Singapore

PATENT SPECIFICATION

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NO DRAWINGS

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Int. Cl.:—C 07 d 87/16 // A 01 n

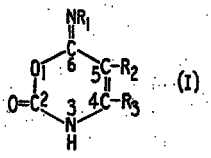
COMPLETE SPECIFICATION

Improvements in or relating to Oxazinone Derivatives

We, E. I. Du Pont De Nemours and Company, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, 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 heterocyclic compounds and more particularly to such compounds having one oxygen atom and one nitrogen atom in the hetero-ring.

According to the invention, we have discovered the following class of compounds, which are referred to as oxazinones:



(I)

and tautomers thereof, where R_1 is hydrogen, alkyl of 1 to 10 carbon atoms, substituted alkyl of 1 to 8 carbon atoms, aryl of 6 to 10 carbon atoms, substituted phenyl, aralkyl of 7 to 13 carbon atoms, substituted aralkyl of 7 to 13 carbon atoms, alkenyl of 3 to 8 carbon atoms, alkynyl of 3 to 8 carbon atoms, furfuryl, cycloalkyl of 3 to 12 carbon atoms, cycloalkenyl of 4 to 12 carbon atoms, cycloalkyl alkyl of 4 to 13 carbon atoms, cycloalkenyl alkyl of 5 to 13 carbon atoms, substituted cycloalkyl, substituted cycloalkenyl or (substituted cycloalkyl) alkyl of 4 to 14 carbon atoms, or (substituted cycloalkenyl) alkyl of 5 to 14 carbon atoms;

R_2 is hydrogen, chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy or t-butoxy; and

R_3 is alkyl of 1 to 5 carbon atoms, chloroalkyl of 1 to 4 carbon atoms or bromoalkyl of 1 to 4 carbon atoms; or in which

R_2 and R_3 are joined together to form $-(CH_2)_n-$, where n is 3, 4 or 5; and salts of said compounds.

Examples of suitable substituted alkyl radicals are bromoalkyl of 1 to 8 carbon atoms, chloroalkyl or 1 to 8 carbon atoms, hydroxyalkyl of 1 to 8 carbon atoms, alkoxyalkyl of 2 to 8 carbon atoms, alkoxy carbonyl alkyl of 3 to 8 carbon atoms, and cyanoalkyl of 2 to 8 carbon atoms.

Suitable aryl and substituted phenyl radicals are, for example, phenyl, naphthyl, biphenyl, chlorophenyl, bromophenyl, alkoxyphenyl, dibromophenyl, dichlorophenyl, fluorophenyl, trichlorophenyl, alkylphenyl of 7 to 11 carbon atoms, dialkylphenyl of 8 to 12 carbon atoms, chloroalkylphenyl of 7 to 10 carbon atoms, nitrochlorophenyl, nitrophenyl, dichloronitrophenyl, chloroalkoxyphenyl of 7 to 11 carbon atoms, trifluoromethylphenyl, tetrahydronaphthyl, and indenyl.

Examples of aralkyl and substituted aralkyl radicals are benzyl, phenylalkyl of 8 to 11 carbon atoms (total), chlorobenzyl, dichlorobenzyl, alkylbenzyl of 8 to 11 carbon atoms (total), dialkylbenzyl of 9 to 13 carbon atoms (total), nitrobenzyl, alkoxybenzyl of 8 to 11 carbon atoms (total), and naphthylmethyl.

Suitable cycloalkyl, cycloalkenyl, cycloalkyl

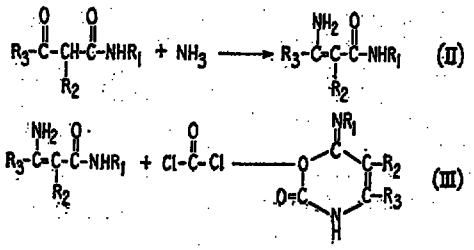
alkyl, and cycloalkenyl alkyl radicals are, for example, cyclohexyl, cyclohexenyl, cyclohexylalkyl, cyclohexenylalkyl, cyclopentyl, cyclopentenyl, cyclopentylalkyl, cyclopentenylalkyl, norbornyl, norbornenyl, norbonylalkyl, norbornenylalkyl, bicyclo(2,2,2)octyl, bicyclo(2,2,2)octenyl, bicyclo(2,2,2)octylalkyl, bicyclo(2,2,2)octenylalkyl, cyclopropyl, cyclobutyl, cyclobutylalkyl, cyclobutenyl, cyclobutenylalkyl, hexahydroindanyl, tetrahydroindanyl, hexahydroindenyl, hexahydroindenyl alkyl, tetrahydroindanyl alkyl, hexahydroindanyl alkyl, hexahydro-4,7-methanoindenyl, tetrahydro-4,7-methanoindanyl, hexahydro-4,7-methanoindanyl, hexahydro-4,7-methanoindenyl alkyl, tetrahydro-4,7-methanoindanyl alkyl, hexahydro-4,7-methanoindanyl alkyl, decahydronaphthyl, decahydronaphthyl alkyl, tetrahydronaphthyl, tetrahydronaphthyl alkyl, decahydro-1,4-methanonaphthyl, decahydro-1,4-methanonaphthyl alkyl, octahydro-1,4-methanonaphthyl, octahydro-1,4-methanonaphthyl alkyl, decahydro-1,4—5,8-dimethanonaphthyl, decahydro-1,4—5,8-dimethonaphthyl alkyl, octahydro-1,4—5,8-dimethanonaphthyl, and octahydro-1,4—5,8-dimethanonaphthyl alkyl.

The cyclic substituents can be further substituted with alkyl groups of 1 to 4 carbon atoms, methoxy groups, chlorine and bromine.

The compounds of the invention in the form of a free base are highly unstable but they can conveniently be prepared in the form of salts with organic or inorganic acids, which are therefore preferred. Examples of preferred salts are the salts of hydrochloric acid, hydrobromic acid, hydroiodic acid, sulphuric acid, sulphamic acid, benzoic acid, acetic acid, phosphoric acid, phthalic acid, citric acid, succinic acid, maleic acid, tartaric acid, propionic acid, dichloroacetic acid, trichloroacetic acid and *alpha,alpha*-dichloropropionic acid.

Further, according to the invention, we provide a method of preparing the compounds defined above which is a simple but remarkable two-step process, and which comprises reacting a substituted acetoacetamide with ammonia to form a substituted *beta*-aminocrotonamide and reacting the resulting *beta*-aminocrotonamide with phosgene to form the corresponding oxazine-2-one hydrochloride salt.

The process proceeds according to the following equations:



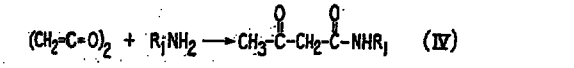
(II)

(III)

R_1, R_2 and R_3 being as defined above. The acetoacetamides used in the reaction with ammonia are prepared either by reaction of an amine with diketone as described below or by reaction of a *beta*-keto ester with excess amine followed by treatment with aqueous acid.

A preferred process in which R_2 is hydrogen and R_3 is methyl is hereinafter described, by way of example only.

The acetoacetamide used as the starting material is prepared by reacting diketene with an amine according to the equation:



(IV)

This procedure is described in greater detail in United States Patent No. 2,615,917.

A solution of the acetoacetamide in water or an inert organic solvent, such as ether, tetrahydrofuran, an alcohol or 1,1,2-trichloroethylene, is then admixed with ammonia and the reaction mass stirred. If water is used as the solvent, the ammonia can conveniently be added as an aqueous solution, for example concentrated aqueous ammonia containing 28—30% by weight ammonia. If an inert organic solvent is used, the ammonia can be introduced as a gas or as an undiluted liquid.

The mol ratio of ammonia to acetoacetamide should be at least 1 to 1. The use of an excess of ammonia results in an increased yield of *beta*-aminocrotonamide, the upper limit of ammonia being largely determined by convenience and economics but no reason is seen to exceed an ammonia to acetacetamide mol ratio of 50 to 1, and a ratio of below 10 to 1 is preferred.

The temperature at which the reaction is carried out is largely a matter convenience but, at ambient pressure, temperatures above about 50°C. are disadvantageous because of undesired loss of ammonia. The reaction temperature is preferably in the range from minus 30° to 30°C. The reaction is generally complete in about 1 to 10 hours, the precise time depending upon the reaction temperature and the system employed.

