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CERTAIN THIOZOLYLUREA COMPOUNDS

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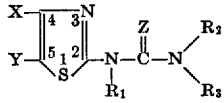
Int. Cl. C07d *91/34*

U.S. Cl. 260—306.8 R 5 Claims

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

ABSTRACT OF THE DISCLOSURE

A thiazole derivative having the general formula

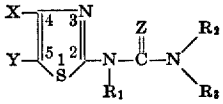


and pesticidal compositions containing the same.

This invention relates to a new family of compounds which are derivatives of thiazole and it relates also to the use of the thiazole derivatives as pesticides and especially as herbicides.

It is an object of this invention to produce and to provide a method for producing thiazole derivatives of the type described and the use of such thiazole derivatives as a pesticide and/or a herbicide.

The thiazole derivatives embodying features of this invention may be characterized by the formula



in which X and Y are groups which may be identical one with the other or different from each other, X and Y are repersentative of such groups as hydrogen, halogen such as chlorine, bromine, iodine, thiocyanate, —CN, —COOH, an alkoxycarbonyl group, —NH_2, —OH, a hydroxyalkyl, alkyl or alkoxy group containing from 1 to 4 carbon atoms such as methyl, ethyl, propyl, butyl, ethoxy, methoxy and the like in which the hydroxyalkyl, alkyl or alkoxy group can be unsubstituted or substituted with a halogen, an aryl group such as phenyl, naphthyl, a halogenated aryl group, an alkaryl group such as benzyl, tolyl and the like, an alkoxy aryl group, a halogenated alkaryl group, a halogenated alkoxyaryl group, an aryloxy group, a halogenated aryloxy group and an alkaryloxy group; in which Z is an atom selected from the group consisting or oxygen and sulphur; in which R_1 is a group such as hydrogen or an alkyl, alkynyl, alkoxy, alkenyl or alkenoxy group having from 1 to 4 carbon atoms, an alkylated acyl residue, a halogenated alkylated acyl residue, an aracyl, a halogenated aracyl (arylated acyl), an alkarylated acyl, or an alkoxy-aryl group; in which R_2 and R_3 is a group selected from hydrogen, an alkyl group, an alkoxy group, an alkenyl group, an alkenoxy group or an alkynyl group in which the groups contain from 1 to 4 carbon atoms, an alkaryl residue, a halogenated alkaryl residue, an aryl group, a halogenated aryl group or an aryloxy group but in which R_2 and R_3 are not both hydrogen in the same compound.

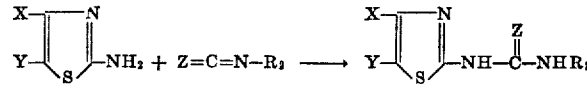
The compounds defined above, which fall within the scope of the invention, may be prepared by a number of

synthetic methods depending somewhat upon the nature of the groups R_1, R_2 and R_3.

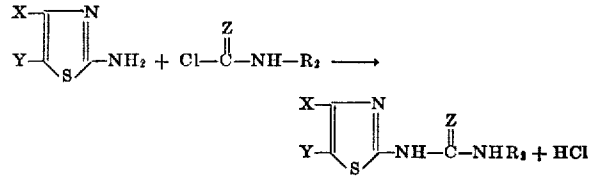
The following will set forth typical examples of methods for the preparation of such compounds:

(1) When two of the three radicals R_1, R_2 and R_3 are hydrogen, for example when R_1 and R_3 are hydrogen while R_2 is alky group, aryl group, or alkaryl group, a halogenated alkaryl group or a halogenated aryl group, two methods of preparation can be employed:

(a) The reaction of an alkyl or aryl isocyanate or isothiocyanate with a 2-aminothiazole in which X and Y are substituted groups, as illustrated in the following equation:

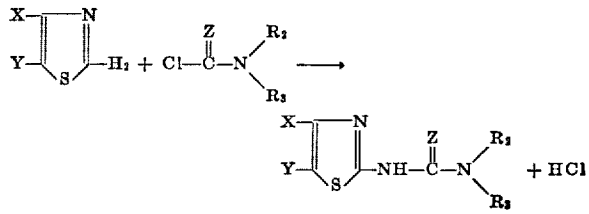


(b) The reaction of a monosubstituted carbamyl or thiacarbamyl halide, in which the halogen is preferably chlorine, with a 2-aminothiazole in the presence of an agent which binds the acid liberated during the reaction, in accordance with the equation:



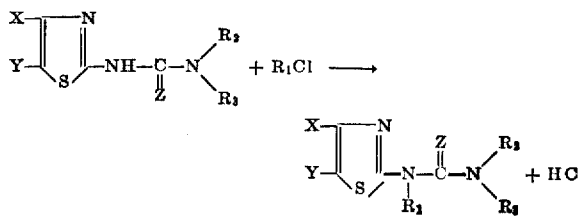
(2) When ony one of the three radicals R_1, R_2 and R_3 is hydrogen, such as when R_1 is hydrogen and R_2 and R_3 represent one of the groups of alkyl, aryl, alkaryl, halogenated alkaryl or halogenated aryl groups, the following process may be employed for the preparation.

