METHOD OF INHIBITING GROWTH OF UNDESIRABLE VEGETATION

Hein L. Klopping, Wilmington, and Harvey M. Loux, Hockessin, Del., assignors to E. L. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Feb. 6, 1964, Ser. No. 343,112
16 Claims. (Cl. 71—58)

This invention relates to heterocyclic compounds and more particularly to such compounds having one oxygen atom and one nitrogen atom in the hetero-ring.

Many of the compounds of this invention are useful in providing control against undesired vegetation. Some of the compounds are effective weed killing agents at rates as low as one-half pound per acre of treated area. Furthermore the compounds of this invention are valuable as intermediates in the preparation of a large variety of uracil derivative compounds which are themselves useful as herbicides.

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

\[
\begin{align*}
R_1 & \text{ hydrogen, alkyl of 1 through 10 carbon atoms,} \\
& \text{substituted alkyl of 1 through 8 carbon atoms, aryl of 6 through 10 carbon atoms, substituted phenyl, aralkyl of 5 through 13 carbon atoms, substituted aroalkyl of 3 through 13 carbon atoms, alkenyl of 3 through 8 carbon atoms, alkynyl of 3 through 8 carbon atoms, cycloalkyl of 3 through 12 carbon atoms, cycloalkenyl of 4 through 13 carbon atoms, substituted cycloalkyl, substituted cycloalkenyl,} \\
& \text{(substituted cycloalkyl) alkyl of 4 through 14 carbon atoms, or (substituted cycloalkenyl) alkyl of 5 through 14 carbon atoms;} \\
R_2 & \text{hydrogen, chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, methoxy, ethoxy, n-propoxy, isopropanoxy, n-butoxy, sec-butoxy or tert-butoxy; and} \\
R_3 & \text{alkyl of 1 through 5 carbon atoms, chloroalkyl of 1 through 4 carbon atoms, or bromoalkyl of 1 through 4 carbon atoms, and} \\
& \text{where} \quad R_3 \text{ and} \quad R_2 \text{ can be joined together to form} \\
& (CH_2)_n \quad \text{where} \quad n \text{ is a positive whole number from 3 through 5, i.e., 4 or 5.}
\end{align*}

In the above, the term "substituted alkyl" is intended to include such radicals as

bromoalkyl of 1 through 8 carbon atoms, chloroalkyl of 1 through 8 carbon atoms, hydroxyalkyl of 1 through 8 carbon atoms, alkoxyalkyl of 2 through 8 carbon atoms, alkoxy carbonyl alkyl of 3 through 8 carbon atoms, and cyanoalkyl of 2 through 8 carbon atoms.

Similarly, the terms "aryl" and "substituted phenyl" embrace radicals such as

phenyl
naphthyl
5 biphenyl
chlorophenyl
bromophenyl
alkoxyphenyl
dibromophenyl
10 dichlorophenyl
fluorophenyl
trichlorophenyl
alkylphenyl of 7 through 11 carbon atoms
diallylphenyl of 8 through 12 carbon atoms
chloroallylphenyl of 7 through 10 carbon atoms
nitrochlorophenyl
nitrophenyl
dichloronitrophenyl
chloroalkoxyphenyl of 7 through 11 carbon atoms
trifluoromethylphenyl
tetrahydrodiphenyl, and
indenyl

The terms "aralkyl" and "substituted aralkyl" are intended to include such radicals as

furfuryl
benzyl
phenylalkyl of 8 through 11 carbon atoms (total)
chlorobenzyl
30 dichlorobenzyl
alkybenzyl of 8 through 11 carbon atoms (total)
diklybenzyl of 9 through 13 carbon atoms (total)
nitrobenzyl
alkoxybenzyl of 8 through 11 carbon atoms (total), and
naphthymethyl

The terms "cycloalkyl," "cycloalkenyl," "cycloalkyl alkyl," and "cycloalkenyl alkyl" will include

cyclohexyl
cyclohexenyl
cyclohexylalkyl
cyclohexenylalkyl
cyclopentyl
cyclopentenyl
cyclopentylalkyl
cyclopentenyalkyl
norbornyl	norbornenyl	norbornylalkyl
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
tetrahydroindenyl alkyl
hexahydroindenyl alkyl
hexahydro-4,7-methanoindenyl
tetrahydro-4,7-methanoindenyl
hexahydro-4,7-methanoindenyl alkyl
tetrahydro-4,7-methanoindenyl alkyl
hexahydro-4,7-methanoindenyl alkyl
decacyclonaphthalyl decahydronaphthyl alkyl
tetrahydronaphthalyl
tetrahydronaphthalyl alkyl
decahydro-1,4-methanonaphthyl
decahydro-1,4-methanonaphthyl alkyl
cyclohexyl-1,4-methanonaphthyl
cyclohexyl-1,4-methanonaphthyl alkyl
decahydro-1,4,5,8-dimethanonaphthyl
decahydro-1,4,5,8-dimethanonaphthyl alkyl
cyclohexyl-1,4,5,8-dimethanonaphthyl, and
cyclohexyl-1,4,5,8-dimethanonaphthyl alkyl

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

The compounds of Formula 1 can conveniently be prepared in the form of salts with organic or inorganic acids. The free base is highly unstable and the salts are therefore highly preferred. Some examples of these preferred salts are the salts of such acids as hydrochloric acid, hydrobromic acid, hydroiodic acid, sulfuric acid, sulfamic acid, benzoic acid, acetic acid, phosphoric acid, phthalic acid, citric acid, succinic acid, maleic acid, trtaric acid, propionic acid, dichloroacetic acid, trichloroacetic acid, alpha, alpha-dichloropropionic acid, and the like.

