968,661

PATENT SPECIFICATION

NO DRAWINGS

968,661

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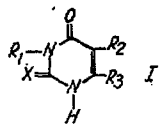
COMPLETE SPECIFICATION

Herbicidal Compositions containing 3-Substituted Uracils

We, E. I. Du Pont De Nemours and Company, a Corporation organised 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:—

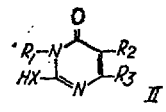
This invention relates to 3-substituted uracils.

It has been discovered that certain 3-substituted uracils have herbicidal activity. These 3-substituted uracils are compounds of the general formula:



I

or the corresponding isomeric formula:



II

wherein R_1 is a covalent organic radical of molecular weight 15 to 250 which is an alkyl group of up to 10 carbon atoms, a substituted alkyl group in which the alkyl group contains up to 3 carbon atoms, a phenyl group, a substituted phenyl group, an aralkyl group of 7 or 8 carbon atoms, a substituted aralkyl group of 7 to 12 carbon atoms, an alkenyl group of 3 to 6 carbon atoms, a propynyl group, a butynyl group, a cycloalkyl group of 5 to 8 carbon atoms, a cycloalkenyl group of 5 to 8 carbon atoms or a cyano group;

R_2 is a hydrogen or halogen atom or an alkyl group of up to 4 carbon atoms, an alkoxy group of up to 3 carbon atoms, a nitro group, an alkoxymethyl group of 2 to 4 carbon atoms, a hydroxy-methyl group, a hydroxyethyl group, an allyl group, a thiocyanato group, a cyano group, a halogenomethyl group or a methyl thiomethyl group;

R_3 is a hydrogen or chlorine atom or an alkyl group of up to 5 carbon atoms, a methoxy group or an ethoxy group;

or R_2 and R_3 together form a divalent alkylene bridge of formula $(CH_2)_n$, wherein n is 3, 4 or 5; and

X is oxygen or sulphur, preferably oxygen;

with the proviso that if R_2 is a hydrogen atom, then either R_3 is an alkyl group of 1 to 5 carbon atoms and R_1 is an alkyl group of 3 to 6 carbon atoms, an allyl group, a propynyl group or a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms, or R_3 is a hydrogen atom and R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms; and metal salts of such uracils.

Within the broad class of 3-substituted uracils defined above are four particular classes which are the subject of our Applica-

[*Price 4s. 6d.*]

tions Nos. 32,469/60, 17,417/64, 17,418/64 and 17,419/64 (Serial Nos. 968,662, 968,663, 968,664 and 968,665). These particular classes, which are defined in detail just before the claims of the present specification, are therefore excluded from the scope of the present invention.

The term "covalent radical" is used to denote a monovalent radical which is attached to the uracil ring by a covalent bond, in contrast to an ionic radical, such as a metal cation, which forms salts with the uracil.

It will be noted that the definition above refers to the isomeric enol form of the uracil, as well as the usual keto form. It is thought that there is a tautomeric equilibrium between the two forms. However, for the sake of convenience the keto form is generally referred to herein.

Examples of substituted alkyl groups in which the alkyl group contains 1 to 3 carbon atoms include such alkyl groups substituted by alkoxy groups, e.g. methoxy groups, or chlorine atoms.

Examples of substituted phenyl groups include phenyl groups substituted by one or more of the following radicals: alkyl groups, e.g. methyl and butyl groups; halogen atoms, e.g. fluorine, chlorine and bromine atoms; nitro groups; alkoxy groups, e.g. methoxy and ethoxy groups; cyano groups; and hydroxy groups.

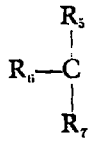
Examples of substituted aralkyl groups containing 7 to 12 carbon atoms include such aralkyl groups substituted by one or more of the following radicals: alkyl groups, as in methylbenzyl and butylphenethyl groups; chlorine atoms, as in chlorobenzyl; nitro groups; and methoxy groups, as in methoxybenzyl.

The metal salts may be, for example, the salts of alkali and alkaline earth metals such as sodium, potassium, which are preferred, and lithium, calcium, magnesium, barium, and strontium, or of other metals such as di- or trivalent iron, manganese and zinc.

Since "uracil" is the commonly accepted name for 2,4 - dihydroxypyrimidine, or, in its keto form, 1,2,3,4 - tetra - hydropyrimidine - 2,4 - dione, the compounds can also be named as pyrimidines. For example, 3 - isopropyl - 5 - bromo - 6 - methyluracil can also be named 3 - isopropyl - 5 - bromo - 6 - methyl - 1,2,3,4 - tetra - hydropyrimidine - 2,4 - dione.

Some of the substituted uracils of the general formula given above are not new compounds, but the following classes of uracils, and their metal salts are believed to be new compounds and as such form part of the present invention:

(1) Compounds of the general formula given above wherein R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms or a group of the formula:



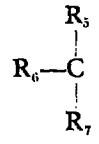
wherein R_5 is a hydrogen atom or a methyl group,

R_6 is a methyl or ethyl group, and

R_7 is an alkyl radical of 1 to 5 carbon atoms; R_2 is a chlorine or bromine atom; and R_3 is a methyl group.

(2) Compounds of the general formula given above wherein R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms; R_2 is hydrogen; R_3 is an alkyl group of up to 5 carbon atoms, preferably a methyl group. R_1 may, for example, be a cyclopentyl, cyclohexyl or cyclopenten - 2 - yl group. Within this class there is a single known compound, 3-cyclohexyl-6-methyl uracil.