A carbamyl or thiacarbamyl halide, preferably the chloride, in which R_2 and R_3 have the meaning given above, is reacted with a suitably substituted 2-aminothiazole in the presence of an agent that takes up the acid liberated according to the equation:



(3) When R_1 is one of the groups selected from an alkylated acyl, halogenated alkylated acyl, arylacyl, halogenated arylacyl, alkylated arylacyl and alkoxylated arylacyl and when R_2 and R_3 are selected from one or more of the groups of hydrogen, alkyl, aryl, alkaryl, halogenated aryl or halogenated alkaryl except that R_2 and R_3 cannot both be hydrogen in the same compound, the following may be employed:

The halide of an aliphatic or aromatic acid, preferably the chloride, R_1Cl, is reacted with thiazolyl or the thiazolyl-thiourea derivative prepared in accordance with method (1) or (2), as illustrated by the following equation:



In the reaction outlined above, in which an acid is formed with an active hydrogen atom, it is preferred to carry out the reactions in the presence of an acid acceptor like a tertiary amine such as triethylamine, dimethylaniline or pyridine.

The derivatives of thiazolylurea or thiazolylthiourea are generally solids which are readily soluble in organic solvents such as dimethyl sulfoxide (DMSO), dimethylformamide, pyridine, tetrahydrofuran and CH_3CN.

The following compounds are given by way of illustration, but not by way of limitation, of the formulations representing compounds of this invention:

N-(2-thiazolyl)-N'-methylurea;
N-(2-thiazolyl)-N',N'-dimethylurea;
N-(2-thiazolyl)-N'-methyl-N'-methoxyurea;
N-(2-thiazolyl)-N'-phenylurea;
N-(2-thiazolyl)-N'-methyl-N'-propenylurea;
N-(2-thiazolyl)-N'-benzoyl-N',N'-dimethylurea;
N-(2-thiazolyl)-N-methyl-N'-phenoxyurea;
N-(2-thiazolyl)-N-butenyl-N'-ethylurea;
N-(2-thiazolyl)-N-trichloroacetyl-N'-butylurea;
N-2(5-chlorothiazolyl)-N',N'-dimethylurea;
N-2(5-chlorothiazolyl)-N'-methylurea;
N-2(5-chlorothiazolyl)-N'-methylthiourea;
N-2(5-chloro-4-methylthiazolyl)-N'-phenylurea;
N-2(5-chloro-4-methylthiazolyl)-N'-methylurea;
N-2(5-chloro-4-methylthiazolyl)-N',N'-dimethylurea;
N-2(4,5-dichlorothiazolyl)-N'-methylurea;
N-(2(4,5-dichlorothiazolyl)-N,N'-dimethylurea;
N-2(4-trifluoromethylthiazolyl)-N'-methyl-N'-methoxyurea;
N-2(4-trifluoromethylthiazolyl)-N'-methylurea;
N-2[4(2-chloro-ethyl)thiazolyl]N'-ethylurea;
N-2(5-bromothiazolyl)-N'-butynylurea;
N-2(4-chlorothiazolyl)-N'-methylurea;
N-2(4-chlorothiazolyl)-N',N'-dimethylurea;
N-2(4-chlorothiazolyl)-N-monochloroacetyl-N'-methyl-N'-phenylurea;
N-2(4-chloromethylthiazolyl)-N',N'-dimethylurea;
N-2(4-chloromethylthiazolyl)-N'-methylurea;
N-2(5-thiocyanatothiazolyl)-N'-methylurea;
N-2(4-phenyl-5-thiocyanatothiazolyl)-N'-propenylurea;
N-2(5-carbethoxy-4-methylthiazolyl)-N'-methylurea;
N-2(4-2-hydroxyethylthiazolyl)-N'-(2,4-dichlorophenoxy)urea;
N-2(4-methylthiazolyl)-N'-methylurea;
N-2(4-methylthiazolyl)-N',N'-dimethylurea;
N-2(4-methylthiazolyl)-N'-phenylurea;
N-2(5-methylthiazolyl)-N'-methylurea;
N-2(5-methylthiazolyl)-N',N'-dimethylurea;
N-2(4-methylthiazolyl)-N'-methyl-N'-methoxyurea;
N-2(4,5-dimethylthiazolyl)-N'-methylurea;
N-2(4,5-dimethylthiazolyl)-N',N'-dimethylurea;
N-2(4-methoxy-5-chlorothiazolyl)-N-acetyl-N'-propenylurea;
N-2(4-p-chlorophenylthiazolyl)-N-methyl-N',N'-dimethylurea;
N-2(4-p-chlorophenylthiazolyl)-N'-methylurea;
N-2(4-p-methoxyphenylthiazolyl)-N'-tolylurea.

The compounds described have been found to have exceptional herbicidal properties. For this purpose, they find widespread application for inhibiting the growth or even destroying of all kinds of plants, pests, such as weeds, brushwood and undesirable shrubbery.

The amount of the compound required to achieve the desired herbicidal effect will depend upon a number of factors such as the nature of the compound itself, the resistance of the species of plants, the composition of the ground, the state of growth of the plant at the time that treatment is effected, that is, a complete kill or only a selective kill.

The compounds may thus be employed as a total herbicide or as a selective herbicide or as a growth regulator. There is a wide range of possible applications depending upon the chemical nature and dosage of the herbicidal compound utilized. The compounds may be applied either prior to the seeding or planting of the cultures or application can be made as a preemergence treatment after seeding but before the cultures or weeds break through the ground or as a post-emergence treatment after the plants break through the ground. In general, the compounds may be applied at any stage of plant growth best adapted to the problem to be solved and the nature of the cultivated plants.

In practice, the substituted thiazolylureas or thiazolylthioureas of the present invention are utilized in amounts within the range of 0.1 to 30 kilograms per hectare and preferably within the range of 0.5 to 20 kilograms per hectare. The optimum dosage will depend upon the intended aim, the type of application, the nature of the plant pests intended to be destroyed and their stage of growth and upon the persistence of the desired herbicidal action.