In accordance with our invention, compounds of Formula 1 above can be prepared in a simple but remarkable two-step process, as follows:

Step 1.—React a substituted acetooctamidate with ammonia to form a substituted beta-aminoacetonitramide.

Step 2.—React the beta-aminoacetonitramide with phosgene to form the corresponding oxazin-2-one hydrochloride salt.

The process proceeds according to the following equations:

**Step 1:**

\[
R_2\text{C}=\text{C}=\text{C}=\text{O}=\text{NHR}_1 + \text{NH}_3 \rightarrow R_2\text{C}=\text{C}=\text{C}=\text{NHR}_1
\]

**Step 2:**

\[
R_2\text{C}=\text{C}=\text{C}=\text{NHR}_1 + \text{Cl}=\text{Cl} \rightarrow R_2\text{C}=\text{C}=\text{C}=\text{NHR}_1
\]

where \( R_2, R_1 \) and \( R_3 \) have the same meaning as in Formula 1.

The acetooctamidates used in Step 1 are prepared either by reaction of an amine with diketene as described below or by reaction of a beta-keto ester with excess amine followed by treatment with aqueous acid.

We shall now describe a preferred exemplary procedure, where \( R_2 \) is hydrogen and \( R_3 \) is methyl.

The acetooctamidate used as the starting material can be prepared by reacting diketene with an amine according to the equation:

\[
(\text{CH}_2=\text{C}=\text{O}=\text{O}) + \text{R}_2\text{NH}_2 \rightarrow \text{CH}_2=\text{C}=\text{C}=\text{NHR}_1
\]

This procedure is described in greater detail in U.S. Patent No. 2,615,917.

The acetooctamidate is then reacted with ammonia. This reaction is carried out by admixing the ammonia with a solution of the acetooctamidate in water or an inert organic solvent such as ether, tetrahydrofuran, an alcohol, 1,2-trichloroethylen, or the like. If water is used as the solvent, the ammonia can conveniently be added as an aqueous solution. For example, concentrated aqueous ammonia on the order of 28-30% by weight ammonia can be used as is. If an inert organic solvent is used, the ammonia can be introduced as a gas or as an undiluted liquid.

The reaction mass is stirred if desired to promote good mixing of the reactants.

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

The temperature at which the amination of the acetooctamidate is carried out is largely a matter of convenience. Ordinarily at ambient pressure temperatures above about 50° C. are disadvantageous because of undesired loss of ammonia above this temperature. The reaction temperature is preferably in the range from minus 30° to 30° C.

The amination reaction generally takes from about 1 to 10 hours, depending as will be understood upon the reaction temperature and the system employed.

The beta-aminoacetonitramide product is recovered by any convenient physical means, such as by filtration, separation of layers, evaporation of the solvent, or the like.

After recovery, the beta-aminoacetonitramide product can be dried and used directly in step 2 of our process or can, if desired, be purified by customary methods such as recrystallization.

The beta-aminoacetonitramide prepared according to Step 1 is converted into the corresponding substituted oxazin-2-one hydrochloride by reaction of the former with phosgene. The preparation of a 6-imino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride from a beta-aminoacetonitramide and phosgene will now be described for purposes of illustration.

A solution of phosgene is prepared in a suitable inert organic solvent such as tetrahydrofuran, dioxane, acetonitrile, 1,1,2-trichloroethylen, or the like. A solvent solution or slurry of the beta-aminoacetonitramide, preferably in the same solvent as the phosgene, is admixed with the phosgene solution.

Equimolar amounts of beta-aminoacetonitramide 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 molals and preferably will not exceed 2 mols for each mol of beta-aminoacetonitramide. It is advantageous to add the crotonitramide solution or slurry to the phosgene solution and maintain phosgene addition to keep the phosgene in excess and the solution saturated with phosgene. Superatmospheric pressure can be used to advantage.

This reaction is highly exothermic and a large amount of heat is evolved during the admixture of the beta-aminoacetonitramide and the phosgene. It is desirable to carry out the admixing at moderate temperatures, say at about 25° to 50° C, in order to minimize vaporization of the phosgene. External cooling means such as a refrigerated condenser can be used if needed to hold the temperature within this range.

Upon completion of the admixture of the beta-aminoacetonitramide and the phosgene, the mixture which now contains a solid as a second phase is heated at a temperature from about 40° to about 100° C. for a period of from about 30 minutes to about 6 hours to complete the reaction. As a result of the reaction, the desired hydrochloride salt of the 6-imino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one is 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 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 salts where R₂ is chlorine or bromine are prepared by conventional halogenation procedures, for example by reaction with the halogen in glacial acetic acid or other solvent.

The oxazinone salts in general do not have distinct melting points. On heating they lose hydrogen chloride and convert to the corresponding uracil as will be described in greater detail hereinafter.

The oxazinone salts 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 1 above, (c) multiple absorption in the range of 1570 to 1660 cm⁻¹, probably due to absorption by >C=O, >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.

