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Baker et al.

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[54] **ANILIDE CARBAMATES AS ALGICIDAL AGENTS**

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[21] Appl. No.: **318,316**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 119,852, March 1, 1971, abandoned.

[52] **U.S. Cl.** ..... **71/67**, 71/106, 71/111, 260/468 C, 260/471 C, 260/479 C

[51] **Int. Cl.** **A01n 9/20**

[58] **Field of Search** 71/67, 106, 111

[56] **References Cited**

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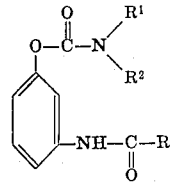
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[57] **ABSTRACT**

This invention relates to the utility of certain anilide carbamates of the general formula:



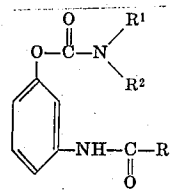
wherein R^1 is hydrogen or alkyl, R^2 is alkyl, alkynyl, cycloalkyl, allyl, phenyl, 3,4-dichlorophenyl or benzyl and R is alkyl, haloalkyl, alkenyl, or cyclopropyl as algicidal agents.

39 Claims, No Drawings

ANILIDE CARBAMATES AS ALGICIDAL AGENTS

This application is a continuation-in-part of copending application Ser. No. 119,852, filed Mar. 1, 1971 now abandoned.

This invention relates to the utility as algicidal agents for the control of algae when used in an algicidally effective amount of certain substituted anilide carbamates of the general formula:



wherein R^1 is hydrogen or alkyl, R^2 is alkyl, alkynyl, cycloalkyl, allyl, phenyl, 3,4-dichlorophenyl or benzyl and R is alkyl, haloalkyl, alkenyl, or cyclopropyl. It was found that these compounds have an algicidal effect and provide beneficial results in controlling the growth of algae.

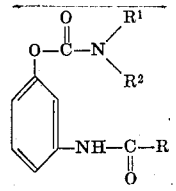
Controlling the growth of algae by employing the compounds described herein can be accomplished by applying an algicidally effective amount to the environment in which algae growth is encouraged. The compounds may be applied to any environmental area which is a host to algae or susceptible to algae attack and growth. By controlling, it is meant the inhibition and prevention of the growth of the organism to be controlled.

The term alkyl as used herein, i.e., both in the specification and claims, contemplates linear and branched chain alkyl radicals containing from one to eight carbon atoms, inclusive, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec.-butyl, tert.-butyl, n-amyl, isoamyl, n-hexyl, n-octyl. The term cycloalkyl as used herein relates to those aliphatic radicals having a cyclic configuration and containing from three to six carbon atoms, inclusive, such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. The term haloalkyl as used herein contemplates linear and branched chain halogen substituted alkyl radicals containing from one to six carbon atoms, inclusive, such as monochloromethyl, dichloromethyl, trichloromethyl, monochloroethyl, dichloroethyl, trichloroethyl, pentachloroethyl, bromomethyl, bromoethyl, iodomethyl, iodoethyl, fluoromethyl, fluoroethyl, chlorofluoromethyl, chlorofluoroethyl, monofluorotetrachloroethyl, and the like.

The term alkenyl as used herein contemplates alkenyl radicals containing at least one double bond and from two to four carbon atoms, inclusive, such as vinyl, allyl, 2-methylvinyl, butenyl-1 and the like. The term alkynyl as used herein preferably includes those members containing at least one triple bond and from three to six carbon atoms, inclusive.

The following compounds in Table I can be used, for example, according to the invention hereindescribed. Compound numbers have been assigned and are used throughout the balance of this application.