(3) Compounds of the general formula given above wherein R_2 and R_3 together form a divalent alkylene bridge of formula $(CH_2)_n$, where n is 3, 4 or 5, R_1 is a cycloalkyl group of 5 to 8 carbon atoms, a cycloalkenyl group of 5 to 8 carbon atoms or a group of the formula



wherein R_5 is a hydrogen atom or a methyl group,

R_6 is a methyl or ethyl group, and

R_7 is an alkyl radical of 1 to 5 carbon atoms; and

X is oxygen or sulphur.

(4) Compounds of the general formula given above wherein R_1 represents a phenyl group, a substituted phenyl group, a cycloalkyl group containing 5 to 8 carbon atoms or a cycloalkenyl group containing 5 to 8 carbon atoms; R_2 represents a halogen atom or a methyl, methoxy methyl or nitro group; and R_3 represents a hydrogen atom.

The 3-substituted uracils can be formulated as herbicidal compositions comprising at least one 3-substituted uracil which is a compound of general formula I or II as defined above or a metal salt thereof, associated with a compatible diluent or surface-active agent, or both. The term "herbicidal composition" is used herein to include both compositions which are ready for use as herbicides and concentrates which require dilution before use as herbicides. The compositions may contain for example 0.5 to 95% by weight of the 3-substituted uracil.

The diluent may be a liquid other than an oil, especially water, or an oil, or a solid carrier. The term "oil" is used herein to denote a liquid which is immiscible with

water and soluble in ether, and which has a boiling point not lower than 125°C. Two or more different types of diluent may be present, as for example in compositions obtained by dispersing a wettable powder in a liquid diluent. Liquid compositions may be in the form of solutions or dispersions.

Examples of oil carriers are aliphatic and aromatic hydrocarbons, for example, hydrocarbons of petroleum origin. Dispersions in oils may be prepared by milling the active material, usually with dispersing agents and suspending agents, with the oil in mills such as pebble mills. The amount of the herbicide in the dispersion may be from 10% or less to 48 and 50% of the oil dispersion. Preferably, the particles in such dispersions range from about 1 to 50 microns, although the majority are preferably in the range of from about 5 to 20 microns in average diameters. In general, the oils used include aliphatic and aromatic hydrocarbons and mixtures thereof, particularly those derived from petroleum and having a boiling point in the range from about 125 to 400°C. A hydrocarbon oil having a boiling point lower than 125°C. should not be used because when sprayed from a nozzle, such a hydrocarbon tends to volatilize undesirably. Furthermore, low-boiling hydrocarbons present a serious fire hazard.

Compositions containing the uracils in association with a solid diluent may be in the form of powdered solids, granules or pellets. Powdered or dust compositions may be prepared by mixing the active material with finely divided inert solid carriers, preferably talcs, natural clays, pyrophyllite, diatomaceous earth, synthetic fine silica, calcium silicate, and flours such as walnut shell, wheat, redwood, soya bean, and cottonseeds, and including also magnesium and calcium carbonates, calcium phosphates, calcium silicate, sulphur and lime, either in powder or granular form.

Granule or pellet compositions may be prepared by mixing the active material in finely divided form with a clay (with or without a water-soluble binder), moistening the mixture with 15—20% water, extruding the mass under pressure through an orifice, and either cutting the extruded material to size before drying to yield pellets, or first drying and then granulating to yield granules. Alternatively granules, but usually not pellets, may be made by spraying active material in solution or suspension upon the surface of a preformed granule of clay, vermiculite, or other suitable granular material. When the active material is soluble in the spray medium so that it can penetrate into the pores of the granular carrier, no binding agent is needed. When it is insoluble and in suspension form, a binder is needed to cause the active material to adhere to the surface. The binder may be soluble such as goulac or dextrin, or colloidally soluble such as swollen starch, glue or polyvinyl alcohol. The final step in either case is to remove the liquid medium, whether solvent or carrier.

The compositions of the invention will usually contain a surface-active agent, in the case of concentrates the amount suitably being sufficient to render the concentrate, e.g. wettable powder, readily dispersible in water or in oil.

The term "surface-active agent" is used herein to include wetting agents, dispersing agents, suspending agents and emulsifying agents. Suitable surface-active agents are listed in, for example, United States Patent Specifications 2,426,417, 2,655,447 and 2,412,510 and British Specification No. 492,742, "Soap and Chemical Specialties", *31*, No. 7, pages 50—61, No. 8, pages 48—61, No. 9, pages 52—67, and No. 10, pages 38—67 (1955), McCutcheon in "Soap and Chemical Specialties", December, 1957; January, February, March, 1958 and Bulletin E—607 of the Bureau of Entomology and Plant Quarantine of the U. S. Department of Agriculture. In general, less than 10% by weight of surface-active agent need be present in herbicidal compositions according to the invention, and the amount of surface-active agent may be 1% by weight or even less.

The herbicidal compositions of this invention may contain two or more of the substituted uracils. They may also be formulated to contain other herbicides in addition to the substituted uracils, for example

2,3,6 - trichlorobenzoic acid and salts thereof
2,3,5,6 - tetrachlorobenzoic acid and salts thereof
2 - chloro - N,N - diallylacetamide
N,N - dipropylthiolcarbamic acid, ethyl ester
2,2 - dichloropropionic acid and salts thereof

methylarsonic acid and salts thereof
borates
chlorates
ammonium sulphamate
2,4 - dichlorophenoxyacetic acid

2,4,5 - trichlorophenoxyacetic acid
N - phenylcarbamic acid, isopropyl ester
N - (*m* - chlorophenyl)carbamic acid, isopropyl ester
trichloroacetic acid
maleic hydrazide