Three tautomeric structures for the compounds are indicated from the above information as follows:

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 weeds, salts of compounds of Formula 1 are preferred where R₂ is other than hydrogen. Particularly preferred for their herbicidal effectiveness are salts of compounds of the following formula:

where R₃ is alkyl of 1 through 10 carbon atoms, substituted alkyl of 1 through 8 carbon atoms, substituted phenyl, aralkyl of 5 through 13 carbon atoms, substituted aralkyl of 5 through 13 carbon atoms, alkenyl of 3 through 8 carbon atoms, alkynyl of 3 through 8 carbon atoms, cycloalkyl of 3 through 12 carbon atoms, cycloalkenyl of 4 through 12 carbon atoms, cycloalkyl alkyl of 5 through 13 carbon atoms, cycloalkynyl alkyl of 5 through 13 carbon atoms, substituted cycloalkyl, substituted cycloalkenyl, (substituted cycloalkyl) alkyl of 4 through 14 carbon atoms, or (substituted cycloalkenyl) alkyl of 5 through 14 carbon atoms;

R₄ is hydrogen, chlorine or bromine;

R₅ is methyl; and where R₆ and R₇ can be joined together to form —(CH₂)ₙ— where n is 3, 4 or 5 and provided that, when R₅ is hydrogen and R₆ is methyl, R₇ is other than methyl or ethyl.

Illustrative of preferred compounds of this invention are salts and particularly the hydrochlorides or hydrobromides of the following oxazinones:

6-sec-butyliminono-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-sec-butyliminono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-norbornylinono-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-norbornyliminono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-norbornyliminono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-ethypropyliminono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-(1,3-dimethylbutyliminono)-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-isopropyliminono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-tert-butyliminono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one
6-phenylinono-5-bromo-3,6-dihydro-4-methyl-2H-1,3-oxazin-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

Preparation of compounds of this invention is illustrated by the following specific examples, which are given for purposes of explanation and not limitation and in which parts and percentages are by weight unless otherwise indicated.

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

To 852 parts of N-sec-butylacetacetamide are added 540 parts (70% excess) of concentrated (25%) aqueous ammonia. The clear solution is stirred and kept about room temperature in order to avoid an excessive loss of ammonia. After about 6 minutes, the solution turns cloudy and an oil begins to separate soon thereafter. Crystallization is induced by scratching the vessel wall. Precipitation of the product beta-amino-N-sec-butyriclonamide is complete in 4 hours. The thick crystal mass is filtered and the solid is washed with ice water and dried in a vacuum oven at 55–60°C. The product is weighed and found to be 69% parts (82% of theory) and melts at 84–88°C. Recrystallization from benzene raises the melting point to 89–90°C.


To a solution of 22 parts of phosgene in 100 parts of tetrahydrofuran is added dropwise with stirring a solution of 31.2 parts of beta-amino-N-sec-butyriclonamide in 75 parts of tetrahydrofuran. A solid precipitates and the temperature rises to 45°C. The mixture is stirred and refluxed for a period of 2 hours, cooled and filtered to obtain 27 parts of 6-sec-butylinono-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride melting at 151.5–162.5°C, with gas evolution.

Analysis.—Calculated for C₉H₈ClN₂O₂: N, 13.2. Found: 12.8.

The infrared spectrum of this material is characterized by a sharp peak at 5.6 microns ascribable to the

\[
\text{C} = \text{C} - \text{O}
\]

where S is methyl, and where R₆ and R₇ can be joined together to form —(CH₂)ₙ— where n is 3, 4 or 5 and provided that, when R₅ is hydrogen and R₆ is methyl, R₇ is other than methyl or ethyl.
moiety, a peak at 3.7 microns (amine hydrochloride) and the absence of NH absorption in the 3 micron region. The solid is soluble in water to the extent of about 27% by weight at room temperature. On prolonged standing of the aqueous solution at room temperature, or much more rapidly on heating, CO₂ evolves, and from the solution can now be isolated ammonium chloride and N-sec-butyl acetamide.

Upon dry heating above the melting point until gas evolution ceases, followed by cooling, a solid is formed which does not depress the melting point of 3-sec-butyl-6-methyluracil (M.P. 118-120°C). The solid has an infrared spectrum identical to that of the uracil.

Upon dissolving the oxazinone in dilute aqueous solutions of NaOH, Na₂CO₃, NaOOCCH₃, or even NaHCO₃, virtually instantaneous rearrangement to the just-mentioned uracil takes place. This uracil, which is present in the solution in the form of its sodium salt, can be isolated by acidifying the solution. The uracil separates as a syrup which crystallizes on rubbing and melts at 118-120°C. Upon recrystallization from alcohol-water.

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

To a solution of 33.6 parts of N-isopropylacetamid in 33.6 parts of water is added 29.3 parts of concentrated (28%) aqueous ammonia. The resulting solution is stirred at ambient temperature for 6 hours during which time beta-amino-N-isopropylcrotononitride precipitates as a white crystalline solid. It is collected by filtration, washed and air dried to give 28.4 parts of material melting at 142-144°C. This material is sufficiently pure for use as described below but if desired can be further purified by recrystallization from ethyl acetate to obtain a purer material melting at 144-145°C. A solution of 56.8 parts of the beta-amino-N-isopropylcrotononitride in 400 parts of dioxane is added over a 5 minute period to a stirred solution of 43.6 parts of propylene in 200 parts of dioxane. The reaction temperature rises to about 50°C and then begins to decrease at which time heat is applied. After 2 hours at 80-100°C the yellow slurry is cooled and the solid collected by filtration. It is washed with dioxane, ether and dried in vacuum at 25-30°C leaving 60.6 parts of dihydropropylamino-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrochloride melting at 156-160°C with gas evolution.

Analysis.—Calculated for C₉H₆ClNO₂: N, 13.69. Found: 13.79.

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

To a stirred solution of 88.6 parts of acetoacetanilide in 1500 parts of water and 150 parts of methanol at 73°C is added 67 parts of concentrated (28%) aqueous ammonia. After several minutes an oil from and crystallizes after initiation by scratching the wall of the vessel. After 2 hours the slurry is cooled in ice and filtered. The solid is washed with 400 parts of cold water and dried in vacuum at 60°C, leaving 69 parts of beta-amino-N-phenylcrotononitride (78% of theory) melting at 140.5-142.3°C.