TABLE I



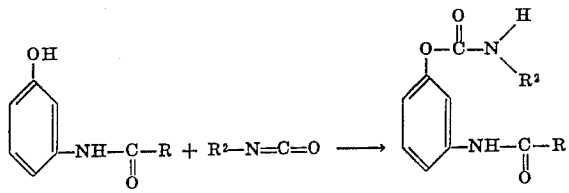
COMPOUND NUMBER	R^1	R^2	R	PHYSICAL CONSTANT m.p. (°C) or n_D^{30}
1	H	CH_3	CCl_3	165–172
2	H	CH_3	$CH{=}CHCH_3$	156–158
3	H	i-C_3H_7	C_2H_5	198–199
4	H	n-C_4H_9	C_2H_5	130–133
5	H	cyclohexyl	C_2H_5	156–159
6	C_2H_5	C_2H_5	C_2H_5	77–78
7	H	C_2H_5	C_2H_5	161–166
8	n-C_3H_7	n-C_3H_7	C_2H_5	55–59
9	H	3,4-diClO	C_2H_5	185–188
10	H	sec.-C_4H_9	C_2H_5	186–188
11	H	t-C_4H_9	C_2H_5	210–213
12	H	$CH_2CH{=}CH_2$	C_2H_5	136–142
13	H	C_2H_5	i-C_3H_2	164–168
14	H	n-C_4H_9	i-C_3H_7	153
15	H	phenyl	CH_3	170–173
16	H	t-C_4H_9	sec.-C_5H_{11}	139–141
17	H	CH_3	CH_3	155–157
18	H	C_2H_5	$CH{=}CHCH_3$	137–140
19	H	C_2H_5	cyclopropyl	191–194
20	H	i-C_3H_7	$CH{=}CHCH_3$	168–173
21	H	i-C_3H_7	cyclopropyl	210–214
22	H	n-C_4H_9	cyclopropyl	160–163
23	H	n-C_4H_9	$CHClCH_3$	153–157
24	H	n-C_4H_9	$CH{=}CHCH_3$	178–183
25	H	n-C_4H_9	CCl_3	170–173
26	H	n-C_4H_9	C_4H_9	146–149
27	H	C_2H_5	CCl_3	184–188
28	H	i-C_3H_7	CCl_3	203–210
29	H	i-C_3H_7	$CHClCH_3$	216–218
30	H	n-C_4H_9	$CH(C_2H_5)_2$	118–120
31	H	n-C_5H_{11}	C_2H_5	108–113
32	H	benzyl	C_2H_5	159–161
33	n-C_3H_7	n-C_3H_7	$C(CH_3)_2C_3H_7$	1.5081
34	C_2H_5	n-C_4H_9	$C(CH_3)_2C_3H_7$	1.5170

TABLE I—Continued

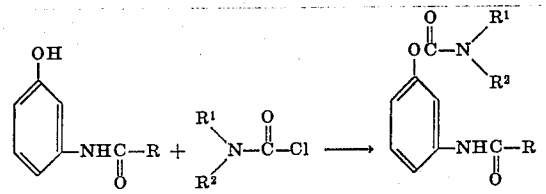
COMPOUND NUMBER	R^1	R^2	R	PHYSICAL CONSTANT m.p. (°C) or n_D^{30}
35	n-C_4H_9	n-C_4H_9	$C(CH_3)_2C_3H_7$	1.5105
36	H	cyclohexyl	CH_3	168–173
37	H	$CH(C_2H_5)_2$	C_2H_5	166–170
38	H	$CH(CH_3)CH_2CH(CH_3)_2$	C_2H_5	148–151
39	H	$CH(CH_3)C(CH_3)_2CH_3$	C_2H_5	182.5–187.5
40	H	$CH(CH_3)C_3H_7$	C_2H_5	154–156
41	H	$CH_2CH(CH_3)_2$	C_2H_5	144–146
42	H	cyclopentyl	C_2H_5	173–177
43	CH_3	i-C_3H_7	C_2H_5	1.5349
44	C_2H_5	i-C_3H_7	C_2H_5	(Gum)
45	C_2H_5	t-C_4H_9	C_2H_5	1.5290
46	H	$C(CH_3)_2$-C≡CH	C_2H_5	156–158
47	CH_3	$CH(CH_3)$-C≡CH	C_2H_5	1.5348
48	H	i-C_3H_7	$C(CH_3)_2C_3H_7$	128–130
49	H	t-C_4H_9	$C(CH_3)_2C_3H_7$	solid

The compounds mentioned thus far, and those contemplated, can be produced, for example, according to the following methods.

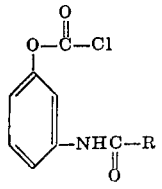
The compounds herein disclosed are prepared by one of several methods. When R^1 is hydrogen and R^2 is alkyl, cyclohexyl, allyl, phenyl, 3,4-dichlorophenyl or benzyl, a convenient method applicable to preparing the compounds is the reaction between an appropriate substituted-m-amido phenol and an appropriate isocyanate.



