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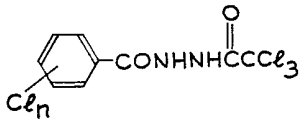
(54) N-TRICHLOROACETYL-N'-CHLOROBENZOYLHYDRAZINE DERIVATIVES

(71) We, KUREHA KAGAKU KOGYO KABUSHIKI KAISHA, a Japanese Corporation, of No. 8, 1-chome, Horidome-cho, Nihonbashi, Chuo-ku, Tokyo, Japan, 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 novel hydrazine derivatives having fungicidal properties, a process for their preparation and fungicidal compositions containing the hydrazine derivatives.

According to the present invention there are provided N-trichloroacetyl-N'-chlorobenzoylhydrazine derivatives having the general formula:



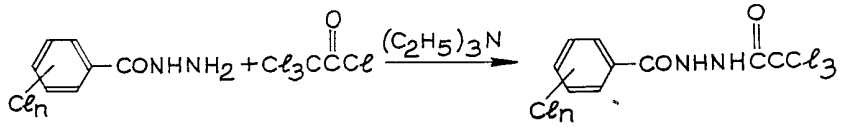
where n represents an integer of 1 or 2.

The hydrazine derivatives of the above general formula are novel compounds which exhibit a pronounced fungicidal effect towards plant diseases.

Accordingly, the present invention includes a fungicidal composition containing, as active ingredient, a hydrazine derivative having the above general formula in a fungicidally effective amount.

The N-trichloroacetyl-N'-chlorobenzoyl hydrazines may be prepared by reacting the corresponding chlorobenzoyl hydrazide with trichloracetyl chloride in the presence of triethylamine.

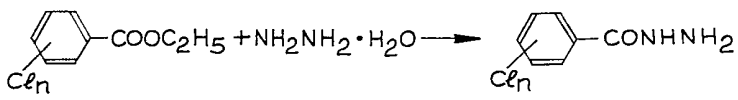
This reaction may be represented by the following equation.



wherein n is 1 or 2.

The reaction is conveniently carried out in an inert solvent, such as benzene, and the trichloroacetyle chloride is added dropwise to the reaction mixture. Preferably the reactants and the triethylamine are used in approximately equimolar amounts and the reaction mixture is agitated at room temperature for 1 to 7 hours.

The chlorobenzoylhydrazine used as starting material in the above reaction is prepared by reacting the corresponding chloro-substituted benzoic acid ester with hydrazine hydrate according to the following equation:

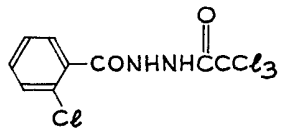
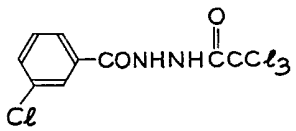
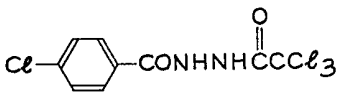
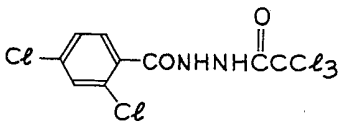
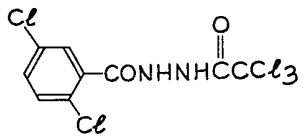
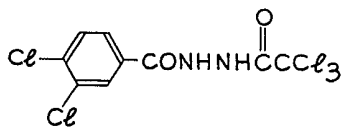


where n is 1 or 2.

Suitable reaction conditions are agitation of the reactants in an inert solvent such as alcohol at elevated temperature.

Certain novel derivatives of the above general formula are listed in the following Table I.

TABLE I

Compound No.	Structural Formula	Chemical Name	M.P.	Yield
1		N-trichloroacetyl-N′-2-chlorobenzoylhydrazine	168–170°C	57%
2		N-trichloroacetyl-N′-3-chlorobenzoylhydrazine	143–144°C	76%
3		N-trichloroacetyl-N′-4-chlorobenzoylhydrazine	165–166°C	70%
4		N-trichloroacetyl-N′-2,4-dichlorobenzoylhydrazine	149–150°C	80%
5		N-trichloroacetyl-N′-2,5-dichlorobenzoylhydrazine	127–130°C	51%
6		N-trichloroacetyl-N′-3,4-dichlorobenzoylhydrazine	183–185°C	50%

The following Examples are given to illustrate the preparation of the novel compounds and their use as fungicides. In the Examples, the number of the compound refers to the numbering in Table I.