A solution of 8.8 parts of the beta-amino-N-phenylcrotononitride in 40 parts of tetrahydrofuran is added over a 10 minute period to a solution of 5.5 parts of phosgene in 25 parts of tetrahydrofuran. The slurry is heated to 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-phenylamino-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrochloride melting at 238-244°C with gas evolution.

Analysis.—Calculated for C₁₉H₁₄ClNO₃: N, 11.74. Found: 11.72.

Examples 4-25

The products of the following Examples 4-16 are 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-aminoacetonitrides and finally the identified product.
Example 26.—6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one

A slurry of 6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride in methylene chloride is stirred with an excess of silver oxide and filtered after 3 minutes. The solution of the free oxazinone thus obtained is placed immediately in a recording infrared spectrophotometer and the region between 5.5 and 6.1 microns is recorded. The spectrum shows 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 is left in the infrared machine and the same region is recorded at various time intervals. The 5.7 micron peak gradually diminishes while a peak at 5.85 microns forms and becomes larger. After 45 minutes the oxazinone peak is all but vanished while the uracil peak is very strong. After one hour and 15 minutes, no trace of the oxazinone peak is left while the uracil peak has reached maximum intensity.

Example 36.—6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride

A slurry of 15 parts by weight of 6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride in 45 milliliters of water is added dropwise 17.6 parts of bromine while stirring. A precipitate forms. The solid after filtration, washing with water and ether, and drying, weighs 8 parts. Recrystallization from acetic acid yields 6.5 parts of white crystals melting at 151–154° C. with decomposition.

Analysis.—Calculated for C₆H₆Br₂N₂O₂: N, 8.2. Found: 8.0.

The infrared spectrum is similar to that of the starting material (sharp peak at 5.6 microns) and contains 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 the following Examples 36–40 are prepared according to the procedure of Examples 35 by replacing the 6-sec-butylamino-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 41.—6-sec-butylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride

A slurry of 15 parts by weight of 6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride in 75 milliliters of glacial acetic acid is stirred at room temperature while chloramine gas is introduced. The slurry becomes thicker at first, and then a thick white precipitate forms which is filtered, washed with acetic acid and acetone, and dried. It weighs 12 parts and melts at 144–150° C.

Analysis.—Calculated for C₆H₆Cl₂N₂O₂: N, 11.1. Found: 10.9.

The infrared spectrum of this product is very similar to that of the starting material (sharp peak at 5.6 microns). It contains an additional peak at 14.5 microns ascribable to the 5-chloro substituent. The chloro compound is 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, Na₂CO₃, NaOOCCH₃ or NaHCO₃. The water solubility of the 5-chloro oxazinone is about 8% by weight at room temperature.

Examples 42–46

The products of the following Examples 42–46 are prepared according to the procedure of Example 41 by replacing the 6-sec-butylamino-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-chloro compound.

Example 42.—6-iso-propylamino-6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride

To a solution of 11 parts of 6-iso-propylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride in 45 milliliters of water is added dropwise 17.6 parts of bromine while stirring. A precipitate forms. The solid

Ex. Starting Oxazinones Product

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Starting Oxazinones</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.</td>
<td>6-sec-butylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one</td>
<td>6-sec-butylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride</td>
</tr>
<tr>
<td>37.</td>
<td>6-iso-propylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one</td>
<td>6-iso-propylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride</td>
</tr>
<tr>
<td>38.</td>
<td>6-methylamino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one</td>
<td>6-methylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride</td>
</tr>
<tr>
<td>39.</td>
<td>6-iso-propylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one</td>
<td>6-iso-propylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride</td>
</tr>
<tr>
<td>40.</td>
<td>6-methylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one</td>
<td>6-methylamino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride</td>
</tr>
</tbody>
</table>
In one very important use for the compounds of Formula 1, they are readily converted to uracils. The conversion of the oxazineone derivative can be carried out using the slurry of the oxazineone hydrochloride salt formed as described above in step 2 of our process from the phosgenation of the aminocrotonamide or, in the alternative, where the oxazineone salt has been recovered in solid crystalline form, the oxazineone 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, such as sodium hydroxide, potassium hydroxide, sodium carbonate, etc. 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 such as sulfuric acid, hydrochloric acid, or the like. Other acids such as acetic acid, formic acid, etc., are also satisfactory as will be understood but are of course more expensive. The uracils are isolated by filtration or, since in some cases they are soluble in the aqueous medium, they are isolated where appropriate by extraction with a suitable solvent such as methylene chloride, ether or the like.

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

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

As will also be understood, we have invented in another important aspect an overall process, which can be carried out in a series of separate or combined steps, a remarkably efficient route for the preparation of uracils from commercially available and relatively inexpensive starting materials. Our overall process thus comprises the steps of:

**Step A.** Reacting a substituted acetocetamidone of the formula

\[
\begin{align*}
\text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} & \rightarrow \text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} \\
\end{align*}
\]

where \( \text{R}_1,\text{ R}_2 \) and \( \text{R}_3 \) have the same meaning as in Formula 1, with ammonia to produce a beta-aminocrotonamide of the formula

\[
\begin{align*}
\text{NH}_3\text{O} & \rightarrow \text{NH}_3\text{O} \\
\text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} & \rightarrow \text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} \\
\end{align*}
\]

**Step B.** Reacting the beta-aminocrotonamide with phosgene

\[
\begin{align*}
\text{O} & \rightarrow \text{O} \\
\text{Cl} & \rightarrow \text{Cl} \\
\end{align*}
\]

to obtain a reaction product, and

**Step C.** Reacting the reaction product of Step B with an inorganic base and, if necessary, an acidifying agent to produce a uracil of the formula

\[
\begin{align*}
\text{R}_1 - \text{N} & \rightarrow \text{R}_1 - \text{N} \\
\text{O} & \rightarrow \text{O} \\
\end{align*}
\]

In a preferred process, the preceding overall process is carried out with the preliminary step of preparing the beta-aminocrotonamide from diketene and an amine.