The *beta*-aminocrotonamide product is recovered by any convenient physical means, such as by filtration, separation of layers or evaporation of the solvent. After recovery, the *beta*-aminocrotonamide product can be dried and then reacted with phosgene, or, if desired, it may be purified by customary methods, such as recrystallization.

The preparation of a 6-amino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride from a *beta*-aminocrotonamide and phosgene will now be described to illustrate this part of the process.

A solution of phosgene is prepared in a

suitable inert organic solvent, such as tetrahydrofuran, dioxane, acetonitrile or 1,1,2-trichloroethylene, and is admixed with a solvent solution or slurry of the *beta*-aminocrotonamide, which is preferably in the same solvent as the phosgene. Equimolar amounts of *beta*-aminocrotonamide and phosgene can be used but for improved efficiency and economy a slight excess of phosgene is preferred. Ordinarily the amount of phosgene used will not exceed 5 mols and preferably will not exceed 2 mols for each mol of *beta*-aminocrotonamide. It is advantageous to add the crotonamide solution or slurry to the phosgene solution and to maintain an excess of phosgene by adding phosgene to keep the solution saturated. Superatmospheric pressure can be used to advantage.

The reaction is highly exothermic and since it is desirable to carry out the admixing at moderate temperatures, for example 25° to 50°C., in order to minimize vaporization of the phosgene, external cooling means, such as a refrigerated condenser, may be employed.

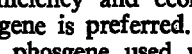
When all the *beta*-aminocrotonamide solution has been added to the phosgene, the mixture contains a solid phase. The reaction may be completed by heating the mixture at a temperature from 40° to 100°C. for 30 minutes to 6 hours, the hydrochloride salt of the 6-imino - 3,6 - dihydro - 4 - methyl - 2H—1,3-oxazin - 2 - one being formed. This compound can be recovered by any convenient means, such as filtration or decantation of the supernatant liquid.

The hydrochloride salt can be converted to other salts of the oxazinone by conventional replacement reactions or by neutralization of the hydrochloride, for example by the use of silver oxide suspended in an inert solvent such as methylene chloride, followed by the filtration of the silver chloride and the addition of the acid required for the desired salt. Salts of acids weaker than hydrochloric acid can be prepared by suspending or dissolving the oxazinone hydrochloride in an inert solvent (or simply in the weaker acid if it is a liquid), adding the appropriate amount of the weaker acid and a salt of the weaker acid, e.g. the sodium salt, and filtering off or otherwise removing the sodium chloride formed.

Those oxazinone compounds when R_2 is chlorine or bromine can be prepared from compounds in which R_2 is hydrogen by conventional halogenation procedures, for example by reaction with the halogen in glacial acetic acid or other solvent.

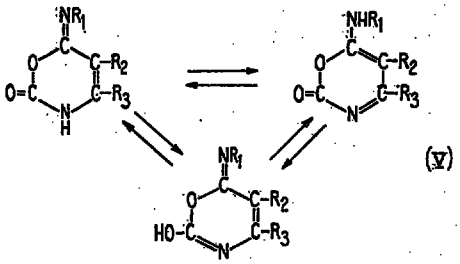
These oxazinone compounds mostly do not have distinct melting points but on heating they lose hydrogen chloride and are converted to the corresponding uracil, as is described in greater detail hereinafter. They are soluble in water and somewhat soluble in highly polar organic solvents such as acetic acid and alcohols, but are insoluble in the less polar organic solvents.

The oxazinone salts exhibit distinctive infrared absorption. Characteristic features are (a) the lack of absorption at the N—H stretching frequency, (b) an intense absorption at 1770—1810 cm.$^{-1}$ which can be attributed to the



moiety of the structure of figure I above, (c) multiple absorption in the range of 1570 to 1660 cm.$^{-1}$, probably due to absorption by >C=C, >C=N— and >C=O, and (d) absorption of medium intensity at 1510—1515 cm.$^{-1}$ which is characteristic of monosubstituted amides. Nuclear magnetic resonance and ultraviolet studies are consistent with the assigned oxazinone ring system.

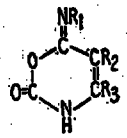
The above information indicates three tautomeric structures for the compounds, viz.



(V)

As mentioned above, many of the compounds of this invention exhibit herbicidal activity. Because of their outstanding usefulness as general purpose herbicides against both broadleaf and grass wedds, salts of compounds in which R_1 is other than hydrogen are preferred.

Salts which are particularly preferred for their herbicidal effectiveness are salts of compounds of the following formula:



(VI)

in which R_1 is as defined above, R_2 is hydrogen, chlorine or bromine; and R_3 is methyl; and where R_2 and R_3 can be joined together to form $—(CH_2)_n—$, where n is 3, 4 or 5, and provided that, when R_2 is hydrogen and R_3 is methyl, R_1 is other than methyl or ethyl.

Particularly preferred compounds are salts, and particularly the hydrochloride and hydrobromide salts, of the following oxazinones:

6 - sec - butylimino - 5 - chloro - 3,6 - dihydro - 4 - methyl - 2H—1,3 - oxazin - 2-one,

6 - sec - butylimino - 5 - bromo - 3,6 - di-

hydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one,
6 - norbornylimino - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazin - 2 - one,
6 - norbornylmethylimino - 5 - bromo - 3,6-dihydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one,
6 - (1 - ethylpropylimino) - 5 - bromo - 3,6-dihydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one,
6 - (1,3 - dimethylbutylimino) - 5 - chloro-3,6 - dihydro - 4 - methyl - 2H — 1,3-oxazin - 2 - one,
6 - isopropylimino - 5 - bromo - 3,6 - dihydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one,
6 - t - butylimino - 5 - bromo - 3,6 - dihydro-4 - methyl - 2H — 1,3 - oxazin - 2 - one,
6 - phenylimino - 5 - bromo - 3,6 - dihydro-4 - methyl - 2H — 1,3 - oxazine - 2 - one,
6 - (3a,4,7,7a - tetrahydro - 4,7 - methanoindan - 2 - ylimino) - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazin - 2 - one,
6 - cyclohexylimino - 5 - bromo - 3,6 - dihydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one,
6 - cyclohexylimino - 4,5 - trimethylene - 3,6-dihydro - 2H — 1,3 - oxazin - 2 - one.

Particular processes for preparing the compounds of this invention are given in the following Examples, in which all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1.

6-sec-Butylimino-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride.

540 parts (70% excess) of concentrated (29%) aqueous ammonia were added to 852 parts of *N*-sec-butylacetoacetamide and the clear solution stirred and kept at room temperature in order to avoid an excessive loss of ammonia. After about 6 minutes, the solution turned cloudy and an oil began to separate. Crystallisation was induced by scratching the vessel wall, and precipitation of the product *beta*-amino-*N*-sec-butylcrotonamide was complete in 4 hours. The resulting thick crystal mass was filtered and the solid washed with ice water and dried in a vacuum oven at 55°—60°C. The product was weighed and found to be 696 parts (82% of theory) and melted at 84°—88°C. Recrystallisation from benzene raised the melting point to 89°—90°C.

Anal. calculated for $C_8H_{16}N_2O$: N, 17.9
Found: N, 17.7

31.2 parts of *beta*-amino-*N*-sec-butylcrotonamide in 75 parts of tetrahydrofuran were added dropwise with stirring to a solution of 22 parts of phosgene in 100 parts of tetrahydrofuran. A solid precipitated and the temperature rose to 45°C. The mixture was stirred and refluxed for 2 hours, cooled and filtered to obtain 27 parts of 6 - sec-butylimino - 3,6 - dihydro - 4 - methyl - 2H—1,3 - oxazin - 2 - one hydrochloride which melted at 151.5°—162.5°C. with gas evolution.

Anal. calculated for $C_9H_{15}ClN_2O_2$: N, 13.2
Found: N, 12.8

The infra-red spectrum of this material is characterised by a sharp peak at 5.6 microns ascribable to the —C(=N)—O—C(=O)— moiety, a peak at 3.7 microns (amine hydrochloride) and the absence of NH absorption in the 3 micron region.

The solid was soluble in water to the extent of about 27% by weight at room temperature and, on prolonged standing at room temperature, the aqueous solution evolved CO_2, the evolution being much more rapid on heating. Ammonium chloride and *N*-sec-butylacetamide could now be isolated from the solution.