An interesting property of certain of the thiazolylureas and thiazolylthioureas of this invention resides in the persistence of their herbicidal action. Compounds of the type described, when suitably formulated, remain effective to prevent weed growth from several weeks to several months. This effectiveness over a long period of time is a very desirable feature of the compounds of this invention since weed control can be maintained throughout the growing season.

Another surprising property of the compounds of this invention is the highly specific character of their action on vegetation. When applied in proper dosages, the compounds are effective to destroy certain weeds which are dicotyledoneae without damaging other cultivated species of dicotyledoneae. Weed plants belonging to the graminaceae family may be destroyed in cereal cultures like wheat, barley, oats and Indian corn, without harming such cultures. The thiazolylureas and thioureas of this invention may be employed alone or in mixtures such as solutions in organic solvents, or as dispersions or emulsions of the oil-in-water or water-in-oil types or as suspensions in aqueous medium. They may be formulated into pastes or mixed with powders for dusting or they may be applied as granules in mixtures containing talcum, kaolin, or other suitable filler.

Such solutions, dispersions, pastes, powders or granules may be formulated to contain different proportions of the active component depending upon the intended use. As previously described, such compositions may be formulated to contain the active ingredient in an amount within the range of 0.5 to 80 percent by weight of the composition.

The compounds of this invention may also be mixed with other additives which are also active or toxic with respect to plants. Certain of these additives may be in the form of solids, as represented by sodium chlorate or the borates or in the form of liquids such as tar oil derivatives (creosotes), substituted or unsubstituted phenols, crude oil derivatives such as kerosene, gas oil, fuel oil and the like. The compounds may be formulated with other useful additives such as fertilizers which contain the usual elements of phosphorus, potassium and nitrogen (with or without trace elements such as Fe, Mn, Zn, Mg, Co and Cu.

In accordance with an important feature of this invention, the thiazolylureas or thioureas may be combined to give a synergistic reaction with other known pesticides in the form of fungicides, bactericides, insecticides and herbicidies to increase the biological activity. It is possible to formulate the treating composition to contain one or more of the pesticides described having different chemical structures and biological activities and which may be selected from the group consisting of nitrophenols, chlorophenols, chloronitrophenols, halogenated aryloxyalkylcarboxylic acids, phenylalkylcarboxylic acids, halogenated benzoic acids and derivatives thereof such as the

corresponding salts, esters amines amides and imides, halogenated carbamates, substituted thiocarbamates and thiolocarbamates, esters of dithiocarbamic acid, alkyl isothiocyanates, mono-or disubstituted amides; di-, tri-, or tetrasubstituted aralkyl ureas, substituted triazines, aminotriazole, substituted benzothiazole, hydrazides, uracil derivatives, pyridinium salts, quaternary ammonium salts, inorganic herbicides such as bichromates, alkali metal cyanates, Na_2AsO_3, $NH_2SO_3NH_4$, etc., as represented by the following specific compounds: pentachlorophenol; dinitrocresol; dinitrobutyl phenol; Na 2,4 - dichlorophenoxyacetate; Na2,3,6-trichlorobenzoate; Na monochloro- or trichloroacetate; isopropyl N-phenylcarbamate; ethyl N,N-dipropylthiolocarbamate; N,N-dimethyldiphenylacetamide; N-phenyl-N',N'-dlimethylurea; 2-chloro-2,6-bis-(ethylamino)-s-tria-zine; 3-amino-1,2,4-triazole; 2,6-dichlorobenzonitrile, maleic hydrazide; 2-chlorobenzothiazole; 1,1'-ethylene dibromide; 2,2'-bipyridinium; methyl isothiocyanate.

In accordance with another feature of the invention, modifications can be made of the various formulations to include one or more surface active agents of the anionic, cationic or nonionic types, as represented by: Na alkylnaphthalenesulfonate, Na cetyl sulfate, Na oleyl sulfate, Na lauryl sulfate, Na N-methyl-N-oleyltaurate, Na oleyl isothionate, Na ligninsulfonate, Na dodecylbenzenesulfonate, alkanolamides of fatty acids, Na di(2-ethylhexyl)sulfosuccinate, sulfonated monoglycerides from coconut oils, alkyltrimethylammonium chlorides, alkylbenzyldimethylammonium chloride, cetyltrimethylammonium bromide, the methoxysulfonate of oleyldiethylmethylethylenediamine; lauryl polyethylene glycol ether; ethers from polyoxyethylene and alkylphenols, polyethylene glycol stearate, polypropylene glycol stearate, condensation products of polypropylene glycol and ethylene oxide, esters of polyethylene glycol and of tall oil acids, sorbitol monopalmitate, sorbitol monooleate, tris(polyoxyethylene)sorbitol monolaurate, tris(polyoxyethylene)-sorbitol monooleate; the condensation product of n-dodecyl mercaptan with ethylene oxide.

The following examples of the preparation and use of the compounds of this invention are given by way of illustration, but not by way of limitation:

EXAMPLE 1

Preparation of N-2(5-chlorothiazolyl)-N'-methylurea

To a thoroughly agitated solution of 9.5 grams of 2-amino-5-chlorothiazole in 35 ml. dimethyl sulfoxide (DMSO), 4.8 grams methyl isocyanate is added dropwise with an accompanying rise in temperature to about 56° C. When the addition is finished, the mixture is cooled to 45° C. and maintained at this temperature for about 1 hour by the addition of heat, if necessary. The solvent is distilled off in vacuum and the reside is taken up in 500 ml. of boiling acetone in the presence of vegetable charcoal. The warm solution is filtered and white shiny crystals are formed in the filtrate upon cooling.

