United States Patent

Teach

[15] **3,670,010**

[45] **June 13, 1972**

[54] **TRIFLUOROMETHYL ACYLATED UREA CARBAMATES**

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[22] Filed: **May 6, 1969**

[21] Appl. No.: **822,316**

[52] **U.S. Cl.** ....**260/479 C,** 71/70, 71/76, 71/107, 260/468 C, 260/472 C

[51] **Int. Cl.** **C07c 125/06**

[58] **Field of Search** ....260/479 C, 468 C, 472 C

[56] **References Cited**

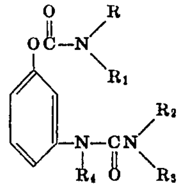
UNITED STATES PATENTS

3,434,822	3/1969	Wilson et al.	71/106

Primary Examiner—James A. Patten
Attorney—Daniel C. Block and Edwin H. Baker

[57] **ABSTRACT**

Acylated urea carbamate compounds having the formula

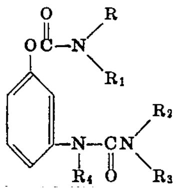


in which R_1 and R_3 are independently selected from an alkyl radical of from 1 to about 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from about 3 to about 4 carbon atoms, inclusive, phenyl and substituted phenyl in which the substituents are lower alkyl, lower alkoxy, nitro and halogen; R and R_2 are independently selected from hydrogen, alkyl of from 1 to about 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from about 3 to about 4 carbon atoms, inclusive, and trifluoroacetyl; provided that at least one of R or R_2 is trifluoroacetyl; and R_4 is selected from hydrogen, methyl or when only one of R or R_2 is trifluoroacetyl then R_4 can be trifluoroacetyl. These compounds are prepared by the reaction of an appropriate carbamoyloxyphenyl urea and trifluoroacetic anhydride. The compounds are useful as herbicides.

4 Claims, No Drawings

TRIFLUOROMETHYL ACYLATED UREA CARBAMATES

This invention relates to certain novel acylated urea carbamates which are useful as herbicides. The compounds of the present invention are new compositions of matter prepared by the reaction of an appropriate carbamoyloxy phenyl urea and trifluoroacetic anhydride and correspond to the formula



in which R_1 and R_3 are independently selected from an alkyl radical of from 1 to about 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from about 3 to about 4 carbon atoms, inclusive, phenyl and substituted phenyl in which the substituents are lower alkyl, lower alkoxy, nitro and halogen; R and R_2 are independently selected from hydrogen, alkyl of from 1 to about 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from about 3 to about 4 carbon atoms, inclusive, and trifluoroacetyl, provided that at least one of R or R_2 is trifluoroacetyl; and R_4 is selected from hydrogen, methyl or when only one of R or R_2 is trifluoroacetyl then R_4 can be trifluoroacetyl. Appropriate carbamoyloxy phenyl ureas useful as starting material are those in which R, R_2 and R_4 are independently hydrogens in the above-defined structure.

In the above description, unless otherwise indicated, the following preferred embodiments are intended for the various groups: alkyl preferably includes those members which contain from 1 to about 8 carbon atoms, inclusive, in both straight chain and branched chain configurations, and lower alkyl preferably includes those members which contain from 1 to about 4 carbon atoms, inclusive, in both straight chain and branched chain configurations. Examples of alkyl and lower alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, n-hexyl, isoamyl, n-heptyl, isooctyl, n-octyl and the like. Examples of lower alkenyl preferably include those members of the group containing from 3 to about 4 carbon atoms having at least one double bond in the 2-position, such as allyl, 2-methylallyl, 2-butenyl and the like. When lower alkenyl appears in substituted phenyl, it also can be a vinyl radical. The term halogen preferably includes fluorine, chlorine, bromine and iodine.

The compounds of this invention have been found to be active herbicides of a general type. That is, certain members of the class have been found to be herbicidally effective against a wide range of plant species. The method of controlling undesirable vegetation of the present invention comprises applying an herbicidally effective amount of the above-described compounds to the area where control is desired.