Upon dry heating above the melting point until gas evolution ceased, followed by cooling, a solid was formed which does not depress the melting point of 3-sec-butyl-6-methyluracil (m.p. 118°—120°C.). The solid had an infra-red spectrum identical to that of the uracil.

When the oxazinone was dissolved in dilute aqueous solutions of NaOH, Na_2CO_3, $NaOOCCH_3$, or even $NaHCO_3$, virtually instantaneous rearrangement to the above-mentioned uracil took place. This uracil, which was present in the solution in the form of its sodium salt, was isolated by acidifying the solution, when the uracil separated as a syrup which crystallised on rubbing. Recrystallisation from an alcohol-water mixture yielded a solid which melted at 118°—120°C.

EXAMPLE 2.

6-Isopropylimino-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride.

29.3 parts of concentrated (28%) aqueous ammonia were added to a solution of 33.6 parts of *N*-isopropylacetoacetamide in 33.6 parts of water and the resulting solution stirred at ambient temperature for 6 hours, during which time *beta*-amino-*N*-isopropylcrotonamide was precipitated as a white crystalline solid. It was collected by filtration, washed and air dried to give 28.4 parts of material melting at 142°—144°C. The material was sufficiently pure for use in the following reaction with phosgene, but if desired it could have been further purified by recrystallisation from ethyl acetate and a purer material melting at 144°—145°C. obtained.

A solution of 56.8 parts of the *beta*-amino-*N*-isopropylcrotonamide in 400 parts of dioxane was added over a 5 minute period to a stirred solution of 43.6 parts of phosgene in 200 parts of dioxane. The reac-

tion temperature rose to about 50°C. and then began to decrease and at this time external heat was applied to maintain the temperature at 30°—100°C. for 2 hours. A yellow slurry formed which was cooled and the solid collected by filtration. It was washed with dioxane and ether and dried in vacuum at 25°—30°C., leaving 60.6 parts of 6 - isopropylimino - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazin - 2 - one hydrochloride, melting at 156°—160°C. with gas evolution.

Anal. calculated for $C_8H_{13}ClN_2O_2$: N, 13.69
Found: N, 13.79.

EXAMPLE 3.

6-Phenylimino-3,6-dihydro-4-methyl-2H—1,3-oxazine-2-one hydrochloride.

67 parts of concentrated (28%) aqueous ammonia were added to a stirred solution of 88.6 parts of acetoacetanilide in 1500 parts of water and 150 parts of methanol at 73°C. After several minutes an oil was formed and crystallisation was initiated by scratching the wall of the vessel. After 2 hours the slurry was cooled in ice, filtered and the solid washed with 400 parts of cold water and dried in a vacuum oven at 60°C., leaving 69 parts of *beta*-amino-*N*-phenyl-crotonamide (78% of theory) melting at 140.5°—142.3°C.

A solution of 8.8 parts of the *beta*-amino-*N*-phenylcrotonamide in 40 parts of tetrahydrofuran was added over a 10 minute period to a solution of 5.5 parts of phosgene in 25 parts of tetrahydrofuran. The slurry was heated at 60°—70°C. for 2 hours, then cooled and the solid collected by filtration, washed with tetrahydrofuran and air dried to give 7.6 parts of 6 - phenylimino - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazin - 2 - one hydrochloride melting at 238°—244°C. with gas evolution.

Anal. calculated for $C_{11}H_{11}ClN_2O_2$: N, 11.74
Found: N, 11.72.

EXAMPLES 4—25.

The products of Examples 4—25 were prepared according to the procedure of Example 3 by replacing the acetoacetanilide of that Example with molecular equivalents of the acetoacetamides indicated to obtain the specified *beta*-aminocrotonamide, and finally the identified product.

Example	Acetoacetamide	Aminocrotonamide	Product
4	*N*-allylacetoacetamide	*beta*-amino-*N*-allyl-crotonamide	6-allylmino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
5	*N*-(*p*-tolyl)acetoacetamide	*beta*-amino-*N*-(*p*-tolyl)-crotonamide	6-(*p*-tolylimino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
6	*N*-octylacetoacetamide	*beta*-amino-*N*-octyl-crotonamide	6-octylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
7	*N*-norbornylaceto-acetamide	*beta*-amino-*N*-norbornyl-crotonamide	6-norbornylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
8	*N*-chloroethylaceto-acetamide	*beta*-amino-*N*-chloro-ethylcrotonamide	6-chloroethylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
9	*N*-benzylacetoacetamide	*beta*-amino-*N*-benzyl-crotonamide	6-benzylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride

Example	Acetoacetamide	Aminocrotonamide	Product
10	*N*-cyclohexenylaceto-acetamide	*beta*-amino-*N*-cyclo-hexenylcrotonamide	6-cyclohexenylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
11	*N*-methylacetoacetamide	*beta*-amino-*N*-methyl-crotonamide	6-methylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
12	*N*-*o*-fluorophenyl-acetoacetamide	*beta*-amino-*N*-*o*-fluoro-phenylcrotonamide	6-(*o*-fluorophenyl-imino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
13	*N*-norbornylmethyl-acetoacetamide	*beta*-amino-*N*-norbornyl-methylcrotonamide	6-norbornylmethyl-imino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
14	*N*-(1-ethylpropyl)-acetoacetamide	*beta*-amino-*N*-(1-ethyl-propyl)crotonamide	6-(1-ethylpropylimino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
15	*N*-(1,3-dimethylbutyl)-acetoacetamide	*beta*-amino-*N*-(1,3-dimethylbutyl)-crotonamide	6-(1,3-dimethylbutyl-imino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
16	*N*-(3a,4,7,7,a-tetra-hydro-4,7-methano-indan-2-yl)aceto-acetamide	*beta*-amino-*N*-(3a,4,7,7a-tetrahydro-4,7-methano-indan-2-yl)crotonamide	6-(3a,4,7,7a-tetrahydro-4,7-methanoindan-2-ylimino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
17	*N*-naphthyl-*alpha*-methylacetoacetamide	*beta*-amino-*alpha*-methyl-*N*-naphthyl-crotonamide	6-naphthylimino-3,6-dihydro-4,5-dimethyl-2H-1,3-oxazin-2-one hydrochloride
18	2-keto-*N*-isopropyl-cyclopentanecarbox-amide	2-amino-*N*-isopropyl-1-cyclopentanecarbox-amide	6-isopropylimino-3,6-dihydro-4,5-trimethylene-2H-1,3-oxazin-2-one hydrochloride
19	*N*-~~(3-methoxy)propyl~~-acetoacetamide	*beta*-amino-*N*-(3-methoxypropyl)-crotonamide	6-(3-methoxypropylimino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
20	*N*-sec-butyl-4-bromo-3-keto-butyramide	*beta*-amino-*N*-sec-butyl-4-bromocrotonamide	6-sec-butylimino-3,6-dihydro-4-bromomethyl-2H-1,3-oxazin-2-one hydrochloride
21	*N*-cyclopropyl-3-keto-2-methylbutyramide	*beta*-amino-*N*-cyclo-propyl-2-methyl-crotonamide	6-cyclopropylimino-3,6-dihydro-4,5-dimethyl-2H-1,3-oxazin-2-one hydrochloride

PATENT OFFICE

(3-methoxypropyl)

Example	Acetoacetamide	Aminocrotonamide	Product
22	*N*-propynyl-2-butyl-3-keto-butyramide	*beta*-amino-*N*-propynyl-2-butylcrotonamide	6-propynylimino-3,6-dihydro-4-methyl-5-butyl-2H-1,3-oxazin-2-one hydrochloride
23	*N*-octen-2-yl-4-chloro-3-keto-2-methoxy-butylamide	*bets*-amino-*N*-octen-2-yl-4-chloro-2-methoxycrotonamide	6-octen-2-yl-imino-3,6-dihydro-4-chloro-alkyl-5-methoxy-2H-1,3-oxazin-2-one hydrochloride
24	*N*-cyclobutenyl-2-butoxy-3-keto-octanamide	*beta*-amino-*N*-cyclo-butenyl-2-butoxyocten-2-amide	6-cyclobutenylimino-3,6-dihydro-4-pentyl-5-butoxy-2H-1,3-oxazin-2-one hydrochloride
25	*N*-cyclooctyl-2-ketocycloheptane-carboxamide	2-amino-*N*-cyclo octyl-cycloheptane-carboxamide	6-cyclooctylimino-3,6-dihydro-4,5-pentanethylene-2H-1,3-oxazin-2-one hydrochloride

EXAMPLE 26.