1,1 - dimethyl - 3 - (3,4 - dichlorophenyl) urea
1,1 - dimethyl - 3 - (*p* - chlorophenyl)urea
1,1 - dimethyl - 3 - phenylurea
1 - *n* - butyl - 1 - methyl - 3 - (3,4 - dichlorophenyl)urea
1 - methoxy - 1 - methyl - 3 - (3,4 - dichlorophenyl)urea

1 - methoxy - 1 - methyl - 3 - (*p* - chlorophenyl)urea
1,1,3 - trimethyl - 3 - (3,4 - dichlorophenyl)urea
2 - chloro - 4,6 - bis(ethylamino) - *s* - triazine
2 - chloro - 4 - ethylamino - 6 - isopropylamino - *s* - triazine
2 - chloro - 4,6 - bis(methoxypropyl - amino) - *s* - triazine
2 - methoxy - 4,6 - bis(isopropylamino) - *s* - triazine
2,4 - bis(isopropylamino) - 6 - methoxy - *s* - triazine
dinitro - *sec.* - butylphenol
2,3,6 - trichlorophenylacetic acid
5,6 - dihydro - (4A,6A) - dipyrido - (1,2-A,2',1'-C) pyrazinium dibromide
2,6 - dichlorobenzonitrile

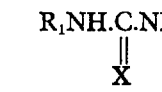
Optionally the compositions may contain conventional additives, e.g. adhesives such as gelatin and blood albumin; resins, for example rosin and alkyd resins, may also be used in certain compositions to increase retention or tenacity of deposits following application.

In a further aspect the invention provides a method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective quantity of at least one 3-substituted uracil which is a compound of general formula I or II as hereinbefore defined or a metal salt thereof. The amount of active compound used will depend on the weeds to be controlled, the formulation used, the mode of application, the climate, season of the year, rainfall and other variables, and because of this it is not possible to state generally a particular rate of application which will be suitable for all situations.

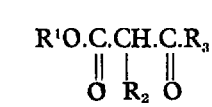
Some of the 3-substituted uracils are especially useful in controlling the growth of weeds on uncultivated areas. Thus in suitable circumstances some of the uracils can be used as soil sterilants and/or in soil-foliage applications; for the latter use rates of at least 2 pounds per acre are generally required, while for tough weeds rates of 10 to 25 or 35 pounds per acre, or even more, up to 80 pounds per acre, may be required.

In suitable cases the 3-substituted uracils can be used to obtain selective control of weeds in the presence of crops. For such use pre-emergence application is usually preferred, in which case rates as low as 0.5 pounds per acre can be effective though up to 2, 3, 4 or 5 pounds per acre or more may be needed in some instances. The uracils can also be used in some cases for post-emergence application.

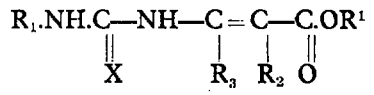
In a still further aspect the invention provides a novel process for the preparation of metal salts of the substituted uracils which comprises (A) heating a urea of the formula:



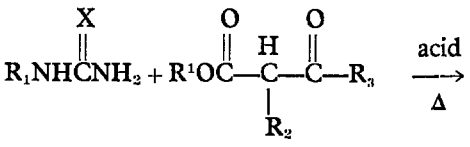
with a β-keto ester of the formula:

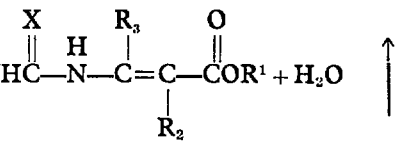


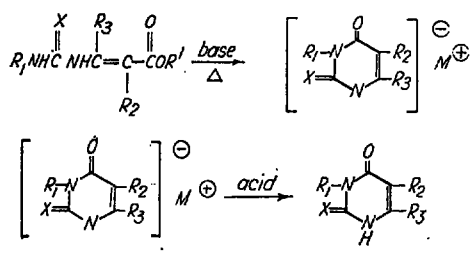
[wherein R^1 is an alkyl group of 1 to 6 carbon atoms and X, R_1, R_2 and R_3 are as defined above, with the proviso that R_1, R_2 and R_3 are such that they do not interfere with the desired reaction in step (A) or the subsequent step (B)] in the presence of an acidic compound and under substantially anhydrous reaction conditions, to produce a 3 - (3 - substituted ureido) - 2,3 - unsaturated ester of the formula:



and (B) heating the said ester under substantially anhydrous conditions in the presence of a strong base to effect ring closure. If desired the salt produced can then be converted to the corresponding substituted uracil by reacting it with an acid. This three-step reaction sequence is illustrated by the following equations:







The ureido unsaturated ester is hydrolysed by water, and it is because of this that the reaction is carried out under substantially anhydrous conditions, i.e. in the presence of insufficient water to cause substantial hydrolysis of the unsaturated ester. Since water is formed in the first step of the reaction, this water must be removed as it is formed, preferably as rapidly as possible, suitably by distillation from the reaction mixture.

It is often preferred to separate the ureido unsaturated ester from the acid before heating it with the strong base, and the process is described by reference to such procedure. However, a technical grade of the uracil salt can be obtained by carrying out the two steps sequentially in the same reaction vessel, sufficient base being added after step (A) to neutralise the acid and also provide the desired amount of base for step (B).

To obtain the best yields the molar ratio of the β-keto ester to the substituted urea should be about 1:1; a slight excess of one reactant or the other is, however, advantageous in that it drives the reaction to completion.

It will be noted that R_1, R_2 and R_3 should be such that they do not interfere with the desired reaction in either step (A) or step (B) under the chosen reaction conditions. For example R_2 is preferably a hydrogen, fluorine, chlorine or bromine atom, an alkoxy group of up to 3 carbon atoms, an allyl group, an alkyl group of up to 4 carbon atoms or a cyano group, all of which are inert.