In a particularly preferred embodiment, our process involves reacting diketene with an amine according to the following:

\[
\begin{align*}
\text{CH}_2\text{O} + \text{R}_2\text{NH}_2 & \rightarrow \text{R}_2\text{NH} - \text{C} = \text{C} - \text{NH}_2 \\
\text{O} & \rightarrow \text{O} \\
\end{align*}
\]

The acetocetamide is then reacted with ammonia in a suitable reaction medium, preferably using from 1 to 10 mols of ammonia for each mol of acetocetamide, at a temperature in the range from -30° to +30° C. as follows:

\[
\begin{align*}
\text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{NH}_2\text{Cl} & \rightarrow \text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{NH}_2\text{Cl} \\
\text{NH}_3\text{O} & \rightarrow \text{NH}_3\text{O} \\
\text{O} & \rightarrow \text{O} \\
\end{align*}
\]

The aminocrotonamide is next phosgenated in suitable medium, preferably using from 1 to 2 mols of phosgene for each mol of aminocrotonamide, at a temperature in the range from 40° to 100° C. for ½ - 6 hours to produce the oxazineone hydrochloride in the system as follows:

\[
\begin{align*}
\text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} & \rightarrow \text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} \\
\text{O} & \rightarrow \text{O} \\
\end{align*}
\]

The oxazineone derivative is next converted at pH 9-10 with a base such as sodium hydroxide to form the corresponding uracil salt which in turn is converted by treatment with an acid such as sulfuric acid to the corresponding uracil of the formula

\[
\begin{align*}
\text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} & \rightarrow \text{R}_1\text{O} + \text{CH} = \text{C}\text{=O} + \text{NH}_2\text{Cl} \\
\text{O} & \rightarrow \text{O} \\
\end{align*}
\]

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, and in particular the uracil of Formula 4, is notably advantageous because it is a rapid, high yield approach to the synthesis of useful uracils employing as the only essential reactants diketene, amines, phosgene and an alkali. None of these starting materials need be converted with extra expense and difficulty to extraneous intermediates before use in this invention.

The following examples are given in addition to those above to illustrate the conversion of oxazineones to corresponding uracils, either directly or through the uracil salt, as well as the embodiment of the overall process of preparation of uracils through the corresponding oxazineone. These examples are likewise given for purposes of illustration only and no unnecessary limitation is intended therefrom. Parts and percentages are by weight unless otherwise indicated.

**Example 47**

To a stirred solution of 10.9 parts of phosgene in 50 parts of tetrahydrofuran is added, over a 15 minute period at ambient temperature, a solution of 15.6 parts of beta-
3,352,662

Amino-N-sec-butylcrotonamide prepared as described in Example 1, in 40 parts of tetrahydrofuran. The temperature rises during the addition to about 50°C and a yellow slurry forms. This slurry is heated at reflux for 2 hours. The solid present in the slurry at this point is 6-sec-butyl-imino-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride. The slurry is then poured into 200 parts of 2 N aqueous sodium hydroxide, with stirring. The resulting solution is extracted twice with 100 parts of methylene chloride to remove alkali-insoluble organics which impurities. The aqueous portion is then acidified with concentrated hydrochloric acid and the resulting 3-sec-butyl-6-methyluracil is isolated by extracting four times with 100 parts each of methylene chloride. Evaporation of the solvent leaves 13.4 parts of the uracil.

Example 48

A solution of 9.6 parts of beta-amino-N-phenyl-crotonamide (prepared as in Example 3) in 40 parts of tetrahydrofuran is added to a stirred solution of 5.5 parts of phosphorus in 25 parts of tetrahydrofuran over a 15 minute period. After the initial exothermic reaction has subsided, the mixture is heated at 63-67°C for 2 hours. It is then cooled and poured into 200 parts of 2 N aqueous sodium hydroxide. After extraction twice with 150 parts each of methylene chloride to remove impurities, the aqueous solution is acidified with concentrated hydrochloric acid. The product is isolated by extraction six times with 100 parts each of methylene chloride, followed by evaporation of the methylene chloride. There is obtained 7.5 parts of 3-phenyl-6-methyluracil, melting at 224-225°C.

As mentioned above the compounds of Formula I and especially those indicated to be preferred are effective herbicides. They exert herbicidal action against both broadleaf and grass weeds, effective against hard-to-kill nutseed and perennial grasses such as quack grass, Johnson grass, and Bermuda grass, and are effective on highly adsorptive substrates such as railroad ballast, heavy clay soil, and soils high in organic matter.

This combination of properties makes these 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 properly selecting an oxazinone of the invention and a rate and time of application, annual grass and broadleaf seedlings in such crops as asparagus, corn, flax, sugar cane, prune, apple, safflower, peanuts, citrus, alfalfa, strawberries, gladiolus, stone fruits and cucurbits can be controlled. By proper selection of 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 the particular end result desired, the use involved, the plant and soil involved, the formulation used, the mode of application, prevailing weather conditions, foliage density and like factors. Since so many variables play a role, it is not possible to indicate a rate of application suitable for all situations. Broadly speaking, the compounds are used at levels of about 0.1 pound per acre to about 25 pounds per acre. For selective weed control in crops, rates of 0.5 to 8 pounds per acre will generally be used. More of the active material can be used to control difficult-to-kill species growing under adverse conditions. Economic factors, such as inaccessibility of the area to be treated, e.g., first breaks in forests, may also favor higher rates, with less frequent treatments.