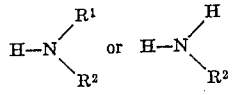
An organic solvent, e.g., chloroform, methylene chloride, ether, dioxane or acetone, can be employed as a reaction medium. Acetone and homologous ketones are found to be particularly convenient when the m-hydroxy alkylanilides are used because such anilides are more soluble in these solvents than in other less polar inert solvents. A tertiary amine, preferably triethylamine, is used in catalytic amounts to promote the reaction. Reaction temperatures are employed that permit operation in the liquid phase. Said reaction temperatures are between room temperature and reflux temperature of the solvent, if any is used. When R^1 is alkyl and R^2 is alkyl, cyclohexyl, allyl, phenyl, 3,4-dichlorophenyl or benzyl, one convenient method applicable for preparing the compounds is the reaction of an appropriately substituted carbamoyl chloride and a 3'-hydroxy-anilide.



Further, the preparation of either type of compound, i.e., wherein R^1 is hydrogen or wherein R^1 is alkyl and R^2 is as described above, is conveniently carried out employing an appropriate amidophenyl chloroformate of the formula



and, either a primary or secondary amine, e.g., the formulae



These later reactions, employing a carbamoyl chloride or a chloroformate, are preferably carried out in the presence of a hydrogen halide acceptor, such as triethylamine, or an excess of an amine starting material, pyridine, picoline, sodium carbonate, potassium carbonate and the like. Temperatures which are employed in these reactions permit operation in a liquid phase and are between about 0°C. and reflux temperature of the solvent, if one is used.

The following illustrated examples describe in detail, without restriction thereto, the preparation of representative compounds.

EXAMPLE I

Preparation of m-(N-methylcarbamoyloxy)acetanilide

In 150 ml. of chloroform, as a solvent, are brought together 15.2 g. of m-hydroxyacetanilide and 6.0 g. methyl isocyanate. To this solution is added 0.3 ml. of triethylamine and a trace of dibutyl tin dilaurate as catalysts. The mixture is refluxed and stirred for 1 hour. A solid product is formed during this period. The solid is separated by filtration. There is obtained 19.2 g. (93.6ξ yield) of the title compound, m.p. 155°–157°C.

EXAMPLE II

Preparation of m-(N-isopropylcarbamoyloxy)propionanilide

In 60 ml. acetone in a round bottom flask equipped with a stirrer, reflux condenser and dropping funnel is dissolved m-hydroxy-propionanilide (3.3 g.). To this solution is added 0.4 ml. of triethylamine. Isopropyl isocyanate (3 g.) is added gradually with good agitation

of the reactants. The precipitation of the product indicates that the reaction is proceeding satisfactorily. When all the isocyanate is added, the mixture is refluxed for 20 minutes, then cooled to room temperature and allowed to stand overnight. A white solid product is recovered by filtration. There is obtained 4.1 g. of the title compound, m.p. 198°–199°C.

EXAMPLE III

Preparation of N,N-dipropylcarbamoyloxy propionanilide

Sixteen and five-tenths (16.5) grams (0.1 mole) of 3'-hydroxy propionanilide is refluxed with 16.3 g. of di-n-propylcarbamoyl chloride and 28 g. of powdered potassium carbonate in 120 ml. of acetone for 4 hours. The mixture is cooled to room temperature and poured into water, taken up in ether, separated, and washed with water, dried over anhydrous magnesium sulfate and stripped under vacuum. There is obtained a pale yellow oil which slowly crystallized overnight. Yield of the crude product is 27.5 g., m.p. 51°–59°C.

EXAMPLE IV

Preparation of 3-propionamidophenyl chloroformate

A solution of 10.1 g. (0.1 mole) of phosgene in 25.9 g. of toluene is prepared and 25.6 g. of this solution is added to 100 ml. of toluene, and 16.5 g. (0.1 mole) of 3'-hydroxy propionanilide is added and dispersed. Triethylamine, 10.1 g. (0.1 mole), is added dropwise and a mildly exothermic reaction results. The temperature is kept under 30°C., with cooling in a water bath. After approximately 70 percent of the triethylamine is added, the remaining phosgene solution is added all at once. The addition of triethylamine is continued. When addition is complete, about 10 ml. of acetone is added and a nearly homogenous yellow solution resulted. It is filtered to remove about 4 g. of starting material and evaporated to a viscous yellow liquid. There is obtained 18.8 g. of the title compound, $n_D^{22} = 1.5437$. Calculated for $C_{10}H_{10}O_3NCl$; Cl = 15.67 percent, found 15.43 percent.