Step (A) of the reaction is preferably carried out in an inert liquid medium, i.e. one which does not react with the reagents or products, is liquid above 7°C., and preferably boils between 60° and 140°C. under the chosen reaction conditions. Suitable inert liquids include benzene, toluene, xylene, chloroform and chlorobenzene and mixtures thereof with a water-miscible liquid such as dioxane. Preferably 1 to 3 parts by weight of the inert liquid are used for each part of reactants, about 1 part being particularly suitable.

Use of an inert liquid medium is preferred so as to avoid the possibility of localized heating of the reaction mixture, and since the water formed during the reaction may be removed rapidly by azeotropic distillation. When using an inert liquid medium, it is convenient to operate at atmospheric pressure and at the boiling point of the inert liquid; the azeotropic distillation may be carried out at reduced pressures, e.g. 12 to 300 mm. Hg, with a correspondingly reduced boiling point. When the reaction is carried on without an inert liquid medium, the reaction temperature is preferably maintained between 80° and 110°C. until approximately the theoretical amount of water has been collected by distillation, preferably under reduced pressure of about 12 to 300 millimetres of mercury.

The reaction is generally continued for 1 to 15 hours, or until water no longer evolves from the reaction. The reaction time will, of necessity, depend upon many variables, such as temperature, pressure, reactants and catalyst, and the rate at which the water distills.

For initiation of the reaction and its successful operation, it is necessary to have an acidic catalyst present. The catalyst is preferably a protonic acid, such as sulphuric, hydrochloric, hydrobromic, hydrofluoric, phosphoric, polyphosphoric, formic or maleic acid, but may also be an acidic salt such as sodium bisulphate; or an acidic ion exchange resin. Sulphuric and phosphoric acids are the preferred catalysts. Generally a mole ratio of acidic catalyst to the mono-substituted urea or thiourea between 0.01:1 and 1:1 is satisfactory.

As stated above rapid removal of the water formed in the first stage is desirable since the unsaturated ester intermediates (and to some extent the ureas) hydrolyze slowly to undesirable by-products when they are in contact with water and the acidic catalyst for prolonged periods. It is therefore preferable to stir the mixture vigorously during the heating to promote removal by distillation of the water as it is formed. To minimize the hydrolysis, it is particularly advantageous to add gradually the appropriate mixture of β-keto ester, mono-substituted urea, and acidic catalyst to a stirred refluxing inert liquid medium and to remove the water formed as quickly as possible from the heated reaction zone by azeotropic distillation.

One can judge the course and completion of the reaction by measuring the weight or volume of the water distillate collected from the reaction. Upon completion of the reaction, the amount of water should be equivalent to the amount of urea or thiourea used.

The reaction residue from the first step is a mixture of the desired intermediate, 3-(3-substituted ureido) - 2,3 - unsaturated ester and the acidic catalyst, with or without an inert liquid carrier. Such mixtures may be used without further treatment for the second stage, or an essentially catalyst-free ureido intermediate can be used, for example, if the reaction is carried out in an inert liquid medium, by decanting or siphoning the hot reaction fluid away from the insoluble catalyst. The inert liquid medium containing the ureido product may be used for the second stage, or, if desired, relatively pure ureido compound may be obtained by distilling the inert liquid, preferably under reduced pressure.

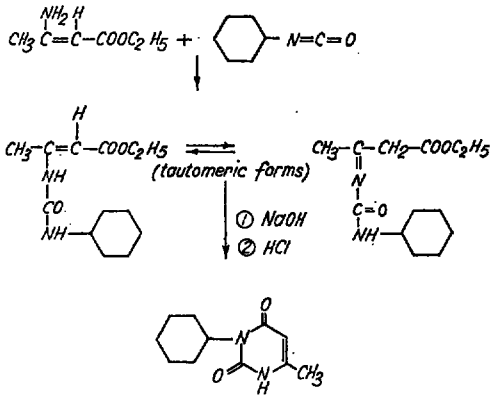
In the second stage of the reaction, the unsaturated ester intermediate may be diluted with an inert liquid, e.g. ethanol, toluene, methanol, isopropanol, acetone, tetrahydrofuran, dioxane, benzene, dimethylformamide, cyclohexanone, or a mixture of two or more of these, particularly if the first stage is carried out without an inert liquid carrier or if the ureido intermediate is isolated after step (A). The reaction mixture is heated for a short time at reflux temperature with an excess (e.g. of 1—5%) of a strong base such as sodium alkoxide, sodium hydroxide, or potassium hydroxide. If the ester intermediate is diluted, then the dilution and the addition of the base are preferably accomplished at the same time

by using a solution of a sodium alkoxide in a non-aqueous liquid. Heating is continued for about 15 to 30 minutes. The reflux temperature is usually from 55° to 155°C. Ring closure occurs rapidly at reflux temperature. The corresponding salt of the desired 3-substituted uracil may be obtained as a residue by removing the liquid medium. These salts can be used directly as aqueous solutions in herbicidal applications.

If it is desired to prepare the corresponding uracil from the salt, the addition of a sufficient amount of an aqueous solution of a protonic acid to lower the pH of the reaction mixture to about 1.0 neutralizes the salts of the 3-substituted uracils and precipitates the acidic forms of these products as solids or oils, which can be easily filtered or separated and dried. For example, the reaction mixture obtained in the second stage, containing the inert liquid, the salts of the desired 3-substituted uracil and the base, may be diluted with sufficient water and stirred to dissolve the salts. The inert, water-immiscible liquid separates and may be removed readily by conventional procedures. The water layer may be treated with acid to neutralize the 3-substituted uracil salt. The acidic form of the substituted uracil then precipitates out of solution as a solid material.