The dried crystals have a melting point of 271–271.5° C. The yield of the compound is about 50 percent by weight calculated on the basis of the starting amine. The following is an analysis in percent by weight of the compound produced in accordance with this example as compared to the theoretical compound calculated for

$C_5H_6ClN_3OS$

Compound of Example 1 (percent): C, 31.83; H, 3.19; Cl, 18.39; S, 16.70. Calculated (percent): C, 31.33; H, 3.15; Cl, 18.50; S, 16.73.

EXAMPLE 2

Preparation of N-2(5-chloro-4-methylthiazolyl)-N'-phenylurea

5 grams of 2-amino-5-chloro-4-methylthiazole is dissolved in 50 ml. of CH_3CN. 4.1 grams of phenyl isocyanate is added dropwise at room temperature with an accompanying rise in temperature to 50° C. This temperature is maintained for 2 hours, the mixture is cooled and the precipitate is collected and dried. It is purified by recrystallization from CH_3CN and decolorized in the presence of vegetable charcoal. 6.75 grams of N-2(5-chloro-4-methylthiazolyl)-N'-phenylurea is obtained in the form of a white powder having a melting point of 252° C., providing a yield of about 75 percent by weight. The compound is given the empirical formula of

$C_{11}H_{10}ClN_3OS$

Compound of Example 2 (percent): C, 49.34; H, 3.76; N, 15.70; Cl, 13.25. Calculated (percent): C, 49.46; H, 3.62; N, 15.90; Cl, 13.29.

EXAMPLE 3

Preparation of N-2(5-methylthiazolyl)-N'-phenylurea

To a suspension of 7 grams of 2-amino-5-methylthiazole in 50 ml. of CH_3CN 7.7 grams of phenyl isocyanate is added slowly with an accompanying temperature rise to about 48° C. The amine becomes dissolved during the course of the addition and the solution is maintained at 48° C. for about 20 minutes. In the course of the reaction, an insoluble product is produced until finally the whole mixture stiffens. The mixture is allowed to remain for about 4 hours after which the crystals are separated and dried and washed with CH_3CN and again dried in vacuum. 12.45 grams of N-2(5-methylthiazolyl)-N'-phenylurea is secured in the form of a white crystalline powder having a melting point of 195–196° C. corresponding to a yield of about 87 percent by weight.

EXAMPLE 4

Preparation of N-2-thiazolyl-N'-phenylurea

The procedure corresponds to that of Example 3 except that 2-aminothiazole is employed instead of the 2-amino-5-methylthiazole. The product N-2-thiazolyl-N'-phenylurea is obtained in the form of a fine white powder having a melting point of about 171° C. which melting point is raised to 173° C. after recrystallization from CH_3COOH of 50% strength. The yield of crude product corresponds to about 96%. The following is the analysis of the compound as compared to the empirical formula $C_{19}H_9N_3OS$:

Compound of Example 4 (percent): C, 54.78; H, 4.14; N, 19.16; S, 14.62. Calculated (percent): C, 54.77; H, 3.91; N, 19.23; S, 14.48.

EXAMPLE 5

Preparation of N-2-thiazolyl-N'-methylurea

To a suspension of 10 grams of 2-aminothiazole in 25 ml. of CH_3CN, containing two drops of triethylamine, 6 grams of methyl isocyanate is slowly added by pouring. The reaction is slightly exothermic and the temperature rises to about 66° C. At the end of the addition, the mixture is cooled to 50° C. and maintained at this temperature for 1¼ hours. The N-2-thiazolyl-N'-methylurea separates in the form of a white crystalline precipitate which is air dried and then dried in vacuum. The yield of crude product, having a melting point of 215° C., is 15.45 grams or about 78%. After recrystallization in absolute alcohol at −30° C., the melting point is raised to 218° C. A final product in the form of shiny white needles is obtained in an overall yield of 94%. The following is the analysis of the compound N-2-thiazolyl-N'-methylurea produced in accordance with this example as compared to the empirical formula $C_5H_7N_3OS$:

Compound of Example 5 (percent): C, 38.20; H, 4.49; N, 28.73; O, 10.18; S, 20.40. Calculated (percent): C, 37.77; H, 4.35; N, 28.84; O, 10.52; S, 20.90.

EXAMPLE 6

Preparation of N-2-(5-thiocyanato)thiazolyl-N'-methylurea

580 ml. of CH_3CN is warmed to 80° C. and 33.6 grams of 2-amino-5-thiocyanatothiazole is dissolved therein. 17.1 grams of methyl isocyanate is added with constant stirring and the stirring is continued while the mixture is maintained at 80° C. for 8 hours.

Upon cooling, the substituted urea precipitates in the form of a fine, slightly pinkish powder which is filtered and dried. The crude N-2-(5-thiocyanato)thiazolyl-N'-methylurea has a melting point of 225° C. and is secured in the amount of 38.9 grams or about 86.5% yield. Recrystallization in methanol yields a final product in the form of small shiny flakes having a yellow coloration and a melting point of 226° C.

The results of the elemental analysis of the compound as compared to the empirical formula $C_6H_6N_4OS_2$ is set forth in the following table:

Compound of Example 6 (percent): C, 33.63; H, 2.82; N, 26.15; S, 29.92. Calculated (percent): C, 33.42; H, 2.74; N, 25.96; S, 29.90.