6-sec-Butylimino-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one.

A slurry of 6 - sec - butylimino - 3,6-dihydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one hydrochloride in methylene chloride was stirred with an excess of silver oxide and filtered after 3 minutes. A solution of the free oxazinone was thus obtained and this was placed immediately in a recording infra-red spectrophotometer, the region between 5.5 and 6.1 microns being recorded. The spectrum showed a characteristic oxazinone peak at 5.7 microns (a shift of 0.1 micron to higher wavelength due to neutralization of the HCl salt), but no peak at 5.85 microns which is characteristic of the corresponding 3-sec-butyl-6-methyluracil. The solution was left in the infra-red machine and the same region recorded at various time intervals. It was observed that the 5.7 micron peak gradually diminished while a peak at 5.85 microns formed and became larger. After 45 minutes the oxazinone peak had all but vanished while the uracil peak was very strong, and after 1 hour and 15 minutes no trace of the oxazinone peak remained, while the uracil peak had reached maximum intensity.

The above observations clearly demonstrate the existence, as well as the relative instability, of the free oxazinones.

Examples 27 to 34 indicate other oxazinones which were prepared by the procedure of Example 26.

Example	Oxazinone
27	6 - phenylimino - 3,6 - dihydro-4 - methyl - 2H — 1,3 - oxazin-2 - one.
28	6 - sec - butylimino - 5 - bromo-3,6 - dihydro - 4 - methyl-2H — 1,3 - oxazin - 2 - one.
29	6 - isopropylimino - 5 - chloro-3,6 - dihydro - 4 - methyl-2H — 1,3 - oxazin - 2 - one.
30	6 - norbornylimino - 3,6 - dihydro-4 - methyl - 2H — 1,3 - oxazin-2 - one.
31	6 - cyclohexylimino - 5 - bromo-3,6 - dihydro - 4 - methyl-2H — 1,3 - oxazin - 2 - one.
32	6 - t - butylimino - 5 - bromo-3,6 - dihydro - 4 - methyl-2H — 1,3 - oxazin - 2 - one.
33	6 - imino - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazin-2 - one.
34	6 - (2 - methylcyclohexylimino)-5 - chloro - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazin-2 - one.

EXAMPLE 35.

6 - sec - Butylimino - 5 - bromo - 3,6-dihydro - 4 - methyl - 2H — 1,3 - oxazin-2 - one hydrobromide.

17.6 parts of bromine were added dropwise to a solution of 11 parts of 6 - sec - butyl-

imino - 3,6 - dihydro - 4 - methyl - 2H—1,3 - oxazin - 2 - one hydrochloride in 45 millilitres of water with stirring. A precipitate was formed which after filtration, washing with water and ether, and drying, weighed 8 parts. Recrystallisation from acetic acid yielded 6.5 parts of large white crystals melting at 151°—154°C. with decomposition.

Anal. calculated for $C_9H_{14}Br_2N_2O_2$: N, 8.2
Found: N, 8.0

The infra-red spectrum was similar to that of the starting material (sharp peak at 5.6 microns) and contained a peak at 15 microns ascribable to the 5-bromo substituent. The bromo compound can be converted to the corresponding 5 - bromo - 3 - sec - butyl - 6-methyluracil (m.p. 157°—159.5°C.) by the same methods described above for the starting material. The bromo compound is less water-soluble than the corresponding chloro compound.

EXAMPLES 36—40.

The products of Examples 36—40 were prepared according to the procedure of Example 29 by replacing the 6 - sec - butylimino - 3,6 - dihydro - 4 - methyl - 2H—1,3 - oxazin - 2 - one hydrochloride of that Example with molecular equivalents of the oxazinones indicated to obtain the specified 5-bromo compound.

Example	Starting Oxazinone	Product
36	6-t-butylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide	6-t-butylimino-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide
37	6-phenylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide	6-phenylimino-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide
38	6-isopropylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide	6-isopropylimino-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide
39	6-methylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide	6-methylimino-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide
40	6-(1,3-dimethylbutylimino)-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide	6-(1,3-dimethylbutylimino)-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrobromide

EXAMPLE 41.

6-sec-Butylimino-5-chloro-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride.

A slurry of 15 parts by weight of 6 - sec-butylimino - 3,6 - dihydro - 4 - methyl-2H — 1,3 - oxazin - 2 - one hydrochloride in 75 millilitres of glacial acetic acid was stirred at room temperature and simultaneously chlorine gas was introduced. The slurry became thinner at first, and then a thick white precipitate formed which was filtered, washed with acetic acid and acetone, and dried. It weighed 12 parts and melted at 144°—150°C.

Anal. calculated for $C_9H_{14}Cl_2N_2O_2$: N, 11.1
Found: N, 10.9.

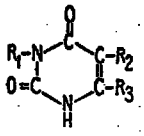
The infra-red spectrum of this product was very similar to that of the starting material (sharp peak at 5.6 microns) but it contained an additional peak at 14.5 microns ascribable to the 5-chloro substituent. The chloro compound was converted to the corresponding 5-chlorouracil (m.p. 152°—153.5°C.) in the same manner as described above for the starting oxazinone by heating above the melting point or treatment with dilute aqueous solutions of NaOH, Na_2CO_3, $NaOOCCH_3$ or $NaHCO_3$. The water solubility of the 5-chloro oxazinone was about 8% by weight at room temperature.

EXAMPLES 42—46.

The products of Examples 42—46 were prepared according to the procedure of Example 41 by replacing the 6 - sec-butylimino - 3,6 - dihydro - 4 - methyl-2H — 1,3 - oxazine - 2 - one hydrochloride of that Example with molecular equivalents of the oxazinones indicated to obtain the specified 5-chloro compound.

Example	Starting Oxazinone	Product
42	6-isopropylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride	6-isopropylimino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
43	6-ethylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride	6-ethylimino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
44	6-imino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride	6-imino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
45	6-norbornylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride	6-norbornylimino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride
46	6-t-butylimino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride	6-t-butylimino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride

One very important use for the oxazinone compounds is for conversion to uracils. This conversion is readily carried out by reacting the reaction product of the *beta*-aminocrotonamide and phosgene with an inorganic base and, if necessary, an acidifying agent to produce a uracil of the formula:



(VII)

The conversion of the oxazinone derivative can be carried out using the slurry of the oxazinone hydrochloride salt formed from the phosgenation of the aminocrotonamide or, alternatively, where the oxazinone salt has been recovered in solid crystalline form, the oxazinone salt can be admixed with a suitable inert liquid such as water or organic solvent to form a solution or slurry.

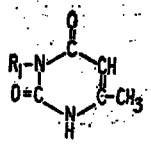
The slurry from either source is admixed with sufficient aqueous base, for example sodium hydroxide, potassium hydroxide or sodium carbonate, to neutralize the acid salt to pH 7 or above and preferably to bring the pH within the range of about 8 to 10. This results in almost immediate conversion to a solution of the uracil salt, which in turn is easily converted to the corresponding uracil with an acid, for example sulphuric acid or hydrochloric acid; other acids, such as acetic acid and formic acid are also satisfactory but they are, of course, more expensive. The uracils are isolated by filtration or, if they are soluble in the aqueous medium, they are isolated by extraction with a suitable solvent, for example methylene chloride or ether.

Instead of proceeding by formation of the uracil salt followed by acidification, the oxazinone can be directly converted to the uracil by admixing with the oxazinone in the liquid system just sufficient base to neutralize the salts, i.e. one mol of base per mol of the oxazinone salt. With weak bases such as sodium bicarbonate, excess base still allows recovery of the free uracil.

We have discovered that the yields of uracil based on the oxazinone compound are essentially quantitative, whether carried out by converting the oxazinone directly to the uracil or first forming the uracil salt and then acidifying.

It will be appreciated that this conversion to uracils provides a remarkably efficient route for the preparation of uracils from commercially available and relatively inexpensive starting materials. Furthermore the process may be carried out in a series of separate or combined steps.

