.6 g.) melting at 216°C.

3 - (3,5 - Dichlorophenyl) - 2 - thiohydantoin, m.p. 258°C., employed as starting material can be prepared according to the method described by Dains, J. Amer. Chem. Soc., 44, 2312 (1922).

Example 37

In accordance with a usual technique there is prepared an emulsifiable solution having the following composition:—

1 - propylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin 400 g.
 Tween 20 10 g.
 Atlox 4855 90 g.
 cyclohexanone - xylene mixture
 (1—3 by volume)
 quantity to make up to 1,000 cc.

Example 38

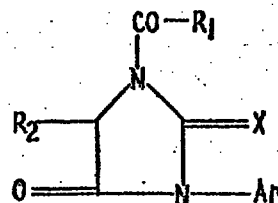
In accordance with a usual technique there is prepared an emulsifiable solution having the following composition:—

1 - propylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin 400 g.
 Tween 20 10 g.
 Atlox 4855 90 g.
 anisole, quantity to make up to 1,000 cc.

"Tween 20" (Registered Trade Mark) is a wetting agent which is a condensate of ethylene oxide with fatty acid esters of sorbitol, and "Atlox 4855" (Registered Trade Mark) is an emulsifying agent which is a polyoxyethylene derivative of an arylsulphonate.

WHAT WE CLAIM IS:—

1. A hydantoin derivative of the general formula:



wherein Ar represents a phenyl radical or a phenyl radical carrying one to five substituents, which may be the same or different, selected

Example 33

Methyl isocyanate (3.2 g.) and triethylamine (0.5 cc.) are added to a suspension of 3 - (3-chlorophenyl) - 2 - thiohydantoin (7 g.) in benzene (100 cc.). After heating for 2 hours under reflux followed by cooling, the precipitate which forms is filtered off, washed with diisopropyl ether (2 x 50 cc.) and dried *in vacuo* over sulphuric acid. There is thus obtained 1 - methylcarbamoyl - 3 - (3-chloro-

phenyl) - 2 - thiohydantoin (6.7 g.) melting at 170°C.

3 - (3 - Chlorophenyl) - 2 - thiohydantoin, m.p. 216°C., employed as starting material can be prepared according to the method described by Dains, J. Amer. Chem. Soc., 44, 2312 (1922).

By proceeding as described above but starting with appropriate compounds of general formulae III and IX there are obtained the following products:—

Example No.	Product	Melting Point (°C.)
34	1-Methylcarbamoyl-3-(dichlorophenyl)-2-thiohydantoin	210
35	1-Ethylcarbamoyl-3-(3,5-dichlorophenyl)-2-thiohydantoin	216

Example 36

A 22.5% (w/v) ethanolic solution of potassium ethoxide (15.4 cc.) is added to a solution of 3 - (3,5 - dichlorophenyl) - 2 - thiohydantoin (10.4 g.) in dimethylformamide (150 cc.). After removal of the ethanol by distillation, dimethylcarbamoyl chloride (4.3 g.) is added. After leaving the reaction mixture overnight at a temperature of about 20°C., the reaction mixture is poured into water (1,500 cc.) and the precipitate which forms is extracted with methylene chloride (1,000 cc.). After chromatography through a column of "Florisil" (an activated magnesium silicate) and recrystallisation from toluene, there is obtained 1 - dimethylcarbamoyl - 3 - (3,5 - dichlorophenyl) - 2 - thiohydantoin (1.6 g.) melting at 216°C. 3 - (3,5 - Dichlorophenyl) - 2 - thiohydantoin, m.p. 258°C., employed as starting material can be prepared according to the method described by Dains, J. Amer. Chem. Soc., 44, 2312 (1922).

Example 37

In accordance with a usual technique there is prepared an emulsifiable solution having the following composition:—

1 - propylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin 400 g.
 Tween 20 10 g.
 Atlox 4855 90 g.
 cyclohexanone - xylene mixture (1—3 by volume)
 quantity to make up to 1,000 cc.

Example 38

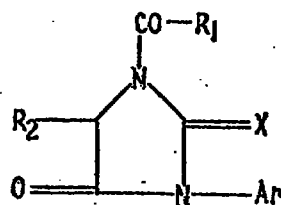
In accordance with a usual technique there is prepared an emulsifiable solution having the following composition:—

1 - propylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin 400 g.
 Tween 20 10 g.
 Atlox 4855 90 g.
 anisole, quantity to make up to 1,000 cc.

"Tween 20" (Registered Trade Mark) is a wetting agent which is a condensate of ethylene oxide with fatty acid esters of sorbitol, and "Atlox 4855" (Registered Trade Mark) is an emulsifying agent which is a polyoxyethylene derivative of an arylsulphonate.