The herbicidal compounds of this invention can be formulated as dusts, as wettable powders, or as soluble powders. In these formulations, care must be taken that diltiens, surface active agents, and other pesticidal additives are neutral in pH and are particularly free of reagent. 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.

In view of the preceding, particularly advantageous results are obtained using the following, where percentages by weight are:

| Active ingredient (oxazinone salt) | 30-60 |
| Non-ion surfactant | 0.1-10 |
| Remainder—inert diluents | 100 |

Substantially anhydrous.

By substantially anhydrous is meant that the maximum amount of water present is 1% by weight based on the weight of the oxazinone salt present.

Suitable diluents for the preparation of dusts and 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, Continental clay, Barnet clay, and Pike’s Peak clay 9T66. Other diluents which can sometime be used are vegetable flours, such as Redwood flour, wheat shell flour, and the like.

When such diluents are to be used in the preparation of herbicidal dusts, the active ingredient will preferably be present in amounts ranging 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 active ingredient may be present in amounts ranging 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 of the surfactants described below.

The surfactants for 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 not be highly alkaline, and with this limitation, surfactants such as salts of alkyl aryl sulfonic acids, and petroleum sulfonates and salts of fatty alcohol sulfates 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 that can be used may be salts of dialkyl esters of sulfocarboxylic acids and fatty acid esters of isothiocylic acids. In some instances, the free acid instead of the salt can also be advantageously used.

Among the very much preferred non-ionic surfactants are polyethylene glycol fatty esters, and polyoxyethylene ethers and thioethers. Other non-ionic compounds are alkoxylphenoxypolyoxyethyleneoxyethanols, such as poyonphenyl adducts with ethylene oxide, trimethyl mono polyethylene 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. Particularly preferred may be polyglycol ethers in which both terminal alcohol groups have been esterified with fatty acids such as lauric, oleic, palmitic, or stearic acids.

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 and the remainder being from 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 lignosulfonates are also useful, especially in the wettable powder compositions of this invention.

FORMULATION WITH OTHER HERBICIDES

The herbicidal compositions of this invention can be formulated to contain two or more of the oxazinones. They can also be formulated to contain other known herbicides in addition to the oxazinones to give compositions which have advantages over the individual components.

Among the known herbicides which can be combined with the compounds of Formula I 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 of this invention 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(ethylenimin)-s-triazine
2-chloro-4-ethylamino-6-isopropylamino-s-triazine
2-chloro-4,6-bis(methoxypropylen)-s-triazine
2-methoxy-4,6-bis(isopropylamino)-s-triazine
2-diethylamino-4-isopropylacetamido-6-methoxy-s-triazine
2-isopropylamino-4-methoxyethylamino-6-methyl-mercapto-s-triazine
2-methylmercapto-4,6-bis(isopropylamino)-s-triazine
2-methylmercapto-4,6-bis(ethylenimin)-s-triazine
2-methylmercapto-4-ethylamino-6-isopropylamino-s-triazine
2-methoxy-4,6-bis(ethylenimin)-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-(2,4,5-trichlorophenoxy)propionic acid and its salts and esters

15

16
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-trichlorobenzoyloxypropanol
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)thiolecarbamic acid, ethyl ester
N,N-di-(n-propyl)thiolecarbamic acid, n-propyl ester
N-ethyl-N-(n-butyl)thiolecarbamic acid, ethyl ester
N-ethyl-N-(n-butyl)thiolecarbamic acid, n-propyl ester
Mixed in a 1:2 to 24:1 ratio, preferably a 1:1 to 12:1 ratio.

F
N-phenylecarbamic 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-trichlorophenoxyacetic 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 propylarsionate
Disodium monomethylarsionate
Octyl-dodecylammoniummethylarsionate
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 chloride
Mixed in a 1:1 to 40:1 ratio, preferably a 2:1 to 20:1 ratio.

G
Ammonia sulfamate
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-di hyd ro-(4,4,6,6A)-d i py ri do-(1,2-A,2'-A',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
Hexachloracetone
Mixed in a 1:2 to 16:1 ratio, preferably a 1:1 to 8:1 ratio.

E
Diphenylacetanilide
N,N-di-methyl-o-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-phosphoramidodithiate
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'-nitrodiphenyl 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 can be found in copending applications Ser. Nos. 233,952, filed Oct. 29, 1962; 241,141, filed Nov. 30, 1962; 221,890, filed Sept. 6, 1962; 232,311, filed Oct. 22, 1962; and 217,521 filed Aug. 17, 1962.

A
3-cyclohexyl-6-methyluracil
3-cyclohexyl-6-ethyluracil
3-cyclohexyl-6-propyluracil
3-norbornyl-6-methyluracil

B
3-cyclohexyl-5,6-trimethyleneuracil
3-sec-butyl-5,6-trimethyleneuracil
3-isopropyl-5,6-trimethyleneuracil
3-isopropyl-5,6-tetramethyleneuracil
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-cyclohexyl-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.

In order that the herbicidal utility aspects of the present invention will be better understood the following illustrative examples are given in addition to those set forth above.