In a preferred process, the *beta*-aminocrotonamide was prepared from diketene and an amine so that R_3 was methyl and R_2 was hydrogen, and this was phosgenated as hereinbefore described to obtain the corresponding oxazinone hydrochloride. This was then converted at pH 9—10 with sodium hydroxide to form the corresponding uracil salt which in turn was converted by treatment with sulphuric acid to the corresponding uracil of the formula:



(VIII)

The class of 3-substituted uracils and 5-halogenated 3-substituted uracils are particularly outstanding herbicides, giving unusually effective control of undesired vegetation at economic rates.

The above-described process for preparing uracils is notably advantageous because it is a rapid, high yield approach to the synthesis of useful uracils employing as the only essential reactants the diketene, amines, phosgene and an alkali, which do not need to be converted with extra expense and difficulty to extraneous intermediates.

The following Examples are given to illustrate the conversion of oxazinones to corresponding uracils, either directly or through the uracil salt. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 47.

A solution of 15.6 parts of *beta*-amino-*N*-sec-butylcrotonamide, prepared as described in Example 1, in 40 parts of tetrahydrofuran was added to a stirred solution of 10.9 parts of phosgene in 50 parts of tetrahydrofuran, over a 15 minute period at ambient temperature. The temperature rose to about 50°C. during the addition and a yellow slurry formed which was heated under reflux for 2 hours. The solid present in the slurry at this point was 6 - sec - butylimino - 3,6 - dihydro - 4-methyl - 2H — 1,3 - oxazine - 2 - one hydrochloride. The slurry was then poured into 200 parts of 2N aqueous sodium hydroxide, with stirring, and the resulting solution extracted twice with 100 parts of methylene chloride to remove alkali-insoluble organic impurities. The aqueous portion was then acidified with concentrated hydrochloric acid and the resulting 3-sec-butyl-6-methyluracil isolated by extracting four times with 100 parts each of methylene chloride. Evaporation of the solvent left 13.4 parts of the uracil.

EXAMPLE 48.

A solution of 9.6 parts of *beta*-amino-*N*-phenylcrotonamide, prepared as in Example 3, in 40 parts of tetrahydrofuran was added to a stirred solution of 5.5 parts of phosgene in 25 parts of tetrahydrofuran over a 15 minute period. After the initial exothermic reaction had subsided, the mixture was heated at 63°—67°C. for 2 hours and then cooled and poured into 200 parts of 2N aqueous sodium hydroxide. After extraction twice with 150 parts each of methylene chloride to remove impurities, the aqueous solution was acidified with concentrated hydrochloric acid and the product isolated by extraction six times with 100 parts each of methylene chloride, followed by evaporation of the methylene chloride. 7.5 parts of 3-phenyl-6-methyluracil, melting at 224°—250°C. were obtained.

As mentioned above, the oxazinone compounds, especially those indicated to be preferred, are effective herbicides. They exert herbicidal action against both broadleaf and grass weeds, are effective against hard-to-kill nutsedge and perennial grasses such as quack grass, Johnson grass, and Bermuda grass, and are effective on highly absorptive substrates such as railroad ballast, heavy clay soil, and soils having a high organic matter content. This combination of properties makes the compounds useful wherever general weed control is required, such as industrial areas, railroad rights-of-way, and areas adjacent to croplands in agricultural areas.

Certain of the compounds of this invention also exhibit selective herbicidal action in crops. By suitable selection of oxazinone compounds and rate and time of application, annual grass and broadleaf seedlings in such crops as asparagus, corn, flax, sugar cane, pineapple, safflower, peanuts, citrus, alfalfa, strawberries, gladiolus, stone fruits and cucurbits can be controlled. With an appropriate rate and time of application, certain of the oxazinones can also be used to control weeds growing in dormant crops.

The precise amounts of oxazinones to be used in any given situation will, of course, vary according to such factors as the particular end result desired, the use involved, the plant and soil involved, the formulation used, the mode of application, prevailing weather conditions and foliage density. Since so many variables play a role, it is not possible to indicate a rate of application suitable for all situations but, broadly speaking, the compounds are used at levels of about ¼ pound per acre to about 25 pounds per acre. For selective weed control in crops, rates of ¼ to 8 pounds per acre are generally used. More of the active material can be used to control difficult-to-kill species growing under adverse conditions or in cases where economic factors, such as inaccessibility of the area to be treated, e.g. fire breaks in forests, may also favour higher rates of application with less frequent treatments.

The herbicidal compounds can be formulated as dusts, as wettable powders, or as soluble powders. In these formulations, care must be taken that diluents, surface active agents, and other pesticidal additives are neutral in pH and are particularly free of reserve alkalinity. It is also important that the formulation ingredients are dry and that during handling of the ingredients, preparation of the compositions, and storage of the compositions, water be rigidly excluded. Insofar as possible, the diluents and surfactants and other additives should also be inert chemically and should be reasonably free of active OH groups.

Particularly advantageous results have been

obtained using the following substantially anhydrous composition, the percentages being by weight:

Active ingredient (oxazinone salt)	30 —60%
Non-ionic Surfactant	0.1—10%
Remainder—Inert Diluents	to 100%

The maximum amount of water which may be present is 1% by weight based on the weight of the oxazinone salt present.

Suitable diluents for the preparation of dusts and ~~wetable~~ Wettable powders are finely divided, pulverulent solids, with neutral or slightly acidic surface reactions such as synthetic fine silicas, diatomaceous earths, and acidic kaolinite clays. Examples of the above are "Hi-Sil", "Celite" 209 (Hi-Sil and Celite are Registered Trade Marks), Continental clay, Barnet clay, and Pike's Peak clay 9T66. Other diluents which can sometimes be used are inert vegetable flours, such as Redwood flour and walnut shell flour.

When such diluents are used in the preparation of herbicidal dusts, the amount of active ingredient present is preferably from 0.5 to 15%, with the remainder primarily being one or more of the above-named diluents. When the composition to be prepared is a wettable powder, the amount of active ingredient present may be from 10 to about 85%, the remainder being diluent except for the presence of from about 0.1 to 5% or 10% of one or more surfactant.

Surfactants for use in these compositions can be of the anionic, cationic, and non-ionic type, although anionic surfactants are preferred and non-ionic surfactants are very much preferred. It is important that the anionic surfactants be not highly alkaline, and with this limitation, surfactants such as salts of alkyl aryl sulphonic acids, and petroleum sulphonates and salts of fatty alcohol sulphates can be used. A list of such surfactants is shown in "Detergents and Emulsifiers Up-to-date 1962" by John W. McCutcheon, Inc. Other anionic surfactants which may be used are salts of dialkyl esters of sulphosuccinates and of fatty acid esters of isethionic acids and, in some instances, the free acid instead of the salt can also be advantageously used.

Polyethylene glycol fatty esters, polyoxyethylene ethers and thioethers are very much preferred non-ionic surfactants. Other non-ionic surfactants are alkylphenoxypolyethyleneoxyethanols, such as nonylphenyl adducts with ethylene oxide, trimethylnonylpolyethylene glycol ethers, polyethylene oxide adducts of fatty and rosin acids, polyethylene oxide adducts of sorbitan esters of fatty and rosin acids, and long-chain alkyl mercaptan adducts with ethylene oxide. Polyglycol ethers in which both terminal alcohol groups have been esterified with fatty acids such as lauric, oleic, palmitic, or stearic acids are particularly preferred.

It is often also desirable to formulate the compounds of this invention as soluble solids. Such compositions consist of from 75 to 95% of the active ingredient with the remainder being one or more of the above-mentioned surface active agents. In order to prepare these compositions, the diluent and/or the surfactant is blended with the active ingredient in the conventional manner in a ribbon blender or similar device, and the mixture is then ground. As stated above, care must be taken to exclude moisture.

Other surface active dispersing agents, such as low viscosity methyl cellulose, or substantially neutral sodium lignosulphonates are also useful, especially in wettable powder compositions.

Formulation with Other Herbicides.