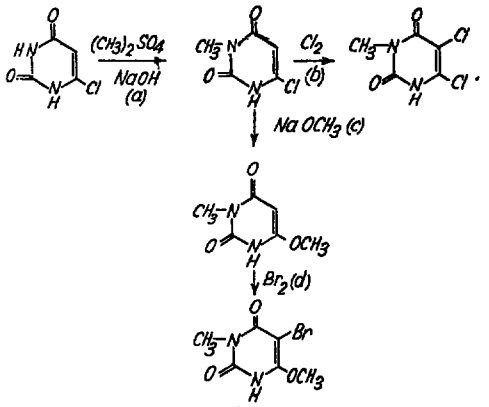
Other processes may also be used for preparing the uracils.

A process for preparing the uracils of class (2) above, in which R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms, R_2 is hydrogen, and R_3 is alkyl of up to 5 carbons, is illustrated in the following equations for the preparation of the known compound 3 - cyclohexyl - 6 - methyl uracil

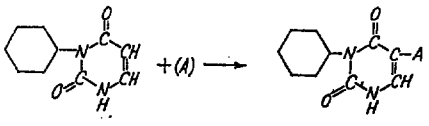


Generally, esters of β - amino - α,β - unsaturated acids can be prepared by reacting the corresponding β-keto esters with aqueous ammonia [Conrad and Epstein, Ber. *20*, 3054 (1887)]. The properly substituted β - amino-α,β - unsaturated esters may then be reacted with a cycloalkyl isocyanate or isothiocyanate in an inert solvent such as toluene or xylene for a short interval of time at reflux temperature, the reaction mixture being chilled and filtered, and the filtrate distilled to remove the solvent. Generally, a viscous liquid or solid residue remains [crude β - (3 - cycloalkyl-ureido) - α,β - unsaturated ester] which can be reacted without further purification with an aqueous alcoholic alkaline solution at reflux temperature to bring about the desired ring closure. At this point the reaction mixture may be made acidic with a strong acid such as hydrochloric acid and distilled to remove most of the alcohol. Upon chilling the remaining aqueous solution, the corresponding substituted uracil separates out as an essentially pure solid. [More general details for related compounds are given in articles by Behrend and Meyer Ann. *314*, 219 (1901) and Ber. *33*, 622 (1900)].

6-Chlorouracil, prepared by acidic hydrolysis of 2,4 - dimethoxy - 6 - chloropyrimidine (see British Specification No. 677,342), may be used as a starting material for the preparation of many of the uracils useful as herbicides according to the present invention, as shown in the following diagram (it will be appreciated that the intermediates shown in the diagram are not suitable for use as active ingredients in the compositions of the invention):



3—5 substituted uracils may be prepared by reacting a 3-substituted uracil with electrophilic reagents according to the following equation:



for example where A is bromine, chlorine, CH_2Cl, CH_2OH, —SCN, or NO_2, analogous methods being described in more detail in the following articles:

J.A.C.S. *61*, 1015 (1939),
Ann. *305*, 314,
Ann. *352*, 242,
Ann. *441*, 192 and
J.A.C.S. *81*, 2674 (1959) for halo groups;

Ann. *385*, 293 (1911) for chloromethyl groups, which may then be reacted with suitable alcohols, water or methyl mercaptide to give alkoxymethyl, hydroxymethyl and methylthiomethyl groups respectively;

J.A.C.S. *63*, 2323 (1941), Org. Syntheses, Coll. Vol II, 574 (1943) and Helv. Chim Acta., *19*, 1411 (1936) for thiocyano groups; and

J.A.C.S. *30*, 1150 (1908) for nitro groups.

The metal salts of the uracils may be prepared directly as has already been mentioned, or may be prepared by known methods, such as dissolving the free uracil in an aqueous or nonaqueous solution of at least an equimolar amount of a base or basic salt containing the desired cation. For example, a sodium salt may be prepared by dissolving the uracil in water containing an equimolar amount of sodium hydroxide. The salt may then be isolated from the solution by removal of the water. The uracil salts which are not soluble in water may be prepared by treating an aqueous solution of an alkali metal salt of the uracil with an aqueous solution of a water-soluble salt of the metal.

The following Examples further illustrate the invention; all parts and percentages are by weight unless otherwise stated. Certain of the 3-substituted uracils used as starting materials in the Examples are new compounds, but they can readily be prepared by the methods hereinbefore described.

EXAMPLE 1

Preparation of 3 - cyclohexyl - 5 - chloro - 6 - methyl - 2 - thiouracil

8.0 parts of chlorine are added to a stirred solution of 22.4 parts of 3 - cyclohexyl - 6 - methyl - 2 - thiouracil is about 100 parts of glacial acetic acid. The temperature is maintained below 30°C. during this addition. The solution is stirred 1/2 hour longer at room temperature, then poured into ice water, whereupon a solid separates. This solid is collected by filtration and washed well with water to give 3 - cyclohexyl - 5 - chloro - 6 - methyl - 2 - thiouracil, which can be purified by recrystallisation.

EXAMPLE 2

Preparation of 5 - bromo - 3 - cyclopentyl - 6 - propyluracil

Seventeen parts of bromine are added over a 20-minute period to a stirred solution of 22.2 parts of 3 - cyclopentyl - 6 - propyluracil in about 100 ml. of glacial acetic acid. The temperature is maintained below 30°C. during this addition. The solution is stirred at room temperature for an additional 1 1/2 hours, then poured into a mixture of ice and water, with stirring. The white solid which separates is collected by filtration, washed well with water, and dried in a vacuum oven, to give 5 - bromo - 3 - cyclopentyl - 6 - propyluracil, which can be purified by recrystallisation.