EXAMPLE 7

Preparation of N-2-(5-carbethoxy-4-methylthiazolyl)-N'-methylurea

By proceeding in accordance with Example 1 but using as the reagents methyl isocyanate and 2-amino-4-methyl-5-carbethoxy-thiazole, the above compound is obtained having a melting point of 262° C. after recrystallization from absolute ethyl alcohol, corresponding to a yield of about 75.5%. The analysis of the compound produced furnished the following values compared to the empirical formula $C_9H_{13}N_3O_3S$:

Compound of Example 7 (percent): C, 44.43; H, 5.38; N, 17.27; O, 19.72; S, 13.17. Calculated (percent): C, 44.03; H, 4.83; N, 17.44; O, 19.92; S, 13.50.

EXAMPLE 8

Preparation of N-2(4-methylthiazolyl)-N'-methylurea

The procedure of Example 5 is followed but in which the reagents are methyl isocyanate and 2-amino-4-methylthiazole. The above compound is obtained in a yield of 93% having a melting point of 212° C. after recrystallization from CH_3CN.

The results of the analysis of the compound produced by the example as compared to the empirical formula $C_6H_9N_3OS$ is as follows:

Compound of Example 8 (percent): C, 42.09; H, 5.30; N, 24.54; O, 9.34; S, 18.73. Calculated (percent): C, 41,81; H, 5.08; N, 24.83; O, 9.32; S, 18.67.

EXAMPLE 9

Preparation of N-2(4-trifluoromethylthiazolyl)-N'-methylurea

The procedure is in accordance with Example 6 but in which the reagents are methyl isocyanate and 2-amino-4-trifluoromethylthiazole. The product identified above has a melting point of 254° C. after recrystallization from isopropanol and is obtained in a yield of about 57%.

The analysis of the compound produced by this example as compared to the emipircal formula $C_6H_6F_3N_3OS$ is set forth in the following table:

Compound of Example 9 (percent): C, 32.00; H, 2.69; N, 18.66; F, 25.31; S, 14.24. Calculated (percent): C, 32.23; H, 2.88; N, 18.76; F, 25.20; S, 14.45.

EXAMPLE 10

Preparation of N-2(4-p-chlorophenylthiazolyl)-N'-methylurea

The procedure is in accordance with Example 5 but the reagents employed are methyl isocyanate and 2-amino-4-(p-chlorophenylthiazole). A yield of 97% is obtained of the compound N-2(4-p-chlorophenylthiazolyl)-N'-methylurea, having a melting point of 232.5° C. after recrystallization from acetonitrile.

The analysis of the compound produced as compared to the empirical formula $C_{11}H_{10}ClN_3OS$ is as follows:

Compound of Example 10 (percent): C, 49.34; H, 3.76; Cl, 13.24; N, 15.69; S, 11.97. Calculated (percent): C, 49.16; H, 3.64; Cl, 13.30; N, 15.52; S, 11.96.

EXAMPLE 11

Preparation of N-2(5-chloro-4-methylthiazolyl)-N'-methylurea

A mixture of 6.1 grams of 2-amino-5-chloro-4-methyl-thiazole chlorohydrate and 25 ml. pyridine is heated to 35–40° C. 2.1 grams of methyl isocyanate is added over a period of 15 minutes. The mixture is heated with stirring for 3 hours to 50° C. and it is then cooled and rapidly poured over 500 grams of ice. The precipitate formed is filtered and recrystallized from CH_3CN. A yield of 75% is obtained of the compound N-2(5-chloro-4-methylthiazolyl-N' - methylurea in the form of a white powder having melting point of 237° C.

The analysis of the compound as compared to the empirical formula $C_6H_8ClN_3OS$ is as follows:

Compound of Example 11 (percent): C, 35.04; H, 3.92; N, 20.43; Cl, 17.24; S, 15.59. Calculated (percent): C, 35.06; H, 3.70; N, 20.23; Cl, 17.09; S, 15.64.

EXAMPLE 12

Preparation of N-2(5-chlorothiazolyl)-N'-methylthiourea

1.5 grams of methyl isothiocyanate and 2.7 grams of 2-amino-5-chlorothiazole are dissolved in 42 grams pyridine. The solution is heated for 5 hours under reflux and then it is cooled and poured into an excess of water.

The formed precipitate is filtered, thoroughly washed with water and dried. The N-2(5-chlorothiazolyl)-N'-methylthiourea that is obtained is recrystallized from acetone in the presence of vegetable charcoal to produce the compound which melts at 199° C.

The following is an analysis of the compound as compared to the empirical formula $C_5H_6ClN_3S_2$:

Compound of Example 12 (percent): C, 28.91; H, 2.91; N, 20.23; Cl, 17.06; S, 30.87. Calculated (percent): C, 29.56; H, 3.0; N, 20.17; Cl, 16.59; S, 31.12.

EXAMPLE 13

Preparation of N-2(5-chloro - 4 - methylthiazolyl) - N', N'-dimethylurea

38.4 grams of pyridine is mixed with 22.7 grams dimethylcarbamyl chloride and cooled to 5° C. 29.7 grams of 2-amino-5-chloro-4-methylthiazole is added in small increments. The reaction is slightly exothermic so that the temperature rises to about 16° C. The materials are allowed to stand for 1 hour and then heated for 3 hours at 60° C. The mixture is then allowed to cool and poured into 1 liter of ice water with thorough stirring so as to prevent the formation of lumps. The product N-2(5-chloro-4 - methylthiazolyl)-N',N' - dimethylurea is separated by filtration and recrystallized from 1.5 liters of CH_3COOH of 50% strength. The crystals are washed with water until made neutral and the resulting compound obtained in a yield of 42.5% has a melting point of 163° C.

The analysis of the compound as compared to the empirical formula $C_7H_{10}ClN_3OS$ is as follows:

Compound of Example 13 (percent): C, 38.26; H, 4.59; Cl, 16.15; S, 14.59. Calculated (percent): C, 38.29; H, 4.22; Cl, 16.15; S, 14.59.