Preparation of m-(N-t-butylcarbamoyloxy)propionanilide

Eighteen and two-tenths (18.2) grams of 3-propionamidophenyl chloroformate in methylene chloride solution (0.08 mole) is cooled to 0°C. and t-butylamine, 24.2 g. (0.16 mole), is added with gentle shaking. A very exothermic reaction took place. The flask is cooled in an ice bath and after 5 minutes it solidifies. The product is treated with 70 ml. of benzene and 50 ml. of cold water is added with stirring. The mixture is filtered and the filter cake is washed with cold water. A nearly white solid is obtained, m.p. 158°–160°C. The product is recrystallized four times from ethyl acetate. There is obtained 2.5 g. of the title compound, m.p. 210°–212°C.

EXAMPLE V

Preparation of 3'-(N-methyl carbamoyloxy)trichloroacetanilide

Methyl isocyanate, 3.2 g. (0.055 mole) is added to 12.7 g. (0.05 mole) of 3'-hydroxy trichloroacetanilide in 150 ml. of methylene chloride containing approximately 0.5 g. of triethylamine as a catalyst. The solution is refluxed for 1 hour. The product precipitates after 30 minutes. The mixture is cooled, and the product filtered off. It is washed with petroleum ether and dried in a vacuum oven. There is obtained 13.3 g. (85 percent of theory) of the title compound, m.p. 165°–172°C.

EXAMPLE VI

Preparation of 3'-(N-butylcarbamoyloxy)crotonanilide.

Nine and nine-tenths (9.9) grams of 3'-hydroxycrotoanilide is dissolved in 100 ml. of acetone, 6 grams of butylisocyanate is added, followed by 4-5 drops of dibutyl tin dilaurate and approximately 100 mg. of triethylenediamine and the mixture heated at reflux for 2 hours. The mixture is poured into water and the product collected and dried. Yield is 10.8 g., m.p. 138°–140°C.

EXAMPLE VII

Preparation of 3'-(N-ethylcarbamoyloxy)cyclopropanecarboxanilide

Ten and six-tenths (10.6) grams of 3'-hydroxycyclopropanecarboxyanilide is dissolved in 100 ml. of acetone and treated with 4.7 g. of ethylisocyanate, 4-5 drops of dibutyl tin dilaurate and approximately 100 mg. of triethylenediamine. The mixture is heated at reflux. After three-fourths hour of reflux, the product crystallizes from the refluxing acetone. The mixture is cooled and the product filtered off. Yield is 11.6 g., m.p. 191°–194°C.

The following examples are given for the purpose of illustrating the effects according to the instant invention:

ALGICIDAL TEST PROCEDURE

Sufficient candidate toxicant is diluted in acetone to give an 0.5 percent mixture which is then diluted into 20 milliliters of warm modified Jack Meyers Agar Medium ("Algae Culture from Laboratory to Pilot Plant," 1953, Page 94). The dilutions are such as to give concentrations of 0.5 and 1.0 μg/ml. of the test compound in 20 × 100 mm. petri dishes. After the agar solidifies, separate petri dishes are innoculated with the desired organism, such as *Scenedesmus obliquus* or *Chlorella pyrenoidosa*. The innoculated samples are then allowed to grow at room temperature under fluorescent lamps using a 14 hour light period each day. After one to two weeks, depending upon the growth of the untreated controls, the results are recorded as to the level necessary to control the specific organism. The results obtained with representative compounds and their concentrations are given in Table II.

TABLE II

ALGICIDE TEST

COMPOUND NUMBER	*Scenedesmus obliquus* (concentration, μg/ml.)
1	(1.0)
2	(1.0)
3	(0.5)
4	0.5
5	0.5
6	(1.0)
7	(1.0)
8	0.5
9	0.5
10	0.5
11	0.5
12	(0.5)
13	(1.0)
14	0.5
15	(0.5)
16	0.5

TABLE II -Continued

ALGICIDE TEST

COMPOUND NUMBER	*Scenedesmus obliquus* (concentration, μg/ml.)
18	(1.0)
19	(1.0)
20	(1.0)
21	(1.0)
22	0.5
23	(1.0)
24	0.5
25	0.5
26	(0.5)
27	(1.0)
28	(1.0)
29	(1.0)
30	(1.0)
31	0.5
32	0.5
33	1.0
34	1.0
35	1.0
36	1.0
37	1.0
38	1.0
39	1.0
40	1.0
41	1.0
42	1.0
43	5.0
44	1.0
45	(1.0)
46	(1.0)
47	(1.0)
48	5.0
49	1.0

( ) denotes partial control at the indicated concentration.