The following compounds can be prepared by the methods described in Examples 1 and 2 by using equivalent amounts of the uracils and halogens set out in the following table instead of the uracils and halogens set out in the Examples.

Ex. No.	Uracil Starting Reagent	Parts by Weight	Halogen	Parts by Weight	Uracil Product
3	3-cycloheptyl-6-butyluracil	26.4	Br	17.0	3-cycloheptyl-5-bromo-6-butyluracil
4	3-cyclopentenyl-6-isobutyluracil	23.4	Cl	8.0	3-cyclopentenyl-5-chloro-6-isobutyluracil
5	3,6-dimethyluracil	14.0	Cl	8.0	3,6-dimethyl-5-chlorouracil
6	3-ethyl-6-methyluracil	15.4	Cl	8.0	3-ethyl-5-chloro-6-methyl-uracil
7	3-octyl-6-methyluracil	23.8	Cl	8.0	3-octyl-5-chloro-6-methyl-uracil
8	3-tert.-octyl-6-methyluracil	23.8	Br	17.0	3-tert.-octyl-6-bromo-6-methyluracil
9	3-heptyl-6-methyluracil	22.4	Cl	8.0	3-heptyl-5-chloro-6-methyl uracil
10	3-decyl-6-methyluracil	26.6	Br	17.0	3-decyl-5-bromo-6-methyl-uracil

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Ex. No.	Uracil Starting Reagent	Parts by Weight	Halogen	Parts by Weight	Uracil Product
11	3-methyl-6-ethyluracil	15.4	Cl	8.0	3-methyl-5-chloro-6-ethyl-uracil
12	3-methyl-6-butyluracil	18.2	Cl	8.0	3-methyl-5-chloro-6-butyl-uracil
13	3,6-diethyluracil	16.8	Br	17.0	3,6-diethyl-5-bromouracil
14	3,6-dibutyluracil	22.4	Cl	8.0	3,6-dibutyl-5-chlorouracil
15	3-phenyl-6-propyluracil	23.0	Cl	8.0	3-phenyl-5-chloro-6-propyl-uracil
16	3-(4-methyl-3-nitrophenyl)-6-methyluracil	26.1	Cl	8.0	3-(4-methyl-3-nitrophenyl)-5-chloro-6-methyluracil
17	3-(3,5-dichloro-4-methylphenyl)-6-ethyluracil	29.9	Cl	8.0	3-(3,5-dichloro-4-methyl-phenyl)-5-chloro-6-ethyluracil
18	3-(*p*-methoxyphenyl)-6-methyl-uracil	23.2	Br	17.0	3-(*p*-methoxyphenyl)-5-bromo-6-methyluracil
19	3-(*m*-fluorophenyl)-6-methyl-uracil	22.0	Cl	8.0	3-(*m*-fluorophenyl)-5-chloro-6-methyluracil
20	3-phenyl-6-butyluracil	24.4	Cl	8.0	3-phenyl-5-chloro-6-butyl-uracil
21	3-(*p*-bromophenyl)-6-methyl-uracil	28.1	Cl	8.0	3-(*p*-bromophenyl)-5-chloro-6-methyluracil
22	3-(3,5-dichloro-4-ethoxyphenyl)-6-methyluracil	31.5	Br	17.0	3-(3,5-dichloro-4-ethoxy-phenyl)-5-bromo-6-methyl-uracil
23	3-(4-methoxy-3-nitrophenyl)-6-methyluracil	27.7	Cl	8.0	3-(4-methoxy-3-nitrophenyl)-5-chloro-6-methyluracil
24	3-(3,4-dichloro-5-nitrophenyl)-6-n-butyluracil	35.8	Cl	8.0	3-(3,4-dichloro-5-nitro-phenyl)-5-chloro-6-n-butyl-uracil
25	3-*p*-tolyl-6-amyluracil	27.2	Cl	8.0	3-*p*-tolyl-5-chloro-6-amyl-uracil
26	3-(3-chloro-4-methylphenyl)-6-methyluracil	25.1	Cl	8.0	3-(3-chloro-4-methylphenyl)-5-chloro-6-methyluracil
27	3-(3-chloro-4-methoxyphenyl)-6-methyluracil	26.7	Br	17.0	3-(3-chloro-4-methoxy-phenyl)-5-bromo-6-methyl-uracil
28	3-(*o*-chlorophenyl)-6-methyl-uracil	23.7	Cl	8.0	3-(*o*-chlorophenyl)-5-chloro-6-~~methyl uracil~~
29	3-(*p*-chlorophenyl)-6-propyluracil	26.5	Cl	8.0	3-(*p*-chlorophenyl)-5-chloro-6-propyluracil
30	3-(3,4-dichlorophenyl)-6-methyl-uracil	27.1	Cl	8.0	3-(3,4-dichlorophenyl)-5-chloro-6-methyluracil