EXAMPLE 1.

Preparation of N-trichloroacetyl-N'-3-chlorobenzoylhydrazine (Compound No. 2)

29.7 g (0.16 mol) of 3-chlorobenzoic ethyl ester and 8.9 g (0.18 mol) of 100%-hydrazine hydrate in 30 ml of ethanol were refluxed for 3 hours with agitation. After cooling the white crystals so formed were filtered and washed with ethyl ether. In this way, 13.0 g of 3-chlorobenzoic acid hydrazine were obtained as white crystals. m.p.: 156—158°C. Yield: 48%.

3.4 g (0.02 mol) of the hydrazide obtained above were suspended in benzene (100 mol) and added to 2.0 g (0.02 mol) of triethylamine and 3.7 g (0.02 mol) of trichloroacetylchloride were added dropwise to the resulting mixture. The reaction mixture was then agitated at room temperature for 5.5 hours. The resulting sedimented crystals were filtered and washed thoroughly with fresh water. The washed product was recrystallized from benzene to provide 4.8 g of N-trichloroacetyl-N'-3-chlorobenzoylhydrazine as white crystals. m.p.: 143—144°C. Yield: 76%.

EXAMPLE 2.

Preparation of N-trichloroacetyl-N'-4-chlorobenzoyl-hydrazine (Compound No. 3)

22 g (0.12 mol) of 4-chlorobenzoic ethyl ester and 6.0 g (0.12 mol) of 100%-hydrazine hydrate were added to 25 mls of ethanol, and the reaction mixture was refluxed for 4.5 hours. After cooling, the sedimented white crystals were added to ethyl ether and thoroughly agitated, pulverized and filtered. The product was then agitated with addition of further ethyl ether, to provide 8.7 g of 4-chlorobenzoic hydrazide as white crystals. m.p.:162—164°C. Yield: 43%.

3.4 g (0.02 mol) of the hydrazide were then suspended in 100 mls of benzene, and added to 2.0 g (0.02 mol) of triethylamine and 3.7 g (0.02 mol) of trichloroacetylchloride were added dropwise to the resulting mixture. The reaction mixture was then agitated for 2.5 hours and the sedimented crystals were filtered and thoroughly washed with fresh water to provide 4.4 g of N-trichloroacetyl-N'-4-chlorobenzoylhydrazide as white crystals. m.p.: 165—166°C. Yield: 70%.

EXAMPLE 3.

Preparation of N-trichloroacetyl-3,4-dichlorobenzoylhydrazine (Compound No. 6)

17.5 g (0.08 mol) of 3,4-dichlorobenzoic ethyl ester and 4.3 g (0.086 mol) of 100%-hydrazine hydrate in 30 mls of ethanol were refluxed for 6.5 hours. After cooling, the sedimented white crystals were added with ethyl ether and the reaction mixture was thoroughly agitated and pulverized. The resulting product was filtered and thoroughly washed with ethyl ether to provide 9.3 g of 3,4-dichlorobenzoic hydrazide as white crystals. m.p.: 168—170°C. Yield: 57%.

The hydrazide so obtained, 4 g (0.02 mol), was suspended in 150 ml of benzene and added to 2.0 g (0.02 mol) of triethylamine and 3.7 g (0.02 mol) of trichloroacetylchloride was added dropwise to the resulting mixture. The reaction mixture was then agitated at room temperature for 7 hours and the sedimented crystals were filtered and thoroughly washed with fresh water to provide 3.5 g of N-trichloroacetyl-N'-3,4-dichlorobenzoic hydrazine as white crystals. m.p.: 183—185°C. Yield: 50%.

The N-trichloroacetyl-N'-chlorobenzoyl -hydrazine derivatives according to this invention show a pronounced fungicidal effect towards various plant disease fungi, especially those of rice blast, tomato late blight and cucumber downy mildew.