WHAT WE CLAIM IS:—

1. A hydantoin derivative of the general formula:



wherein Ar represents a phenyl radical or a phenyl radical carrying one to five substituents, which may be the same or different, selected



from halogen atoms, alkyl and alkoxy radicals containing 1 to 4 carbon atoms and the trifluoromethyl radical, R_1 represents an alkoxy radical containing 1 to 4 carbon atoms or a

5 grouping $-NR_3R_4$, in which R_3 and R_4 are the same or different and each represents a hydrogen atom, an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms, R_2 represents a

10 hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms, and X represents an oxygen or sulphur atom.

2. A hydantoin derivative according to claim 1 wherein R_1 represents an alkoxy radical containing 1 to 4 carbon atoms or a grouping

15 $-NR_3R_4$, in which R_3 and R_4 are the same or different and each represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms.

20 3. A hydantoin derivative according to claim 1 or 2 wherein Ar represents the phenyl radical or a phenyl radical carrying one or two substituents selected from chlorine and fluorine atoms, alkyl radicals containing 1 to 4 carbon atoms and the trifluoromethyl radical.

25 4. A hydantoin derivative according to claim 1 wherein Ar represents the 3,5 - dichlorophenyl radical, R_1 represents a grouping

30 $-NR_3R_4$, in which R_3 represents a hydrogen atom and R_4 represents an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms, and

35 R_2 and X are as defined in claim 1.

5. 1 - Propylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin.

6. 1 - Allylcarbamoyl - 3 - (3,5 - dichlorophenyl)hydantoin.

7. 1 - Isopropylcarbamoyl - 3 - (3,5 - dichlorophenyl)hydantoin.

8. 1 - Methylcarbamoyl - 3 - (3,5 - dichlorophenyl)hydantoin.

9. 1 - Ethylcarbamoyl - 3 - (3,5-dichlorophenyl)hydantoin.

10. 1 - Methylcarbamoyl - 3 - (3,5 - dichlorophenyl) - 2 - thiohydantoin.

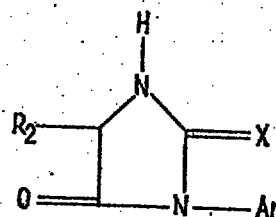
11. 1 - Ethylcarbamoyl - 3 - (3,5-dichlorophenyl) - 2 - thiohydantoin.

12. A hydantoin derivative conforming to the general formula specified in claim 1 obtained as product in any one of Examples 1 to 11, 14, 15, 18, 20 to 33 and 36.

13. A process for the preparation of a hydantoin derivative as claimed in claim 1 which comprises reacting a compound of the general



(wherein Hal represents a halogen atom and R_1 is as defined in claim 1) with a hydantoin compound of the general formula:



wherein Ar, R_2 and X are as defined in claim 1.

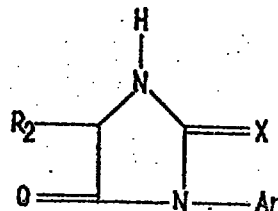
14. A process according to claim 13 wherein Hal represents a chlorine atom.

15. A process according to claim 13 or 14 in which the reaction is carried out in a basic organic solvent, or in an organic solvent in the presence of a strong base, at a temperature between 0°C. and the boiling temperature of the reaction mixture.

16. A process for the preparation of a hydantoin derivative as claimed in claim 1 wherein R_1 represents a grouping $-NR_3R_4$, in which R_3 represents a hydrogen atom and R_4 represents an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms, which comprises reacting an isocyanate of the general formula:



wherein R_4' represents an alkyl radical containing 1 to 4 carbon atoms or an alkenyl radical containing 2 to 4 carbon atoms) with a hydantoin compound of general formula:



(wherein Ar, R_2 and X are as defined in claim 1) by known methods for the preparation of ureas.

17. A process according to claim 16 in which the reaction is carried out by heating the reactants in an organic solvent in the presence of a basic condensation agent.

18. A process for the preparation of a hydantoin derivative of the general formula specified in claim 1 substantially as described in any one of Examples 1 to 36.

19. A hydantoin derivative of the general formula specified in claim 1 when prepared by the process claimed in any one of claims 13 to 18.

20. A fungicidal composition which comprises, as active ingredient, at least one hydantoin derivative as claimed in any one of claims



1 to 12 in association with one or more diluents or adjuvants compatible with the hydantoin derivative.

5 21. A fungicidal composition according to claim 20 in which the amount of hydantoin derivative is between 0.005% and 80% by weight of the composition.

10 22. A fungicidal composition according to claim 20 or 21 which contains a wetting, dispersing or emulsifying agent.

23. A fungicidal composition according to claim 22 in which the wetting, dispersing or emulsifying agent is a non-ionic compound.

15 24. A fungicidal composition as claimed in claim 20 substantially as hereinbefore described with especial reference to Example 37 or 38.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



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