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Ex. No.	Uracil Starting Reagent	Parts by Weight	Halogen	Parts by Weight	Uracil Product
31	3-(*p*-butylbenzyl)-6-methyl-uracil	27.2	Cl	8.0	3-(*p*-butylbenzyl)-5-chloro-6-methyluracil
32	3-(3,4-dichlorophenyl)-6-ethyl-uracil	28.5	Cl	8.0	3-(3,4-dichlorophenyl)-5-chloro-6-ethyluracil
33	3-(β-phenethyl)-6-methyluracil	23.0	Cl	8.0	3-(β-phenethyl)-5-chloro-6-methyluracil
34	3-(*p*-tolyl)-6-ethyl-2-thiouracil	24.6	Br	17.0	3-(*p*-tolyl)-5-bromo-6-ethyl-2-thiouracil
35	3-(3-chloro-4-nitrophenyl)-6-propyl-2-thiouracil	32.5	Cl	8.0	3-(3-chloro-4-nitrophenyl)-5-chloro-6-propyl-2-thiouracil
36	3-propynyl-6-propyl-2-thiouracil	20.8	Br	17.0	3-propynyl-5-bromo-6-propyl-2-thiouracil
37	3-isopropyl-6-chlorouracil	18.8	Cl	8.0	3-isopropyl-5,6-dichlorouracil
38	3-cyclohexyl-6-methoxyuracil	22.4	Br	17.0	3-cyclohexyl-5-bromo-6-methoxyuracil
39	3-cyclopentyl-6-chlorouracil	21.4	Br	17.0	3-cyclopentyl-5-bromo-6-chlorouracil
40	3-allyl-6-ethoxyuracil	19.6	Cl	8.0	3-allyl-5-chloro-6-ethoxyuracil
41	3-cyclohexyluracil	19.4	Cl	8.0	3-cyclohexyl-5-chlorouracil
42	3-cyclohexyluracil	19.4	Br	17.0	3-cyclohexyl-5-bromouracil
43	3-cyclopentyluracil	18.0	Cl	8.0	3-cyclopentyl-5-chlorouracil
44	3-cyclopentyluracil	18.0	Br	17.0	3-cyclopentyl-5-bromouracil
45	3-cyclooctyluracil	22.2	Cl	8.0	3-cyclooctyl-5-chlorouracil
46	3-cyclooctyluracil	22.2	Br	17.0	3-cyclooctyl-5-bromouracil
47	3-cyclopentenyluracil	17.8	Cl	8.0	3-cyclopentenyl-5-chlorouracil
48	3-cyclopentenyluracil	17.8	Br	17.0	3-cyclopentenyl-5-~~bromouraci~~ bromouracil
49	3-isopropyluracil	15.4	Cl	8.0	3-isopropyl-5-chlorouracil
50	3-isopropyluracil	15.4	Br	17.0	3-isopropyl-5-bromouracil
51	3-hexyluracil	19.7	Cl	8.0	3-hexyl-5-chlorouracil
52	3-phenyluracil	18.8	Br	17.0	3-phenyl-5-bromouracil
53	3-(3,4-dichlorophenyl)uracil	25.9	Br	17.0	3-(3,4-dichlorophenyl)-5-bromouracil
54	3-benzyluracil	20.2	Br	17.0	3-benzyl-5-bromouracil
55	3-cyanouracil	13.7	Br	17.0	3-cyano-5-bromouracil

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Ex. No.	Uracil Starting Reagent	Parts by Weight	Halogen	Parts by Weight	Uracil Product
56	3-ethyluracil	14.0	Cl	8.0	3-ethyl-5-chlorouracil
57	3-(3-methoxypropyl)uracil	17.4	Br	17.0	3-(3-methoxypropyl)-5-bromouracil
58	3-sec. amyluracil	18.2	Br	17.0	3 sec. amyl-5-bromouracil
59	3-allyluracil	15.2	Cl	8.0	3-allyl-5-chlorouracil
60	3-butyluracil	16.8	Br	17.0	3-butyl-5-bromouracil
61	3-decyluracil	25.2	Br	17.0	3-decyl-5-bromouracil
62	3-(2-chloroethyl)uracil	17.6	Cl	8.0	3-(2-chloroethyl)-5-chlorouracil

EXAMPLE 63

Preparation of 3 - butyl - 6 - methyl - 5 - nitrouracil

A solution of 40 parts by volume of fuming nitric acid and 40 parts by volume of fuming sulphuric acid (20% SO_3) is stirred at 25—30°C. while 20 parts by weight of 3 - butyl - 6 - methyluracil are added portion-wise over a 30-minute period. The solution is stirred an additional 30 minutes, then poured slowly into 4 volumes of a stirred ice-water mixture. The uracil separates out as a pale yellow solid. It is collected by filtration, washed well with water, and air-dried. One recrystallisation from 1,1,1 - trichloroethane gives analytically pure 3 - butyl - 6 - methyl - 5 - nitrouracil, melting at 170—171°C.

The following 5-nitro substituted uracils can be prepared as in Example 63 by substituting equivalent amounts of the substituted uracil starting reagents set forth in the following table for the 3 - butyl - 6 -methyluracil in Example 63.