Compounds Number 5, 17 and 38 controlled *Cholorella pyrenoidosa* at 1.0 μg/ml. Compound Number 39 also gave partial control of *Chlorella pyrenoidosa* at 1.0 μg/ml.

The manner in which the water area may be treated for the control of algae will vary with the specific problems encountered. An acute problem in the storage and utilization of industrial process water is the fouling of such water and systems in which the water is used by the growth of algae. Entire areas such as a pond or lake may be treated. Drainage ditches and other water-flowing sites may be treated.

In addition to use in ponds and lakes, this invention is applicable to the control of algae in industrial cooling towers and other water recirculating systems as used in paper manufacturing processes, for example.

The substances to be employed according to the present invention can be used as such or in the form of formulations with carrier vehicles. Examples and emulsifiable concentrates, spray powders, pastes, soluble powders, and the like. Suitable carrier vehicles or assistants are mainly: Solvents, such as, optionally chlorinated, aromatic hydrocarbons (e.g., xylene, benzene, chlorobenzenes), paraffins (e.g., petroleum fractions), alcohols, (e.g., methanol, ethanol, butanol), amines (e.g., ethanolamine, dimethylformamide), as well as water; finely divided solid carriers, for example, natural and synthetic stone meals or powders (kaolin, alumina, chalk, i.e., calcium carbonate, talc, highly disperse silicic acid, silicates, e.g., alkali silicates); emulsifiers, such as non-ionic and anionic emulsifiers (e.g., polyoxyethylene fatty acid esters and polyoxyethylene fatty alcohol ethers, alkyl sulfonates and aryl sulfonates) especially magnesium stearate, sodium oleate, etc., and dispersing agents such as lignin, sulfite waste liquors and methyl cellulose.

As already mentioned above, the active compounds or agents to be employed according to the instant invention can be present in the aforesaid formulations in mixture with one another and with other known active substances.

The algicidal compositions of the invention also comprise aqueous emulsions. The aqueous emulsions can be prepared by dissolving a surfactant of the type noted hereinabove and pouring the emulsifiable concentrate so obtained into water with vigorous agitation. The aqueous emulsions of the invention can also be prepared by dissolving the active ingredient in a water-miscible solvent such as Carbitol (diethylene glycol monoethyl ether), acetone, a lower alkanol, Cellosolve (ethylene glycol monoethyl ether), dioxan, and the like, if desired, in association with a surfactant such as noted above, to obtain an emulsifiable concentrate which is poured into water with vigorous agitation. The aqueous emulsions of the invention can also be prepared by dissolving the active ingredient and a surfactant such as noted above in an organic solvent which is immiscible with water. The resulting emulsifiable concentrate is then admixed with water with vigorous agitation to form an emulsion. The water-immiscible organic solvents which are suitable for use include cyclohexanone, summer oils, aromatic hydrocarbons such as benzene, toluene, xylene, and high-boiling petroleum hydrocarbons such as kerosene, diesel soil, and the like.

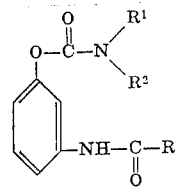
The aqueous emulsions of the invention can be supplied to the user in the form of the emulsifiable concentrates described above which require dilution with water before use. Both the concentrated compositions and the diluted compositions are included within the scope of the present invention.

Formulations contain, in accordance with the present invention, in general from 0.1 to 95, preferably 0.5 to 90, percent by weight of active compound or agent. The agents according to the present invention or their preparations are applied in the usual way, e.g., by spraying, dusting, sprinkling or atomizing. The active substances can be applied, according to the purpose in view, in a concentration of 5 to 0.0005 percent. In special cases it is, however, possible or even necessary to go below or above these concentrations. The remainder of active algicidal composition being an adjuvant which can be a liquid extending agent or surface active agent, but preferably is an admixture thereof.

Various changes and modifications are possible without departing from the spirit and scope of the invention described herein and will be apparent to those skilled in the art to which it pertains.