The herbicidal compositions of this invention can be formulated to contain two or more of the oxazinone salts, or to contain other known herbicides in addition to the oxazinones, to give compositions which have advantages over the individual components. Examples of known herbicides which can be combined with the compounds of formula 1 are:

Substituted Ureas

3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea

3 - (4 - chlorophenyl - 1,1 - dimethylurea

3 - phenyl - 1,1 - dimethylurea

3 - (3,4 - dichlorophenyl) - 3 - methoxy-1,1 - dimethylurea

3 - (4 - chlorophenyl) - 3 - methoxy - 1,1-dimethylurea

3 - (3,4 - dichlorophenyl) - 1 - n - butyl-1 - methylurea

3 - (3,4 - dichlorophenyl) - 1 - methoxy - 1-methylurea

3 - (4 - chlorophenyl) - 1 - methoxy - 1-methylurea

3 - (3,4 - dichlorophenyl) - 1,1,3 - trimethylurea

3 - (3,4 - dichlorophenyl) - 1,1 - diethylurea

3 - (*p* - chlorophenoxyphenyl) - 1,1 - dimethylurea.

These ureas can be mixed with the oxazinones in proportions of from 1:4 to 4:1, respectively, the preferred ratio being 1:2 to 2:1.

Substituted Triazines

2 - chloro - 4,6 - bis(ethylamino) - s-triazine

2 - chloro - 4 - ethylamino - 6 - isopropylamino - s - triazine

2 - chloro - 4,6 - bis(methoxypropylamino)-s - triazine

2 - methoxy - 4,6 - bis(isopropylamino)-s - triazine

2 - diethylamino - 4 - isopropylacetamido-6 - methoxy - s - triazine

2 - isopropylamino - 4 - methoxyethylamino - 6 - methylmercapto - s - triazine
2 - methylmercapto - 4,6 - bis(isopropylamino) - s - triazine
2 - methylmercapto - 4,6 - bis(ethylamino)-s - triazine
2 - methylmercapto - 4 - ethylamino - 6-isopropylamino - s - triazine
2 - methoxy - 4,6 - bis(ethylamino) - s-triazine
2 - methoxy - 4 - ethylamino - 6 - isopropylamino - s - triazine
2 - chloro - 4,6 - bis(isopropylamino) - s-triazine.

These triazines can be mixed with the compounds of this invention in proportions of from 1:4 to 4:1, respectively, the preferred ratio being 1:2 to 2:1.

Phenols

Dinitro - *o* - sec - butylphenol and its salts
Pentachlorophenol and its salts.

These phenols can be mixed with the compounds of this invention in the proportions of 1:10 to 20:1, respectively, the preferred ratio being 1:5 to 5:1.

Carboxylic Acids and Derivatives

The following carboxylic acids and derivatives can be mixed with the compounds of this invention in the listed proportions:

A. 2,3,6 - trichlorobenzoic acid and its salts
2,3,5,6 - tetrachlorobenzoic acid and its salts
2 - methoxy - 3,5,6 - trichlorobenzoic acid and its salts
2 - methoxy - 3,6 - dichlorobenzoic acid and its salts
3 - amino - 2,5 - dichlorobenzoic acid and its salts
3 - nitro - 2,5 - dichlorobenzoic acid and its salts
2 - methyl - 3,6 - dichlorobenzoic acid and its salts
2,4 - dichlorophenoxyacetic acid and its salts and esters
2,4,5 - trichlorophenoxyacetic acid and its salts and esters
(2 - methyl - 4 - chlorophenoxy)acetic acid and its salts and esters
2 - (2,4,5 - trichlorophenoxy)propionic acid and its salts and esters
2 - (2,4,5 - trichlorophenoxy)ethyl - 2,2-dichloropropionate
4 - (2,4 - dichlorophenoxy)butyric acid and its salts and esters
4 - (2 - methyl - 4 - chlorophenoxy)butyric acid and its salts and esters
2,3,6 - trichlorobenzyloxypropanol

Mixed in a 1:16 to 8:1 ratio, preferably a 1:4 to 4:1 ratio.

B. 2,6 - dichlorobenzonitrile

Mixed in a 1:4 to 4:1 ratio, preferably a 1:3 to 3:1 ratio.

C. Trichloroacetic acid and its salts

Mixed in a 1:2 to 25:1 ratio, preferably a 1:1 to 8:1 ratio.

D. 2,2 - dichloropropionic acid and its salts

Mixed in a 1:4 to 8:1 ratio, preferably a 1:2 to 4:1 ratio.

E. *N,N* - di - (n - propyl)thiolcarbamic acid, ethyl ester
N,N - di(n - propyl)thiolcarbamic acid, n - propyl ester
N - ethyl - *N* - (n - butyl)thiolcarbamic acid, ethyl ester
N - ethyl - *N* - (n - butyl)thiolcarbamic acid, n - propyl ester

Mixed in a 1:2 to 24:1 ratio, preferably a 1:1 to 12:1 ratio.

F. *N* - phenylcarbamic acid, isopropyl ester
N - (*m* - chlorophenyl)carbamic acid, isopropyl ester
N - (*m* - chlorophenyl)carbamic acid, 4 - chloro - 2 - butynyl ester

Mixed in a 1:2 to 24:1 ratio, preferably a 1:1 to 12:1 ratio.

G. 2,3,6 - trichlorophenylacetic acid and its salts

Mixed in a 1:12 to 8:1 ratio, preferably a 1:4 to 4:1 ratio.

H. 2 - chloro - *N,N* - diallylacetamide
Maleic hydrazide

Mixed in a 1:2 to 10:1 ratio, preferably a 1:1 to 5:1 ratio.

Inorganic and Mixed Inorganic-Organic Salts

The following salts can be mixed with the oxazinones in the listed proportions:

A. Calcium propylarsonate
Disodium monomethylarsonate
Octyl-dodecylammoniummethylarsonate
Dimethylarsinic acid

Mixed in a 1:4 to 4:1 ratio, preferably a 1:2 to 2:1 ratio.

B. Sodium arsenite

Mixed in a 1:5 to 40:1 ratio, preferably a 1:4 to 25:1 ratio.

C. Lead arsenate
Calcium arsenate

Mixed in a 150:1 to 600:1 ratio, preferably a 100:1 to 400:1 ratio.

D. Sodium tetraborate hydrated, granulated
Sodium metaborate
Sodium pentaborate
Polyborchlorate
Unrefined borate ore, such as borascu

Mixed in a 3:1 to 1500:1 ratio, preferably a 6:1 to 1000:1 ratio.

E. Ammonium thiocyanate

Mixed in a 1:10 to 20:1 ratio, preferably a 1:5 to 5:1 ratio.

F. Sodium chlorate

Mixed in a 1:1 to 40:1 ratio, preferably a 2:1 to 20:1 ratio.

G. Ammonium sulphamate

Mixed in a 1:1 to 100:1 ratio, preferably a 1:1 to 50:1 ratio.

Other Organic Herbicides

These organic herbicides can be mixed with the oxazinone salts in the listed proportions:

A. 5,6 - dihydro - (4A,6A) - dipyrido-(1,2 — A,2',1' — C)pyrazinium dibromide

Mixed in a 1:20 to 16:1 ratio, preferably a 1:5 to 5:1 ratio.

B. 3 - Amino - 1,2,4 - triazole

Mixed in a 1:20 to 20:1 ratio, preferably a 1:5 to 5:1 ratio.

C. 3,6 - endoxohexahydrophthalic acid

Mixed in a 1:3 to 20:1 ratio, preferably a 1:2 to 10:1 ratio.

D. Hexachloroacetone

Mixed in a 1:2 to 16:1 ratio, preferably a 1:1 to 8:1 ratio.

E. Diphenylacetonitrile

N,N - dimethyl - α,α - diphenylacetamide

N,N - di - n - propyl - 2,6 - dinitro-4 - trifluoromethylaniline

N,N - di - n - propyl - 2,6 - dinitro-4 - methylaniline

Mixed in a 1:10 to 30:1 ratio, preferably a 1:5 to 20:1 ratio.

F. *O* - (2,4 - dichlorophenyl) - *O* - methyl-isopropyl - phosphoramidothiate

2,3,5,6 - tetrachloroterephthalic acid, dimethyl ester

Mixed in a 1:4 to 20:1 ratio, preferably a 1:3 to 15:1 ratio.

G. 2,4 - dichloro - 4' - ~~nitrophenyl~~ ether

Mixed in a 1:10 to 30:1 ratio, preferably a 1:5 to 20:1 ratio.

Substituted Uracils

These oxazinone salts can be mixed with substituted uracils, in the proportions listed below. All of the indicated ratios are weight ratios. Methods for the preparation of the listed uracils are described in our copending application No. 46342/62.