Since these novel products contain no heavy metal atoms, which are very harmful to human health, but also have no adverse effect on cultured plants, the fungicidal compositions of the invention are highly effective and advantageous for use in the control of various fungal plant diseases.

It is possible to use one or more of the aforementioned novel compounds as the effective fungicidal ingredient in the compositions according to the invention. The fungicidal compounds may be applied to the plants in an undiluted state or in a suitable diluent or carrier, including water, organic solvents, liquid dispersants or solid carrier to form powders, granules, emulsion suspensions or solutions.

The fungicidal compounds may be used per se, or in combination with conventional additives and/or auxiliary agents such as wet extenders, emulsifying

solvents and adhesives for enhancing the fungicidal action.

It has been further found that any other horticultural and agricultural remedies and/or fertilizers may be used in combination with the above novel fungicidal compounds without inviting decomposition or deterioration of the former. These substances used in conjunction with the fungicidal compounds of the invention may be other fungicides or insecticides. For this purpose, a mixture of these substances may be applied to the plants or they may be employed concurrently.

The following Examples illustrate the preparation of fungicidal compositions and their use for treatment of plants and control of fungal diseases.

EXAMPLE 4.

Application in the form of powder

Active Compound

N-trichloroacetyl-N'-2-chlorobenzoylhydrazine (Compound No. 1) m.p.: 168—170°C.

Agricultural Fungicidal composition

Formulation:

compound no. 1	3 wt. parts
clay	40 wt. parts
talc	57 wt. parts

These components are mixed together and pulverized to provide a fine powder which may be dispensed by means of a puffer.

EXAMPLE 5.

Application in the form of an aqueous suspension

Active Compound

N-trichloroacetyl-N'-4-chlorobenzoylhydrazine (Compound No. 3) m.p.: 165—166°C.

Agricultural fungicidal composition

Formulation:

compound no. 3	50 wt. parts
polyoxyethylene alkylaryl ether	6 wt. parts
kieselguhr	44 wt. parts

These components are mixed together and pulverized and used in the form of an aqueous suspension by addition with an appropriate amount of water to give a desired final concentration of the active ingredient.

EXAMPLE 6.

Pot Tests for Control of Rice Blast

A large number of porous porcelain pots, each having a diameter of 10 cm, were cultured with "Japonica" — waterfield rice plants of *Oryza sativa* L, "variety: SASANISHIKI" to the four leaf stage. Each pot was planted with twenty stems of the rice plant. Three pots consisted of a treating area. These plants were thoroughly treated with the wettable powder set forth in Example 5, diluted with a sufficient amount of water to provide an aqueous suspension of the desired concentration. The suspension was applied onto the plants by means of a liquid spray so as to thoroughly soak all the leaves. After drying, the leaves were inoculated with spores of rice blast fungi, Piricularia oryzae, by spraying an aqueous suspension thereof. Then the treated pots were placed in an atmosphere of high humidity at 27—28°C for four days.

The uppermost leaves of rice plant stems per three pots were carefully examined and the observed number of lesions were counted. An equal number of untreated pots were inoculated with the same rice blast fungi to serve as a control. The number of lesions were counted, and the control rate was found by the following formula.

$$\text{Control rate, } \% = \left(1 - \frac{\text{number of lesions on treated leaves}}{\text{number of lesions on untreated leaves}}\right) \times 100$$

The procedure was repeated except that suspensions were prepared in accordance with Example 5 using each of the other compounds listed in Table 1. The results thus determined are shown in Table II below:

TABLE II

Compound used	Concentration (ppm)	Number of infected leaf spots	Infection Suppression Rate (%)
No. 1	500	177	77.6
No. 2	500	15	98.1
No. 3	500	28	96.5
No. 4	500	126	84.0
No. 5	500	0	100
No. 6	500	0	100
non-treated (Control)	–	789	–

The Compound Numbers in the above Table II are same as those set forth in the foregoing Table I.

EXAMPLE 7.