An herbicide is used herein to mean a compound which controls or modifies the growth of plants. By a "growth controlling amount" is meant an amount of of compound which causes a modifying effect upon the growth of plants. Such modifying effects include all deviations from natural development, for example, killing, retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation dwarfing and the like. By "plants" it is meant germinant seeds, emerging seedlings, and established vegetation including the roots and above-ground portions.

The compounds of the present invention are prepared by several different methods depending upon the nature of the starting materials and products desired. The following general method is applicable to preparing all of the compounds herein disclosed. An appropriately substituted mono-N-substituted carbamoyloxy phenyl urea is treated with trifluoroacetic anhydride. Sulfuric acid may be used as a catalyst for the reaction. The reaction is usually performed in a suitable solvent, such as benzene. After the reaction is completed, the solvent is removed and the product recovered therefrom. Upon recovery of the crude product, final recovery is by normal workup procedures, such as distillation in the case of liquids and recrystallization for solids.

The mono-N-substituted carbamoyloxy phenyl urea starting material employed in this synthesis may be prepared by methods employed for the synthesis of carbamates and of urea derivatives, further described and exemplified in British Pat. No. 1,106,064.

The compounds of the present invention are preparable by the following more particularly illustrated example. Following the example is a table of compounds which are preparable according to the procedures described herein.

EXAMPLE

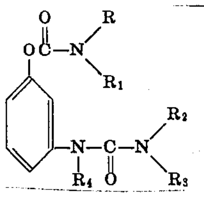
Reaction of 1-(3′-N-methyl carbamoyloxy phenyl)-3-methyl urea and trifluoroacetic anhydride.

There are three potential reactive hydrogen sites in the starting material. This example describes the reaction of about a 1:1 mole ratio of reactants to prepare a product. It is possible that in this reaction each hydrogen site enters into the reaction alone or at the same time that other active hydrogen sites enter the reaction. Such that at least one trifluoroacetyl group is present at one of the reactive hydrogen sites in the product. Present in the reaction product in varying amounts are 1-(3′-N-methyl-N-trifluoroacetyl-carbamoyloxy phenyl) 3-methyl urea, 1-(3′-N-methyl-N-trifluoroacetyl-carbamoyloxy phenyl)-3-trifluoroacetyl-3-methyl urea and 1-(3′-N-methyl carbamoyloxy phenyl)-1,3-di-trifluoroacetyl-3-methyl urea.

Fifteen and six-tenths grams (0.07 mole) of 1-(3′-N- methyl carbamoyloxy phenyl)-3-methyl urea is treated with 15 g. of trifluoroacetic anhydride in 10 ml. of benzene containing five drops of sulfuric acid. The clear solution formed on addition of the anhydride is refluxed for 30 minutes, diluted with additional benzene, washed with sodium bicarbonate solution and water and dried. The benzene is removed under vacuum to yield 19.7 g. of a gummy solid m.p. 84°–87° C. The herbicidal activity of this product will be reported below in the Herbicidal Screening Test results as Compound No. 1.

When a 2:1 mole ratio of trifluoroacetic anhydride to carbamoyloxy-phenyl urea is reacted, a product is obtained which is believed to contain an average of at least two trifluoroacetyl groups per molecule. That is, a mixture of 1-(3′-N-methyl-N-trifluoroacetyl carbamoyloxy phenyl)-3-trifluoroacetyl-3-methyl urea and 1-(3′-N-methyl carbamoyloxy phenyl)-1,3-ditrifluoroacetyl-3-methyl urea. The herbicidal activity of this product will be reported below in the Herbicidal Screening Test results as Compound No. 2.

Representative of compounds falling within the generic formula of products presented herein, which are preparable by the aforedescribed procedures and which may be formulated into herbicidal compositions and applied as illustrated below are:



R	R_1	R_2	R_3	R_4
$COCF_3$	n-Butyl	Hydrogen	Methyl	Hydrogen.
$COCF_3$	n-Propyl	do	do	Do.
$COCF_3$	n-Hexyl	Methyl	do	Do.
$COCF_3$	Neopentyl	do	do	Do.
$COCF_3$	Isopropyl	Hydrogen	Isopropyl	Do.
$COCF_3$	Methyl	do	Ethyl	Do.
$COCF_3$	n-Octyl	Methyl	Methyl	Do.
$COCF_3$	2-methylallyl	do	do	Do.