EXAMPLE 14

Preparation of N-2(4,5-dimethylthiazolyl)-N'-methylurea

By using the method of Example 5 but employing as reagents 2-amino-4,5-dimethylthiazole and methyl isocyanate, the compound N-2(4,5 - dimethylthiazolyl) - N'-methylurea is obtained in a yield of 84%, having a melting point of 184.5° C. after recrystallization from acetone.

The elemental analysis of the compound as compared to the empirical formula $C_7H_{11}N_3OS$ is as follows:

Compounds of Example 14 (percent): C, 45.38; H, 5.98; N, 22.67; O, 8.63. Calculated (percent): C, 45.33; H, 5.66; N, 22.97; O, 8.83.

EXAMPLES 15–20

Biological experiments and tests were conducted with various greenhouse plants using N-2(5-chlorothiazolyl-N'-methylurea in four different dosages, as set forth in the following tables. Two techniques of treatment were employed, as follows:

(a) the pre-emergence treatment, i.e. after seeding but before the plants break through the ground (see Tables 1 to 3);

(b) the post-emergence treatment, i.e. after the plants have broken through the soil, when each seed has developed into a young plant of between 5 and 15 cm. in height (see Tables 4 to 6).

The active product was formulated into an aqueous suspension from a wettable powder containing 20% by weight of the active compound and applied to the plants by atomization.

The results noted and the evaluations are set forth in the following tables as percent of destruction of the treated vegetation.

TABLE 1.—PRE-EMERGENCE TREATMENT OF SEVERAL PLANTS WHICH BELONG TO THE GRAMINACEAE AND WERE CULTIVATED IN A GREENHOUSE, THE RESULTS AND EVALUATIONS BEING MADE 37 DAYS AFTER TREATMENT

Species of treated plants	Doses in kg./hectare of active material			
	0.5	1	2	4
Barley (*Hordeum distichum*)	0	15	15	100
Indian corn (*Zea mays*)	0	[25] 15	20	80
Oats (*Arena sativa*)	0	20	100	100
Wheat (*Triticum vulgare*)	0	35	100	100
Wild oats (*Avena fatua*)	5	30	100	100
Wild millet (*Echinochloa crusgalli*)	5	65	98	98
Millet (*Panicum miliaceum*)	5	98	100	100
Rye-grass (*Lolium italicum*)	75	98	100	100
Slender Foxtail (*Alopecurus agrestis*)	90	100	100	100

TABLE 2.—PRE-EMERGENCE TREATMENT OF VARIOUS PLANTS WHICH ARE DICOTYLEDONEAE AND WERE CULTIVATED IN A GREENHOUSE, THE EVALUATIONS BEING MADE 37 DAYS AFTER TREATMENT

Species of plant treated	Doses of the active material in kg./hectare			
	0.5	1	2	4
Peas (*Pisum salivum*)	0	0	0	3
Tomatoes (*Solanum esculentum*)	0	0	0	95
Carrots (*Daucus carotta*)	15	100	100	100
Linseed (*linum usitalissimum*)	20	100	100	100
Buckwheat (*Polygonum fagopyrum*)	98	98	100	100
Amaranth (*Amaranthus species*)	98	100	100	100
Rape (*Brassica napus*)	100	100	100	100

In Table 3, the active product is applied in the form of a sludge containing 5% by weight of a wettable powder of N-2(5-chlorothiazolyl)-N'-methylurea.

TABLE 3

Plant species treated	Results after 10 days doses in kg./hectare of active material				Results after 30 days doses in kg./hectare of active material			
	10	15	20	30	10	15	20	30
Mustard, wild (*Sinapis arcensis*)	80	100	.....	100	100	100	100	100
Great nasturtium (*Tropaeolum majus*, variety Nanum)	0	0	.....	0	0	0	.....	0
Oats (*Avena sativa*)	40	75	.....	75	100	100	100	10

For the great nasturtium, as recognizable from this table, no destruction occurred, but a slight phytotoxicity was noted starting with the dosage of 10 kg./hectare of the active material.

Tables 1 to 3 show that N-2(5-chlorothiazolyl)-N'-methylurea has exceptional herbicide effect which can destroy species belonging both to the graminaceae as well as to the dicotyledoneae. Thus it is applicable against a wide- spectrum of plants. Furthermore, this herbicide enjoys exceptional efficiency because it is able to destroy up to 100% of such species as slender foxtail, rape and buckwheat when employed in dosages as low as 0.5 kg./hectare in the pre-emergence treatment. This compound also exhibits a selective herbicidal action due to an unexpected and remarkable fact. For example, when applied in the dosage of 0.5 kg./hectare, 90% of the foxtail is destroyed whereas the wheat remains undamaged. This herbicide shows a good selectivity with respect to peas and tomatoes in pre-emergence treatment, whereas, at the same dosage, other dicotyledoneae such as carrots, linseed and rape are completely destroyed. At dosages of 4 kg./hectare, all of the test plants with the exception of the peas and the great nasturtium, are practically destroyed. Of considerable interest is the fact that the compound can function as a total weed removal agent.

The following Tables 4 and 5 present the results of post-emergence treatments of various plants which are, respectively, graminaceae in Table 4 and dicotyledoneae in Table 5. The experiments were undertaken on greenhouse cultures with a wettable powder containing 20% of the active ingredient N-2(5-chlorothiazolyl)-N'-methylurea. The evaluations set forth in the tablet were made 34 days after treatment.