A. 3 - cyclohexyl - 6 - methyluracil

3 - cyclohexyl - 6 - ethyluracil

3 - cyclohexyl - 6 - sec - butyluracil

3 - norbornyl - 6 - methyluracil

3 - cyclopentyl - 6 - methyluracil

3 - cyclohexyl - 6 - isopropyluracil

Mixed in a 1:4 to 4:1 ratio, preferably a 1:2 to 2:1 ratio.

B. 3 - cyclohexyl - 5,6 - trimethyleneuracil

3 - sec - butyl - 5,6 - trimethyleneuracil

3 - isopropyl - 5,6 - trimethyleneuracil

3 - isopropyl - 5,6 - tetramethyleneuracil

3 - isopropyl - 5,6 - pentamethyleneuracil

Mixed in a 1:6 to 6:1 ratio, preferably a 1:4 to 4:1 ratio.

C. 3 - cyclohexyl - 5 - bromouracil

3 - cyclohexyl - 5 - chlorouracil

3 - isopropyl - 5 - bromouracil

3 - sec - butyl - 5 - bromouracil

3 - sec - butyl - 5 - chlorouracil

Mixed in a 1:6 to 6:1 ratio, preferably a 1:2 to 2:1 ratio.

D. 3 - isopropyl - 1 - trichloromethylthio-5 - bromo - 6 - methyluracil

3 - cylcohexyl - 1 - trichloromethylthio-5 - bromo - 6 - methyluracil

3 - sec - butyl - 1 - acetyl - 5 - bromo-6 - methyluracil

3 - isopropyl - 1 - acetyl - 5 - bromo-6 - methyluracil

3 - isopropyl - 1 - trichloromethylthio-5 - chloro - 6 - methyluracil

Mixed in a 1:4 to 4:1 ratio, preferably a 1:2 to 2:1 ratio.

E. 3 - sec - butyl - 5 - bromo - 6 - methyluracil

3 - isopropyl - 5 - bromo - 6 - methyluracil

3 - sec - butyl - 5 - chloro - 6 - methyluracil

3 - phenyl - 5 - bromo - 6 - methyluracil

3 - (1,3 - dimethylbutyl) - 5 - bromo-6 - methyluracil

3 - (1 - ethylpropyl) - 5 - chloro - 6-methyluracil

3 - cyclohexyl - 5 - bromo - 6 - methyluracil

Mixed in a 1:4 to 4:1 ratio, preferably a 1:2 to 2:1 ratio.

The following Examples illustrate the herbicidal utility of compositions of this invention, all parts and percentages being by weight except where otherwise indicated.

EXAMPLE 49.

N-Norbornylmethylimino-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride	80%
Polyethylene glycol dioleate	5%
"Hi-Sil"	15%

The above ingredients were blended and ground in a hammer mill until the particle size of substantially all the active ingredients was below 50 microns.

The wettable powder was used for the control of annual broadleaf and grass weeds growing around telephone poles and highway markers. An application of 5 pounds of active ingredient per acre in 40 gallons of water gave excellent control of crab grass, water grass, black-eyed susan, carpetweed, and chickweed.

EXAMPLE 50.

6-t-Butylimino-5-bromo-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrobromide	80.0%
Sodium lauryl sulphate	0.6%
Partially desulphonated sodium lignin sulphonate	1.0%
Calcined, non-swelling montmorillonoid type clay (Pikes Peak clay)	18.4%

A wettable powder was prepared by blending the above components and then micropulverizing them until substantially all the particles are below 50 microns in size. 20 pounds of active ingredient per acre in 100 gallons of water was used for weed control around oil tank installations and on railroad ballast. Excellent control of quack grass, crab grass, goose grass, Johnson grass, bitterweed, ox-eye daisy, mare's-tail, maple oak, and willow brush was obtained.

30 pounds of active ingredient per acre, as a spot treatment, provided excellent control of such deep-rooted weeds as bindweed and Canada thistle.

EXAMPLE 51.

6-isopropylimino-5-bromo-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrobromide	80.0%
Sodium lauryl sulphate	0.6%
~~Sidium~~ lignin sulphonate	2.0%
Kaolin clay	17.4%

The above components were blended and micropulverized until the solids were substantially all below 50 microns in particle size and the mixture then reblended until it is homogeneous.

The wettable powder was used as a general purpose weed killer on industrial sites and railroad ballast. 10 to 20 pounds of active ingredient per acre in 100 gallons of water gave excellent control of goldenrod, evening primrose, pokeweed, ox-eye daisy, cocklebur, goose grass, crab grass, and love grass.

20 pounds of active ingredient per acre in 50 gallons of water gave excellent control of nutsedge.

EXAMPLE 52.

6-sec-butylimino-5-bromo-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrobromide	95%
polyethylene glycol ester of fatty and rosin acids concreted with urea	5%

The above ingredients were mixed and ground and then mixed with water for prompt spray application as a solution.

The formulation was used at 1 to 2 pounds of active ingredient per acre in 30 gallons of water for the post-emergence control of annual weeds in sugar cane. A directed spray to seedling crab grass, water grass, pigweed, and lamb's quarters gave excellent control of these weeds.

EXAMPLE 53.

6-norbornylmethylimino-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride	40%
Soya lecithin	3%
Substantially aliphatic, low viscosity mineral oil, e.g. kerosene or diesel oil	57%

An oil suspension was prepared by pregrinding the active material and mixing it with the other components with agitation and, alternatively, by blending all the components together, then pebble-milling or sand-milling them to reduce the particle size of the active component. The product was suitable for dilution with weed oils to form an oil spray.

When diluted with 80 gallons of Lion Herbicidal Oil No. 6 and applied at 12 pounds of active ingredient per acre for general overall weed control along cyclone fences and railroad ballast, good control of quack grass, cheat, witch grass, buttonweed, and jimson weed was obtained for several months.

EXAMPLE 54.

6-cyclohexylimino-5-chloro-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride	90.0%
Alkyl naphthalene sulphonate, Na salt	2.0%
Low viscosity methyl cellulose	0.3%
Attapulgite clay	7.7%

The above components were blended and micropulverized until the particles of uracil had been reduced to about 10 microns in diameter and then reblended.

This formulation gave excellent weed control when applied, either pre-emergence or post-emergence, at rates of 4 pounds per acre to crab grass, wild oats, wild mustard, volunteer alfalfa, foxtail and lamb's quarters.

EXAMPLE 55.

6-sec-butylimino-5-chloro-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrochloride	10%
"Celite" 209 ("Celite" is a Registered Trade Mark	10%
kaolinite clay (acidic)	80%

The active ingredient and the "Celite" were blended and ground in a hammer mill until the mixture was uniform and the particle size

of substantially all the material was below 50 microns. The dust concentrate was then mixed with the kaolinite clay and the mixture deagglomerated in an Entoleter mill to obtain a smooth free-flowing uniform dust.

The composition was used for the control of mixtures of annual and perennial weeds growing around farm buildings. An application of 15 pounds of active material per acre gave excellent control of pepper grass, wild mustard, burdock, quack grass and crab grass.

EXAMPLE 56.

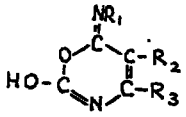
6-sec-butylimino-5-bromo-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrobromide	25%
Granular 8—15 mesh attapulgite clay	75%

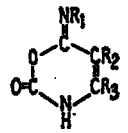
A granular composition was prepared by suspending the active ingredient in acetone, spraying this solution on the attapulgite granules while they were tumbled and drying the resulting granules.

The granules were applied by hand for "spot treatment" of undesirable bunch grasses growing in agricultural areas. An application of 20 to 30 pounds of active ingredient per acre gave good control of Dallis and vasey grass.