Continued

R	R_1	R_2	R_3	R_4
$COCF_3$	t-Butyl	do	do	Do.
$COCF_3$	do	Hydrogen	Isopropyl	Do.
$COCF_3$	Methyl	Ethyl	Ethyl	Do.
$COCF_3$	t-Butyl	Hydrogen	t-Butyl	Do.
$COCF_3$	Methyl	Allyl	Methyl	Do.
$COCF_3$	Isopentyl	Ethyl	do	Do.
$COCF_3$	Isopropyl	Methyl	Cyclohexyl	Do.
$COCF_3$	Allyl	do	Methyl	Do.
$COCF_3$	Cyclohexyl	Hydrogen	do	Do.
$COCF_3$	Phenyl	do	do	Do.
$COCF_3$	p-Tolyl	do	Ethyl	Do.
$COCF_3$	Methoxyphenyl	do	Methyl	Do.
$COCF_3$	m-Nitrophenyl	do	do	Do.
$COCF_3$	p-Chlorophenyl	do	do	Do.
$COCF_3$	n-Butyl	Trifluoroacetyl	do	Do.
$COCF_3$	n-Propyl	do	do	Do.
$COCF_3$	Methyl	do	Ethyl	Do.
$COCF_3$	do	do	do	Methyl.
$COCF_3$	Phenyl	do	Methyl	Hydrogen.
$COCF_3$	do	do	do	Methyl.
$COCF_3$	t-Butyl	Methyl	do	Trifluoroacetyl.

Herbicidal Screening Tests

As previously mentioned, the herein described compounds produced in the above-described manner are phytotoxic compounds which are useful and valuable in controlling various plant species. Compounds of this invention are tested as herbicides in the following manner.

Pre-emergence herbicide test

On the day preceding treatment, seeds of seven different weed species are planted in individual rows using one species per row across the width of the flat. The seeds used are hairy crabgrass (*Digitaris sanguinalis* (L.) Scop.), yellow foxtail (*Setaria glauca* (L.) Beauv.), water grass (*Echinochloa crusgalli* (L.) Beauv.), California red oat (*Avena sativa* (L.) redroot pigweed (*Amaranthus retroflexus* (L.), Indian mustard (*Brassica juncea* (L.) Coss.) and curly dock (*Rumex crispus* (L.). Ample seeds are planted to give about 20 to 50 seedlings per row, after emergence, depending upon the size of the plants. The flats are watered after planting. The spraying solution is prepared by dissolving 50 mg. of the test compound in 3 ml. of a solvent, such as acetone, containing 1 percent Tween 20 (polyoxyethylene sorbitan monolaurate). The following day each flat is sprayed at the rate of 20 pounds of the candidate compound per 140 gallons of solution per acre. An atomizer is, used to spray the solution onto the soil surface. The flats are placed in a greenhouse at 80° F. and watered regularly. Two weeks later the degree of weed control is determined by comparing the amount of germination and growth of each weed in the treated flats with weeds in several untreated control flats. The rating system is as follows:

−= no significant injury (0–15 percent control)
+= slight injury (25–35 percent control)
++= moderate injury (55–65 percent control)
+++= severe injury or death (85–100 percent control)

An activity index is used to represent the total activity on all seven weed species. It is the sum of the number of plus marks, so that an activity index of 21 represents complete control of all seven weeds. Compound No. 1 has an index value of 21 and Compound No. 2 has an index value of 19.