TABLE 4

Species of plant treated	Doses per hectare, in kg.of active material			
	0.5	1	2	4
Wheat	0	0	0	0
Barley	0	0	0	0
Wild oats	0	0	0	10
Oats	0	0	0	20
Indian corn	0	0	0	25
Rye grass	5	85	90	96
Slender foxtail	10	92	98	98
Wild millet	80	100	100	100

TABLE 5

Species of plant treated	Doses per hectare, in kg. of active material			
	0.5	1	2	4
Peas	0	0	0	0
Rape	0	0	0	5
Linseed	5	20	35	70
Carrots	5	40	80	98
Buckwheat	15	60	65	90

TABLE 6.—POST-EMERGENCE TREATMENT OF VARIOUS PLANTS WITH AQUEOUS DISPERSIONS CONTAINING 5% BY WEIGHT OF THE ACTIVE MATERIAL

	Doses per hectare in kg. of active material	Species of plant treated: Wild mustard	Great nasturtium	Oats
Results after 10 days	2.5	0	0	0
	5	0	0	0
	10	80	0	15
	15	80	0	20
	20	80	---	20
	30	80	0	20
Results after one month	2.5	100	0	0
	5	100	0	20
	10	100	0	95
	15	100	0	100
	20	100	---	100
	30	100	0	100

It will be recognized from the above table that for the great nasturtium no destruction occurs at any of the dosages although a slight phytotoxicity appears with the dosage of 10 kg./hectare of active material.

The results set forth in Tables 4 to 6 indicate that post-emergence treatment with the herbicide destroys 92% of the slender foxtail when applied in a dosage of 1 kg./hectare and that it is still fully selective in that it does not destroy wheat, barley and wild oats even at twice the dosage. At a dosage of 2.5 kg./hectare, wild mustard is completely destroyed within one month after treatment whereas oats remains unaffected.

EXAMPLES 21–23

Field experiments were conducted with N-2(5-chlorothiazolyl)-N'-methylurea as the active material applied to the plants in the same manner as described in Examples 15–20.

(a) Barley in spring.—As the stage of development of three leaves, barley is treated by applying 0.75 to 1.25 kg./hectare of active material. The accompanying weeds were represented by goosefoot (Chemopodium species) and by wild radish (Raphanus raphanistrum). The effectiveness of weed removal was very good 64 days after treatment.

(b) Wheat in autumn.—The pre-emergence treatment in dosages of 1.5 kg./hectare was employed and it was noted that after three months the weed-killing effect was selective with respect to wheat. Slender foxtail and wild radish were destroyed substantially completely.

(c) With peas.—Treatment was made as soon as the plants broke through the ground by application of the active material in dosages of 1 to 2 kg./hectare. The selectivity was perfect in that 45 days after treatment the herbicidal efficiency was exhibited by the fact that knotweed (Polygonum aviculare), black bindweed (Polygonum convulvulus) and goosefoot (Chenopodium species) was completely destroyed without harm to the pea plants.

EXAMPLES 24–27

The biological activity of N-2(5-chloro-4-methylthiazolyl)-N'-methylurea upon various plants in the greenhouse was tested with four different dosages, as indicated in the following tables. Two different treatments were employed, namely, a pre-emergence treatment after the seeding but before the plants broke through the ground, a post-emergence treatment after the plants had broken through the ground and when each plant was present as a young plant (seedling) which was approximately between 5 to 15 cm. in height.

The active material was applied by spraying from an aqueous suspension containing 20% by weight of the active material as a wettable powder. The results observed as expressed in the following table in percent of destruction of the treated plants.

TABLE 7.—PRE-EMERGENCY TREATMENT OF VARIOUS PLANTS WHICH ARE GRAMINACEAE, SETTING FORTH OBSERVATIONS 41 DAYS AFTER TREATMENT

Species of treated plants	Doses in kg./hectare of active materials: 1	2	4	8
Wheat	0	0	0	0
Indian corn	0	0	0	0
Wild millet	0	0	0	15
Barley	0	0	0	70
Oats	0	0	10	25
Millet	0	0	10	98
Rye grass	0	20	90	100
Slender foxtail	0	5	55	95

TABLE 8.—PRE-EMERGENCY TREATMENT OF VARIOUS DICOTYLEDONEAE, OBSERVATIONS BEING MADE 41 DAYS AFTER TREATMENT

Species of treated plants	Doses in kg./hectare of active materials: 1	2	4	8
Peas	0	0	0	0
Green bean (*Phaseolus vulgaris*)	0	0	0	0
Tomatoes	0	0	0	25
Common sunflower (*Helianthus annuus*)	0	5	0	35
Buckwheat	0	0	5	40
Rape	0	0	10	98
Linseed	0	65	100	100
Carrots	0	98	100	100

The following Tables 9 and 10 set forth the results from post-emergence treatments of various graminaceae in Table 9 and dicotyledoneae in Table 10, in the greenhouse. The results are those observed 42 days after treatment.

TABLE 9

Species of treated plants	Doses in kg./hectare of active materials: 1	2	4	8
Indian corn	0	0	0	0
Millet	0	0	0	50
Wild millet	0	0	20	30
Oats	0	0	30	100
Slender foxtail	0	0	70	90
Barley	0	20	50	100
Wheat	0	24	50	98
Italian wild rye grass	0	70	95	100

TABLE 10

Species of treated plants	Doses in kg./hectare of active materials: 1	2	4	8
Peas	0	0	0	0
Rape	0	0	0	0
Sunflower	0	0	0	50
Green beans	0	30	40	40
Tomatoes	0	30	70	90
Buckwheat	60	60	60	80
Linseed	60	60	90	95
Carrots	60	80	90	100

It will be seen from Tables 7 to 10 that a clearcut activity is achieved both for the pre-emergence as well as for the post-emergence treatments when application is made in dosages between 4 to 8 kg./hectare of the active material. In the pre-emergence treatment, a selective weed killing is observed in that wheat, Indian corn, green beans and peas remain undamaged (Tables 7 and 8) whereas the slender foxtail is destroyed in the amounts of 55–95% and the Italian wild rye grass in the amounts of 90–100%. In the post-emergence treatment, a selective weed killing is obtained without harm to Indian corn and peas (Tables 9 and 10) while foxtail is destroyed in amounts up to 70–90% and wild rye grass in amounts up to 95–100%.