Example 49

Percent
6-norbornylmethylinolar 3,6-di hydro-4-methyl-2H-1,3-ox azin-2-one hydrochloride 80
Polyethylene glycol dioleate 5
"Hi-Sil" 15
The ingredients are blended and ground in a hammer mill until the particle size of substantially all the active ingredients is below 50 microns.
This wettable powder is 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 gives excellent control of crab grass, water grass, black-eyed susan, carpetweed, and chickweed.

Example 50

Percent
6-tert-butylimino-5-bromo-3,6-di hydro-4-methyl-2H,1,3-ox azin-2-one hydrobromide 80.0
Sodium lauryl sulfate 0.6
Partially desulfonated sodium lignin sulfonate 1.0
Calcined, non-swelling montmorillonoid type clay (Pikes Peak clay) 18.4
A wettable powder is prepared by blending the com-
3,352,662

Component and then micropulverizing them until substantially all the particles are below 50 microns in size. This formulation is used at 20 pounds of active ingredient per acre in 100 gallons of water 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 is obtained. At 30 pounds of active ingredient per acre as a spot treatment, excellent control of such deep-rooted weeds as bindweed and Canada thistle is obtained.

**Example 51**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-isopropylmimino-5-bromo-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrobromide</td>
<td>80.0</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.6</td>
</tr>
<tr>
<td>Sodium lignin sulfonate</td>
<td>2.0</td>
</tr>
<tr>
<td>Kaolin clay</td>
<td>17.4</td>
</tr>
</tbody>
</table>

These components are blended and micropulverized until the solids are substantially all below 50 microns in particle size. The mixture is then reblended until it is homogeneous. This wettable powder is used as a general purpose weed killer on industrial sites and railroad ballast. Ten to twenty pounds of active ingredient per acre in 100 gallons of water gives excellent control of goldenrod, evening primrose, pokeweed, ox-eye daisy, cocklebur, goose grass, crabgrass, and love grass.

Twenty pounds of active ingredient per acre in 50 gallons water gives excellent control of nutsedge.

**Example 52**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-sec-butilmimino-5-bromo-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrobromide</td>
<td>95</td>
</tr>
<tr>
<td>Polyethylene glycol ester of fatty and rosin acids concreted with urea</td>
<td>5</td>
</tr>
</tbody>
</table>

The ingredients are mixed and ground and can then be mixed with water for prompt spray application as a solution. This formulation is 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 gives excellent control of these weeds.

**Example 53**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-norborylmethylmimino-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrochloride</td>
<td>50</td>
</tr>
<tr>
<td>Soya lecithin</td>
<td>3</td>
</tr>
<tr>
<td>Substantially aliphatic, low viscosity mineral oil, e.g. kerosene or diesel oil</td>
<td>57</td>
</tr>
</tbody>
</table>

The oil suspension is prepared by pregrinding the active material and mixing it with the other components with agitation, or by blending all the components together, then pebble-milling or sand-milling them to reduce the particle size of the active component. The product is suitable for dilution with weed oils to form an oil spray. This formulation is diluted with 80 gallons of an herbicidal oil such as 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 is obtained for several months. Quack grass, cheat, witch grass, buttonweed, and jimson weed are controlled.

**Example 54**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-cyclohexylmimino-5-chloro-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrochloride</td>
<td>90.0</td>
</tr>
<tr>
<td>Alkyl naphthalene sulfonate, Na salt</td>
<td>2.0</td>
</tr>
<tr>
<td>Low viscosity methyl cellulose</td>
<td>0.3</td>
</tr>
<tr>
<td>Attapulgite clay</td>
<td>7.7 75</td>
</tr>
</tbody>
</table>

These components are blended and micropulverized until the particles of uracil have been reduced to about 10 microns in diameter, then reblended. This formulation gives excellent weed control when applied 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**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-sec-butilmimino-5-chloro-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrochloride</td>
<td>10</td>
</tr>
<tr>
<td>&quot;Celtex&quot; 209</td>
<td>20</td>
</tr>
<tr>
<td>Kaolinite clay (acidic)</td>
<td>80</td>
</tr>
</tbody>
</table>

The active ingredient and the "Celtex" are blended and ground in a hammer mill until the mixture is uniform and the particle size of substantially all of the material is below 50 microns. This dust concentrate is then mixed with the kaolinite clay and the mixture is deagglomerated in a device such as an Entoliter mill to obtain a smooth free-flowing uniform dust.

This composition is 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 gives excellent control of pepper grass, wild mustard, burdock, quack grass, and crab grass.

**Example 56**

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-sec-butilmimino-5-bromo-3,6-dihydro-4-methyl-2H,1,3-oxazin-2-one hydrobromide</td>
<td>25</td>
</tr>
<tr>
<td>Granular 8-15 mesh attapulgite clay</td>
<td>75</td>
</tr>
</tbody>
</table>

A granular composition is prepared by suspending the active ingredient in acetone and spraying this solution on the attapulgite granules while they are tumbled. The resulting granules are then dried. The granules are 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 gives good control of Dallis and vaezy grass.