Post-emergence herbicide test

Seeds of five weed species including hairy crabgrass, watergrass, California red oats, Indian mustard, and curly dock and one crop, pinto beans (*Phaseolus vulgaris*), are plated in flats as described above for pre-emergence screening. The flats as described above are placed in the greenhouse at 72°–85° F. and watered daily with a sprinkler. About 10 to 14 days after planting when the primary leaves of the bean plant are almost fully expanded and the first trifoliate leaves are just starting to form, the plants are sprayed. The spray is prepared by weighting out 50 mg. of the test compound, dissolving it in 5 ml. of acetone containing 1 percent Tween 20 (polyoxyethylene sorbitan monolaurate) and then adding 5 ml. of water. The solution is sprayed on the foliage using an atomizer. The spray concentration is 0.5 percent and the rate would be approximately 20 pounds per acre if all of the spray was retained on the plant and the soil, but some spray is lost so it is estimated that the application rate is approximately 12.5 pounds per acre.

Beans are used to detect defoliants and plant growth regulators. The beans are trimmed to two or three plants per flat by cutting off the excess weaker plants several days before treatment. The treated plants are placed back in the greenhouse and care is taken to avoid sprinkling the treated foliage with water for 3 days after treatment. Water is applied to the soil by means of a slow stream from a watering hose taking care not to wet the foliage.

Injury rates are recorded 14 days after treatment. The rating system is the same as described above for the pre-emergence test were (−), (+), (++) and (+++) are used for the different rates of injury and control. The injury symptoms are also recorded. The maximum activity index for complete control of all the species in the post-emergence screening test is 18 which represents the sum of the plus marks obtained with the six plant species used in the test. Compound No. 1 has an index value of 18 and Compound No. 2 has an index value of 18.

The compound of the present invention can be used as pre-emergence or post-emergence herbicides and applied in a variety of ways at various concentrations. In practice, the compounds herein defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the adjuvants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may effect the activity of the material in a given application. Thus, these active herbicidal compounds may be formulated as granules of relatively large particle size, as wettable powders, as emulsifiable concentrates, as powdery dusts, as solutions, or as any of several other known types of formulations, depending upon the desired mode of application. Preferred formulations for both pre- and post-emergence herbicidal applications are wettable powders, emulsifiable concentrates and granules. These formulations may contain as little as about 0.5 percent to as much as about 95 percent or more by weight of active ingredient. The amount applied depends upon the nature of the seeds or plants to be controlled and the rate of application varies from 1 to approximately 50 pounds per acre.

Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersant. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include fuller's earth, kaolin clays, silicas and other readily wet organic or inorganic diluents. Wettable powders normally are prepared to contain about 5 to about 95 percent of the active ingredient by weight and usually also contain a small amount of wetting, dispersing or emulsifying agent to facilitate wetting and dispersion.

Emulsifiable concentrates are homogeneous liquid compositions which are dispersible in water or other dispersant, and may consist entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone and other non-volatile organic solvents. For herbicidal application, these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredients may vary according to the manner in which the composition is to be applied, but in general comprises about 0.5 to 95 percent of active ingredient by weight of the herbicidal composition.

Granular formulations, wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, bentonite clays, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are prepared to contain about 5 to about 25 percent of active ingredient and may also contain small amounts of other ingredients which may include surface-active agents such as wetting agents, dispersing agents or emulsifiers; oils such as heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as dextrins, glue or synthetic resins.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; polyhydric alcohols; and other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1 to 15 percent by weight of the herbicidal compositions.

Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporating applications.

Pastes, which are homogeneous suspensions of a finely divided solid toxicant in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5 to about 95 percent of active ingredient by weight, and may also contain small amounts of wetting, dispersing or emulsifying agent to facilitate dispersion. For application, the pastes are normally diluted and applied as a spray to the area to be affected.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene or other organic solvents. Pressurized sprays, typically aerosols, wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freons, may also be used.

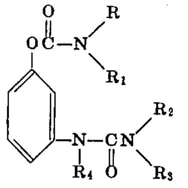
The phytotoxic compositions of this invention are applied to the plants in the conventional manner. Thus, the dust and liquid compositions can be applied to the plant by the use of powerdusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because they are effective in very low dosages. In order to modify or control growth of germinating seeds or emerging seedlings, as a typical example, the dust and liquid compositions are applied to the soil according to convention methods and are distributed in the soil to a depth of at least one-half inch below the soil surface. It is not necessary that the phytotoxic compositions be admixed with the soil particles and these compositions can be applied merely by spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid formulations applied to the surface of the soil can be distributed below the surface of the soil by conventional means such as discing, dragging or mixing operations.