EXAMPLES 28–33

According to the method used in Examples 15–20, the which form the subject matter of this invention were tested with respect to plants using a dosage of 8 kg./hectare of active material. Tables 11 and 12 set forth the results obtained, expressed in percent destruction of the treated plants.

TABLE 11.—PRE-EMERGENCE TREATMENT OF VARIOUS GRAMINACEAE IN WHICH THE RESULTS SET FORTH WERE OBSERVED 46 DAYS AFTER TREATMENT

	Example		
	28	29	30
Active material tested	N-2(4-methyl-thiazolyl)-N'-methylurea	N-2(5-chloro-4-methylthiazolyl)-N',N'-dimethyl-urea	N-2(4-trifluoro-methylthiazol) N'-methylurea
Species of plants treated:			
Indian corn	0	0	0
Wheat	0	0	60
Barley	0	0	20
Oats	20	0	90
Millet	0	20	100
Wild millet	10	80	20
Wild rye	20	70	60
Foxtail	40	95	98

TABLE 12.—PRE-EMERGENCE TREATMENT OF VARIOUS DICOTYLEDONEAE, IN WHICH THE RESULTS WERE OBSERVATIONS MADE 46 DAYS AFTER TREATMENT

	Example		
	31	32	33
Active material tested	N-2(4-methyl-thiazolyl)-N'-methylurea	N-2(5-chloro-4-methylthiazolyl)-N',N'-dimethyl-urea	N-2(4-trifluoro-methylthiazolyl)-N'-methylurea
Species of plant tested:			
Peas	20	0	95
Green beans	0	0	70
Sunflower	95	0	100
Tomatoes	20	40	100
Buckwheat	90	30	100
Rape	85	60	100
Linseed	95	95	100
Carrots	98	100	100

Examples 29 and 32 show that treatment is selective in that it does not destroy wheat, Indian corn, oats and barley, green beans, peas and sunflower, whereas destruction is observed of slender foxtail up to 95%, Italian wild rye grass up to 70% and wild millet up to 80%.

The compounds of Examples 30 and 33 show herbicidal activity but without too much selectivity. All of the millet and rape are destroyed and only Indian corn remains fully resistant.

The compounds of Examples 28 and 31 are selective in that wheat, Indian corn, millet, barley and green beans are not destroyed while herbicidal effect in the order of 85% is secured with respect to rape.

EXAMPLE 34

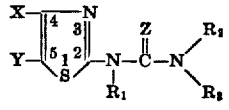
Treatment is effected in accordance with Examples 15–20 but at a dosage of 10 kg./hectare, using as the active ingredient N - 2 - thiazolyl - N' - methylurea. The active ingredient completely destroyed millet in a pre-emergence treatment.

It will be seen from the foregoing that a new series of compounds are provided which have shown marked activity as a herbicide in managing plant growth and in the destruction of undesirable weeds and plants connected with plant growth. The compounds of this invention exhibit an important degree of selectivity with respect to their herbicidal activity with various plants and combinations of plants.

It will be understood that changes may be made in the details of formulation and application without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. A thiazole derivative having the formula



in which X and Y are selected from the group consisting of hydrogen, halogen, alkyl, alkoxy or halogenated alkyl in which the alkyl and alkoxy groups contain from 1–4 carbon atoms and in which at least one of the groups X and Y is halogen, R_1 is selected from the group consisting of hydrogen, alkyl containing from 1–4 carbon atoms and alkenyl containing from 1–4 carbon atoms, R_2 and R_3 are selected from the group consisting of hydrogen, alkyl, alkenyl and alkynyl in which the alkyl, alkenyl and alkynyl contain from 1–4 carbon atoms, and Z is selected from the group consisting of oxygen and sulphur.

2. A thiazole derivative as claimed in claim 1 in which the compound is N-2-(5-chlorothiazolyl)-N'-methylurea.

3. A thiazole derivative as claimed in claim 1 in which the compound is N - 2 (5 - chloro - 4 - methylthiazolyl)-N'-methylurea.

4. A thiazole derivative as claimed in claim 1 in which the compound is N - 2(5 - chlorothiazolyl) - N' - methylthiourea.

5. A thiazole derivative as claimed in claim 1 in which the compound is N - 2(5 - chloro - 4 - methylthiazoyly)-N',N'-dimethylurea.

References Cited

The following references, cited by the Examiner, are of record in the patented file of this patent or the original patent.

UNITED STATES PATENTS

2,755,285 7/1956 O'Neill et al. ..... 260—306.8

FOREIGN PATENTS

14,593 10/1963 Japan ..... 260—306.8

OTHER REFERENCES

DeGering, An Outline of Organic Nitrogen Compounds (Michigan, 1950), p. 438.

Bhargava et al., Bull. Chem. Soc. Japan, vol. 38, pp. 905–9 (1965).

Tefas et al., Chem. Abstracts, vol. 54, cols. 17376–7 (1960).

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CERTIFICATE OF CORRECTION

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Inventor(s) Jean-Claude Guillot et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

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Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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