What is claimed is:

I. The method of inhibiting growth of undesired vegetation comprising applying to the locus to be treated a herbicidally effective amount of a compound of the formula:

```
NR C g-R, C-Rs
```

where R is selected from the group consisting of hydrogen; alkyl of 1 through 10 carbon atoms; substituted alkyl of 1 through 8 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, hydroxy, alkoxyl, alklyoxycarbonyl, and cyano; aryl of 6 through 10 carbon atoms; substituted phenyl wherein said substituent is selected from the group consisting of chloro, bromine, fluorne, alkoxyl of 1 through 5 carbon atoms, alky of 1 through 6 carbon atoms, nitro, trifluoromethyl, 1,2-tetramethylenyl, and 1,2-trimethylenyl; aralkyl of 5 to 13 carbon atoms, substituted aralkyl of 5 through 13 carbon atoms wherein said substituent is selected from the group consisting of chloro, nitro, alkyl and alkoxy; arlenyl of 3 through 8 carbon atoms; alkynyl of 3 through 8 carbon atoms; cycloalkyl of 3 through 12 carbon atoms; substituted cycloalkyl of 3 through 12 carbon atoms wherein said substituent is selected from the group consisting of bromine, fluorne, methoxy and alkyl, cycloalkenyl of 4 through 12 carbon...
atmos; substituted cycloalkenyl of 4 through 12 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, methoxy, and alkyl; cycloalkyl alkyl of 4 through 13 carbon atoms; cycloalkenyl alkyl of 5 through 13 carbon atoms; substituted cycloalkenyl alkyl of 4 through 14 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, methoxy and alkyl; (substituted cycloalkenyl)alkyl of 5 through 14 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, methoxy, and alkyl; R₃ is selected from the group consisting of hydrogen, chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, and tert-butoxy; and R₄ is selected from the group of alkyl of 1 through 5 carbon atoms, chloroalkyl of 1 through 4 carbon atoms, and bromoalkyl of 1 through 4 carbon atoms; with the proviso that R₂ and R₃ can be joined together to form —(CH₂)n— where n is a positive whole number of 3 through 5; and acid salts of said compound.

2. The method of inhibiting growth of undesired vegetation comprising applying to the locus to be treated a herbicidally effective amount of a compound as set forth in claim 1 wherein R₁ is as defined and other than hydrogen.

3. The method of inhibiting growth of undesired vegetation comprising applying to the locus to be treated a herbicidally effective amount of a compound as set forth in claim 2 wherein R₁ is methyl, provided that when R₂ is hydrogen, R₃ is other than methyl and ethyl.

4. The method of inhibiting growth of undesired vegetation comprising applying to the locus to be treated a herbicidally effective amount of a compound of the formula:

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{R₁} & \quad \text{C} \\
\text{H} & \quad \text{C} \\
\end{align*}
\]

wherein R₁ is selected from the group consisting of alkyl of 1 through 10 carbon atoms; substituted alkyl of 1 through 8 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, hydroxy, alkoxycarbonyl, and cyanide; aryl of 6 through 10 carbon atoms; substituted phenyl wherein said substituent is selected from the group consisting of chlorine, bromine, fluorine, alkoxy of 1 through 5 carbon atoms, alkyl of 1 through 6 carbon atoms, nitro, trifluoromethyl, 1,2,4-trimethyleneyne, and 1,2,3-trimethyleneyne; alkoxy of 5 to 13 carbon atoms, substituted aralkyl of 5 through 13 carbon atoms wherein said substituent is selected from the group consisting of chlorine, nitro, alkyl and alkoxy; alkenyl of 3 through 8 carbon atoms; alkenyl of 3 through 8 carbon atoms; cycloalkyl of 3 through 12 carbon atoms; substituted cycloalkenyl of 3 through 13 carbon atoms wherein said substituent is selected from the group consisting of bromine, fluorine, methoxy and alkyl, cycloalkenyl of 4 through 12 carbon atoms; substituted cycloalkenyl of 4 through 12 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, methoxy, and alkyl; cycloalkyl of 4 through 13 carbon atoms; cycloalkenyl of 5 through 13 carbon atoms; (substituted cycloalkenyl)alkyl of 4 through 14 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, methoxy and alkyl; and (substituted cycloalkenyl)alkyl of 5 through 14 carbon atoms wherein said substituent is selected from the group consisting of bromine, chlorine, methoxy, and alkyl; R₂ is selected from the group consisting of hydrogen, chlorine and bromine; and R₃ is methyl; with the proviso that R₂ and R₃ can be joined together to form —(CH₂)n— where n is a positive whole number of 3 through 5; and with the further proviso that when R₂ is hydrogen, R₃ is other than methyl and ethyl; and acid salts of said compound.

5. The method of inhibiting growth of undesired vegetation comprising applying to the locus to be treated a herbicidally effective amount of 6-sec-butylinino-5-chloro-3,6-dihydro-4-methyl-2H-1,3-oxazin-2-one hydrochloride. (References on following page)
<table>
<thead>
<tr>
<th>Reference Number</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,329,619</td>
<td>9/1943</td>
<td>Jayne et al.</td>
<td>260—244</td>
</tr>
<tr>
<td>2,447,822</td>
<td>8/1948</td>
<td>Senkus</td>
<td>260—244</td>
</tr>
<tr>
<td>2,758,994</td>
<td>8/1956</td>
<td>Lacey</td>
<td>260—244</td>
</tr>
<tr>
<td>2,797,217</td>
<td>6/1957</td>
<td>Safir et al.</td>
<td>260—244</td>
</tr>
<tr>
<td>3,022,150</td>
<td>2/1962</td>
<td>Weed</td>
<td>71—2.5</td>
</tr>
<tr>
<td>3,037,853</td>
<td>6/1962</td>
<td>Luckenbaugh</td>
<td>71—2.5</td>
</tr>
</tbody>
</table>

References Cited

UNITED STATES PATENTS

3,210,355 10/1965 deStevens
3,223,707 12/1965 Brokke
3,235,357 2/1966 Loux

LEWIS GOTTS, Primary Examiner.
WALTER A. MODANCE, JAMES O. THOMAS, Jr., Examiners.
ROBERT T. BOND, Assistant Examiner.