The phytotoxic compositions of this invention can also contain other additaments, for example, fertilizers, pesticides and the like used as adjuvant or in combination with any of the above-described adjuvants. Other phytotoxic compounds useful in combination with the above-described compounds include, for example, 2,4-dichlorophenoxyacetic acids, 2,4,5-trichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives, such as 2,4-bis(3-methoxypropylamino)-6-methylthio-S-triazine; 2-chloro-4-ethylamino-6-isopropylamino-S-triazine, and 2-ethylamino-4-isopropylamino-6-methylmercapto-S-triazine, urea derivatives, such as 3-(3,4-dichlorophenyl)-1,1-dimethyl urea and 3-(p-chlorophenyl)-1,1-dimethyl urea and acetamides such as N,N-diallyl-α-chloroacetamide, N-(α-chloroacetyl)hexamethylene imine, and N,N-diethyl-α-bromoacetamide, and the like; benzoic acids such as 3-amino-2,5-dichlorobenzoic and; thiocarbamates, such as S-propyl dipropylthiocarbamate; S-ethyl-dipropylthiocarbamate, S-ethyl-cyclohexylethyl-thiocarbamate, S-ethyl hexahydro-1H-azepine-1-carbothioate and the like. Fertilizers useful in combination with the active ingredients include, for example, ammonium nitrate, urea and superphosphate. Other useful additaments include materials in which plant organisms take root and grow such as compost, manure, humus, sand and the like.

The concentration of a compound of the present invention, constituting an effective amount in the best mode of administration in the utility disclosed is readily determinable by those skilled in the art.

What is claimed is:

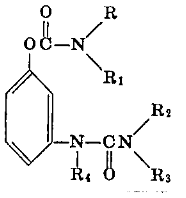
1. Acylated urea carbamate compounds having the formula



of

in which R_1 and R_3 are independently selected from an alkyl radical of from 1 to 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from 3 to 4 carbon atoms, inclusive, phenyl and substituted phenyl in which the substituents are lower alkyl, lower alkoxy, nitro and halogen; R and R_2 are independently selected from hydrogen, alkyl of from 1 to 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from 3 to 4 carbon atoms, inclusive, and trifluoroacetyl, provided that at least one or R or R_2 is trifluoroacetyl; and R_4 is selected from hydrogen, methyl or when only one of R or R_2 is trifluoroacetyl then R_4 can be trifluoroacetyl.

2. Acylated urea carbamate compounds having the formula



in which R_1 is selected from an alkyl radical of from 1 to 8 carbon atoms, inclusive, lower alkenyl of from 3 to 4 carbon atoms, inclusive; R_3 is selected from an alkyl radical of from 1 to 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from 3 to 4 carbon atoms, inclusive, phenyl and substituted phenyl in which the substituents are lower alkyl, lower alkenyl, lower alkoxy, nitro and halogen; R is selected from hydrogen, alkyl of from 1 to 8 carbon atoms, inclusive, lower alkenyl of from 3 to 4 carbon atoms, inclusive, and trifluroacetyl; and R_2 is selected from hydrogen, alkyl of from 1 to 8 carbon atoms, inclusive, cyclohexyl, lower alkenyl of from 3 to 4 carbon atoms, inclusive and trifluoroacetyl, provided that at least one of R or R_2 is trifluoroacetyl; and R_4 is selected from hydrogen, methyl or when only one of R or R_2 is trifluoroacetyl then R_4 can be trifluoroacetyl.

3. A compound according to claim 2 in which R is trifluoroacetyl, R_1 is methyl, R_2 is hydrogen, R_3 is methyl and R_4 is hydrogen.

4. A compound according to claim 2 in which R is trifluoroacetyl, R_2 is trifluoroacetyl, R_1 is methyl, R_3 is methyl and R_4 is hydrogen.

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