Pot test for control of downy mildew on cucumber plants

A number of pots of 10 cm diameter, were used for the culture of cucumber plants to the two leaf stage, variety: SAGAMI hampaku. Each plant was planted in a pot. Each group of three pots was used as one treating area. These plants were treated with an aqueous suspension of the wettable powder of Example 5, which had been diluted with water. The application was made by means of a liquid spray. After drying, all the leaves were inoculated with spores of downy mildew fungi, Pseudoperonospora cubensis, by spraying. Then, the plants were kept in an atmosphere of high humidity at 22—23°C for 24 hours and then in a greenhouse for 5 days. After the elapse of 5 days after the inoculation, the degree of infection was determined in accordance with the following classification, as per one leaf per pot and per three pots for each treating area. The procedure was repeated using similar suspensions containing the other compounds listed in Table 1.

Classification

Index of infection	*State of infection*
"0"	no infection
"0.5"	less than 10% infection in terms of inoculated leaf area.
"1"	10—20% infection in terms of inoculated leaf area.
"2"	20—40% infection in terms of inoculated leaf area.
"3"	40—60% infection in terms of inoculated leaf area.
"4"	60—80% infection in terms of inoculated leaf area.
"5"	over 80% infection in terms of inoculated leaf area.

The test results are shown in Table III below.

TABLE III

Compound used	Concentration (ppm)	Mean Index of Infection	Chemical Harmful Effect
No. 1	500	2	none
No. 2	500	0.5	none
No. 3	500	0.5	none
No. 4	500	0.5	none
No. 5	500	2	none
No. 6	500	0	none
non-treated (Control)	—	5	—

The Compounds Numbers shown above are the same as those set forth in Table 1.

EXAMPLE 8.

Pot test for the control of late blight on tomato plants

A number of pots, each being of 10 cm diameter as before, were planted each with a tomato plant at its four leaf stage, the variety being FUKUJU No. 2. Each group of three pots formed one treating area. The cultured plants were sprayed with an aqueous suspension of the wettable powder as set forth in Example 5. After drying, an aqueous suspension of spores of tomato late blight fungi, Phytophthora infestans, preparatorily cultured on potato tubers were sprayed over the above treated tomato leaves. The thus-conditioned plants were kept in a greenhouse at 20—22°C for two days. After the lapse of four days after the said inoculation, the index of infection was determined in accordance with the foregoing classification, so as to estimate the respective mean index of infection per plant. The procedure was repeated using similar fungicidal suspensions containing as the active ingredient the other compounds listed in Table 1. The test results are shown in the following Table IV.

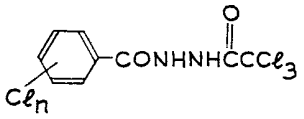
TABLE IV

Compound used	Concentration (ppm)	Mean Index of Infection	Chemical Harmful Effect
No. 1	500	2	none
No. 2	500	0	none
No. 3	500	0.5	none
No. 4	500	0.3	none
No. 5	500	1	none
No. 6	500	0	none
non-treated	—	5	—

The Compound Numbers shown above are the same as those set forth in Table I above.

WHAT WE CLAIM IS:—

1. N-trichloroacetyl-N'-chlorobenzoylhydrazine derivatives having the general formula:



where n represents an integer of 1 or 2.

2. A fungicidal composition which contains as the active ingredient a N-trichloroacetyl-N'-chlorobenzoylhydrazine derivative having the general formula set forth in claim 1 in a fungicidally effective amount.

3. A composition as claimed in claim 2, wherein the active ingredient is N-trichloroacetyl-N'-3,4-dichlorobenzoylhydrazine.

4. A process for the manufacture of a N-trichloroacetyl-N'-chlorobenzoylhydrazine having the general formula set forth in claim 1 which comprises reacting the corresponding chlorobenzoylhydrazide with trichloroacetylchloride in the presence of triethylamine.

5. A process as claimed in claim 4, in which the chlorobenzoylhydrazide is prepared by reacting the corresponding chloro-substituted benzoic acid ester with hydrazine hydrate.

6. A process for the manufacture of N-trichloroacetyl-N'-chlorobenzoylhydrazines substantially as described with reference to Examples 1 to 3.

7. A fungicidal composition substantially as described with reference to Examples 4 and 5.

8. A method of combatting fungal diseases in plants which comprises applying to the foliage a composition as claimed in claim 2, 3 or 7.

9. A method of combatting fungal diseases in plants substantially as described with reference to Examples 6 to 8.

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