What is claimed is:

1. The method for inhibiting and preventing algae growth in water, which comprises adding to the algae environment an algicidally effective amount of a compound of the formula



wherein R^1 is hydrogen or alkyl having one to eight carbon atoms, inclusive, R^2 is alkyl having one to eight carbon atoms, inclusive, alkynyl having at least one triple bond and three to six carbon atoms, inclusive, cycloalkyl having three to six carbon atoms, inclusive, allyl, phenyl, 3,4-dichlorophenyl or benzyl and R is alkyl having one to eight carbon atoms, inclusive, haloalkyl in which halo is chloro, fluoro, iodo and bromo and having from one to six carbon atoms, inclusive, alkenyl having at least 1 double bond and from two to four carbon atoms, inclusive, or cyclopropyl.

2. The method according to claim **1** in which R^1 is hydrogen, R^2 is alkyl and R is alkyl.

3. The method according to claim **2** in which R^2 is isopropyl and R is ethyl.

4. The method according to claim **2** in which R^2 is n-butyl and R is ethyl.

5. The method according to claim **2** in which R^2 is ethyl and R is ethyl.

6. The method according to claim **2** in which R^2 is sec.-butyl and R is ethyl.

7. The method according to claim **2** in which R^2 is tert.-butyl and R is ethyl.

8. The method according to claim **2** in which R^2 is n-butyl and R is isopropyl.

9. The method according to claim **2** in which R^2 is tert.-butyl and R is sec.-amyl.

10. The method according to claim **2** in which R^2 is 1,2,2-trimethylpropyl and R is ethyl.

11. The method according to claim **2** in which R^2 is n-amyl and R is ethyl.

12. The method according to claim **2** in which R^2 is methyl and R is methyl.

13. The method according to claim **2** in which R^2 is sec.-amyl and R is ethyl.

14. The method according to claim **2** in which R^2 is 1,3-dimethylbutyl and R is ethyl.

15. The method according to claim **2** in which R^2 is 1-methylbutyl and R is ethyl.

16. The method according to claim **2** in which R^2 is isobutyl and R is ethyl.

17. The method according to claim **2** in which R^2 is isopropyl and R is 1,1-dimethylbutyl.

18. The method according to claim **2** in which R^2 is tert.-butyl and R is 1,1-dimethylbutyl.

19. The method according to claim **1** in which R^1 is hydrogen, R^2 is cycloalkyl and R is alkyl.

20. The method according to claim **19** in which R^2 is cyclohexyl and R is ethyl.

21. The method according to claim **19** in which R^2 is cyclopentyl and R is ethyl.

22. The method according to claim **1** in which R^1 is alkyl, R^2 is alkyl and R is alkyl.

23. The method according to claim **22** in which R^1 is n-propyl, R^2 is n-propyl and R is ethyl.

24. The method according to claim **22** in which R^1 is methyl, R^2 is isopropyl and R is ethyl.

25. The method according to claim **22** in which R^1 is ethyl, R^2 is isopropyl and R is ethyl.

26. The method according to claim **22** in which R^1 is ethyl, R^2 is tert.-butyl and R is ethyl.

27. The method according to claim **1** in which R^1 is hydrogen, R^2 is 3,4-dichlorophenyl and R is ethyl.

28. The method according to claim **1** in which R^1 is hydrogen, R^2 is alkyl and R is cyclopropyl.

29. The method according to claim **28** in which R^2 is n-butyl.

30. The method according to claim **1** in which R^1 is hydrogen, R^2 is alkyl and R is alkenyl.

31. The method according to claim **30** in which R^2 is n-butyl and R is 2-methylvinyl.

32. The method according to claim **1** in which R^1 is hydrogen, R^2 is alkyl and R is haloalkyl.

33. The method according to claim **32** in which R^2 is n-butyl and R is trichloromethyl.

34. The method according to claim **32** in which R^2 is ethyl and R is trichloromethyl.

35. The method according to claim **32** in which R^2 is isopropyl and R is 1-chloroethyl.

36. The method according to claim **1** in which R^1 is hydrogen, R^2 is alkynyl and R is alkyl.

37. The method according to claim **36** in which R^2 is 1,1-dimethylprop-2-ynyl and R is ethyl.

38. The method according to claim **1** in which R^1 is alkyl, R^2 is alkynyl and R is alkyl.

39. The method according to claim **38** in which R^1 is methyl, R^2 is 1-methylprop-2-ynyl and R is ethyl.

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