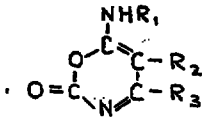
WHAT WE CLAIM IS:—

1. A compound having one of the three tautomeric formulae:





and



in which R_1 is hydrogen, alkyl of 1 to 10 carbon atoms, substituted alkyl of 1 to 8 carbon atoms, aryl of 6 to 10 carbon atoms, substituted phenyl, aralkyl of 7 to 13 carbon atoms, substituted aralkyl of 7 to 13 carbon atoms, alkenyl of 3 to 8 carbon atoms, alkynyl of 3 to 8 carbon atoms, furfuryl, cycloalkyl of 3 to 12 carbon atoms, cycloalkenyl of 4 to 12 carbon atoms, cycloalkyl alkyl of 4 to 13 carbon atoms, cycloalkenyl alkyl of 5 to 13 carbon atoms, substituted cycloalkyl, substituted cycloalkenyl or (substituted cycloalkyl) alkyl of 4 to 14 carbon atoms or (substituted cycloalkenyl) alkyl of 5 to 14 carbon atoms;

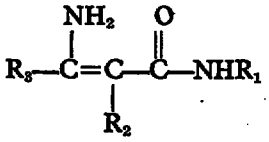
R_2 is hydrogen, chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy and t-butoxy; and

R_3 is alkyl of 1 to 5 carbon atoms, chloroalkyl of 1 to 4 carbon atoms or bromoalkyl of 1 to 4 carbon atoms; or in which

R_2 and R_3 are joined together to form $-(CH_2)_n-$, where n is 3, 4 or 5; and salts of said compound.

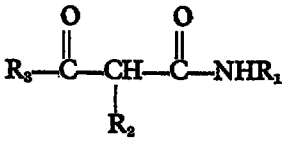
2. A compound according to claim 1 in which R_1 is other than methyl or ethyl, R_2 is hydrogen and R_3 is methyl.

3. A process for preparing a compound as claimed in claim 1 or 2 which comprises reacting a substituted *beta*-aminocrotonamide of the formula:



with phosgene.

4. A process according to claim 3 in which the *beta*-crotonamide is obtained by reacting a substituted acetoacetamide of the formula:



with ammonia.

5. A process according to claim 4 in which R_2 is hydrogen and R_3 is methyl, in which the acetoacetamide is prepared by reacting diketene with an amine of the formula NH_2R_1.

6. A process according to any of claim 4 in which acetoacetamide is reacted with a molar excess of ammonia at a temperature between −30°C. and 30°C.

7. A process according to any of claim 3 in which 1 mol of *beta*-aminocrotonamide is reacted with 1 to 2 moles of phosgene in an inert organic solvent.

8. A process according to claim 7 in which the reaction mixture is heated for 30 minutes to 6 hours at a temperature of 40°C. to 100°C.

of substantially all the material was below 50 microns. The dust concentrate was then mixed with the kaolinite clay and the mixture deagglomerated in an Entoleter mill to obtain a smooth free-flowing uniform dust.

The composition was used for the control of mixtures of annual and perennial weeds growing around farm buildings. An application of 15 pounds of active material per acre gave excellent control of pepper grass, wild mustard, burdock, quack grass and crab grass.

EXAMPLE 56.

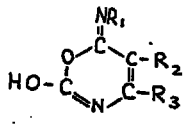
6-sec-butylimino-5-bromo-3,6-dihydro-4-methyl-2H—1,3-oxazin-2-one hydrobromide	25%
Granular 8—15 mesh attapulgite clay	75%

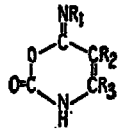
A granular composition was prepared by suspending the active ingredient in acetone, spraying this solution on the attapulgite granules while they were tumbled and drying the resulting granules.

The granules were applied by hand for "spot treatment" of undesirable bunch grasses growing in agricultural areas. An application of 20 to 30 pounds of active ingredient per acre gave good control of Dallis and vasey grass.

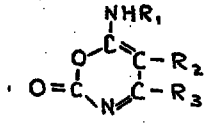
WHAT WE CLAIM IS:—

1. A compound having one of the three tautomeric formulae:





and



in which R_1 is hydrogen, alkyl of 1 to 10 carbon atoms, substituted alkyl of 1 to 8 carbon atoms, aryl of 6 to 10 carbon atoms, substituted phenyl, aralkyl of 7 to 13 carbon atoms, substituted aralkyl of 7 to 13 carbon atoms, alkenyl of 3 to 8 carbon atoms, alkynyl of 3 to 8 carbon atoms, furfuryl, cycloalkyl of 3 to 12 carbon atoms, cycloalkenyl of 4 to 12 carbon atoms, cycloalkyl alkyl of 4 to 13 carbon atoms, cycloalkenyl alkyl of 5 to 13 carbon atoms, substituted cycloalkyl, substituted cycloalkenyl or (substituted cycloalkyl) alkyl of 4 to 14 carbon atoms or (substituted cycloalkenyl) alkyl of 5 to 14 carbon atoms;

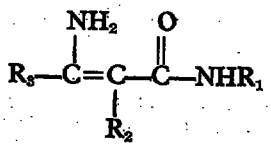
R_2 is hydrogen, chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy and t-butoxy; and

R_3 is alkyl of 1 to 5 carbon atoms, chloroalkyl of 1 to 4 carbon atoms or bromoalkyl of 1 to 4 carbon atoms; or in which

R_2 and R_3 are joined together to form $-(CH_2)_n-$, where n is 3, 4 or 5; and salts of said compound.

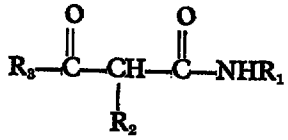
2. A compound according to claim 1 in which R_1 is other than methyl or ethyl, R_2 is hydrogen and R_3 is methyl.

3. A process for preparing a compound as claimed in claim 1 or 2 which comprises reacting a substituted *beta*-aminocrotonamide of the formula:



with phosgene.

4. A process according to claim 3 in which the *beta*-crotonamide is obtained by reacting a substituted acetoacetamide of the formula:



with ammonia.

5. A process according to claim 4 in which R_2 is hydrogen and R_3 is methyl, in which the acetoacetamide is prepared by reacting diketene with an amine of the formula NH_2R_1.

6. A process according to any of claim 4 in which acetoacetamide is reacted with a molar excess of ammonia at a temperature between −30°C. and 30°C.

7. A process according to any of claim 3 in which 1 mol of *beta*-aminocrotonamide is reacted with 1 to 2 moles of phosgene in an inert organic solvent.

8. A process according to claim 7 in which the reaction mixture is heated for 30 minutes to 6 hours at a temperature of 40°C. to 100°C.

* C L M S *

9. A process according to any of claim 3, 7 or 8 in which when R_2 represents hydrogen, the oxazinone compound formed is further treated with a halogenating agent to produce an oxazinone compound in which R_2 is halogen.

10. A substantially anhydrous herbicidal composition comprising a compound as claimed in claim 1 or 2 as active ingredient and an inert diluent therefor.

11. A composition according to claim 10, containing 30 to 60% by weight of the active ingredient.

12. A composition according to claim 10 or 11 which includes 0.1 to 10% by weight of a non-ionic surfactant.

13. A herbicidal composition comprising a herbicidally effective amount of a compound as claimed in claim 1 or 2 and at least one of the following compounds: herbicidal substituted ureas; herbicidal substituted triazines; herbicidal phenols; herbicidal carboxylic acids and derivatives thereof; herbicidal inorganic salts; herbicidal uracils; 5,6-dihydro - (4A,6A) - dipyrido - (1,2—A,2',1' — C) - pyrazinium dibromide; 3-amino - 1,2,4 - triazole; 3,6 - endoxhexahydrophthalic acid; hexachloroacetone; diphenylacetonitrile; *N,N*-dimethyl-*alpha,alpha*-diphenylacetamide; *N,N* - di - n - propyl-2,6 - dinitro - 4 - trifluoromethylaniline; *N,N* - di - n - propyl - 2,6 - dinitro - 4-methylaniline; O - (2,4 - dichlorophenyl)-O - methyl - isopropylphosphoramidothiate; and 2,3,5,6 - tetrachloroterephthalic acid, dimethyl ester.

14. A method of destroying or inhibiting the growth of undesired vegetation which comprises applying thereto a herbicidally effective amount of a compound as claimed in claim 1 or 2.

15. A process for converting an oxazinone compound as claimed in claim 1 to the corresponding uracil which comprises reacting the oxazinone compound with a base at a pH above 7.

16. An oxazinone compound substantially as herein described.

17. A process for preparing an oxazinone compound substantially as herein described.

18. A herbicidal composition according to claim 10 substantially as herein described.

19. A method of destroying or inhibiting the growth of undesired vegetation substantially as herein described.

20. A process for converting an oxazinone compound to the corresponding uracil substantially as herein described.

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