Ex. No.	Uracil Starting Reactant	5-Nitrouracil Product
64	3-ethyl-6-methyluracil	3-ethyl-6-methyl-5-nitrouracil
65	3-cyclohexyl-6-chlorouracil	3-cyclohexyl-5-nitro-6-chlorouracil
66	3-allyl-6-methyl-2-thiouracil	3-allyl-6-methyl-6-nitro-2-thiouracil
67	3-(*p*-chlorophenyl)-6-propyluracil	3-(*p*-chlorophenyl)-5-nitro-6-propyluracil
68	3-(β-phenethyl)-6-ethyluracil	3-(β-phenethyl)-6-ethyl-5-nitrouracil
69	3-benzyl-6-methyl-2-thiouracil	3-benzyl-6-methyl-5-nitro-2-thiouracil
70	3-decyl-6-butyluracil	3-decyl-6-butyl-5-nitrouracil
71	3-cyclohexyl-6-methyluracil	3-cyclohexyl-6-methyl-5-nitrouracil
72	3-cyclopentenyl-6-butyl-2-thiouracil	3-cyclopentenyl-6-butyl-5-nitro-2-thiouracil
73	3-cyclooctyl-6-propyluracil	3-cyclooctyl-6-propyl-5-nitrouracil
74	3-cyclohxeyl-6-ethyluracil	3-cyclohexyl-6-ethyl-5-nitrouracil
75	3-cyclohexyluracil	3-cyclohexyl-5-nitrouracil
76	3-isopropyluracil	3-isopropyl-5-nitrouracil
77	3-*sec.* amyluracil	3-*sec.* amyl-5-nitrouracil
78	3-phenyluracil	3-phenyl-5-nitrouracil
79	3-allyluracil	3-allyl-5-nitrouracil
80	3-*sec.* butyluracil	3-*sec.* butyl-5-nitrouracil
81	3-cyclooctyluracil	3-cyclooctyl-5-nitrouracil
82	3-allyl-2-thiouracil	3-allyl-5-nitro-2-thiouracil
83	3-cyclopentenyluracil	3-cyclopentenyl-5-nitrouracil
84	3-butyluracil	3-butyl-5-nitrouracil

EXAMPLE 85

Preparation of 3 - amyl - 6 - methyl - 5 - thiocyano - 2 - thiouracil

A suspension of 39 parts by weight of lead thiocyanate in 200 parts by volume of carbon tetrachloride is treated slowly and with vigorous agitation with 17.6 parts by weight of bromine. Occasional external cooling is required to hold the temperature of the reaction mixture at 15—20°C. At the end of the addition, stirring is continued until the bromine colour is discharged, after which the solution is filtered rapidly, preferably in the absence of moisture. To this solution is added 21.2 parts by weight of 3 - amyl - 6 - methyl - 2 - thiouracil, and the resulting mixture is stirred at room temperature for 5 hours. At the end of this time, the solvent is removed, leaving behind essentially pure 3 - amyl - 6 - methyl - 5 - thiocyano - 2 - thiouracil.

The following compounds are prepared as in Example 85 by substituting equivalent amounts of the appropriate uracil starting reagents for the 3 - amyl - 6 - methyl - 2 - thiouracil in Example 85.

Example No.	Product
86	3-ethyl-6-hexyl-5-thiocyanouracil
87	3-heptyl-6-ethyl-5-thiocyano-2-thiouracil
88	3-(3,4-dichlorophenyl)-6-methyl-5-thiocyanouracil
89	3-(*m*-nitrophenyl)-6-butyl-5-thiocyanouracil
90	3-benzyl-6-methyl-5-thiocyanouracil
91	3-allyl-6-propyl-5-thiocyanouracil
92	3-(β-phenethyl)-6-methyl-5-thiocyanouracil
93	3-cyclohexyl-6-methyl-5-thiocyanouracil
94	3-cyclopentyl-6-butyl-5-thiocyanouracil
95	3-cycloheptenyl-6-ethyl-5-thiocyano-2-thiouracil
96	3-cyclohexyl-6-amyl-5-thiocyanouracil
97	3-isopropyl-5-thiocyanouracil
98	3-cyclopentenyl-5-thiocyanouracil
99	3-allyl-5-thiocyanouracil
100	3-cyclooctyl-5-thiocyanouracil
101	3-phenyl-5-thiocyanouracil
102	3-sec. butyl-5-thiocyanouracil
103	3-benzyl-5-thiocyanouracil
104	3-(*m*-nitrophenyl)-5-thiocyanouracil
105	3-(β-phenethyl)-5-thiocyanouracil
106	3-cyano-5-thiocyanouracil
107	3-cyclohexyl-5-thiocyano-2-thiouracil
108	3-sec. amyl-5-thiocyano-2-thiouracil

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EXAMPLE 109

Preparation of 3 - isopropyl - 5,6 - dimethyl-2 - thiouracil

A mixture of 23.6 parts of isopropylthiourea, 28.8 parts of ethyl 2 - methyl - 3 - ketobutyrate, about 0.5 part of 85% orthophosphoric acid, and about 200 parts of benzene was heated at reflux. Water was collected in a Dean Stark trap. After 24 hours, about 2.5 parts of water had been collected and there appeared to be no more separating. The solution was decanted and evaporated to a mixture of viscous oil and solid, which was taken up in about 200 parts of ethanol containing about 10.5 parts of sodium methoxide and heated at reflux for 10 minutes. Most of the ethanol was removed under reduced pressure and the residue was taken up in just sufficient water to dissolve it. Concentrated hydrochloric acid was added to lower the pH to 4 and the resulting white solid was collected by filtration. This was recrystallized to give pure 3 - isopropyl - 5,6 - dimethyl - 2 - thiouracil.

The following compounds are prepared as in Example 109 by substituting equivalent amounts of the ureas and thioureaus and equivalent amounts of the β-keto esters set forth in the following table for the isopropylthiourea and ethyl 2 - methyl - 3 - ketobutyrate in Example 109.

Ex. No.	β-Keto Ester	Parts by Weight	Urea	Parts by Weight	Uracil Product
110	ethyl 2-butyl-3-ketovalerate	39.8	amylurea	26.0	3-amyl-5-butyl-6-ethyl-uracil
111	ethyl 2-ethyl-3-ketovalerate	34.2	propylthiourea	23.6	3-propyl-5,6-diethyl-2-thiouracil
112	ethyl 2-methyl-3-ketobutyrate	28.8	allylurea	20.0	3-allyl-5,6-dimethyluracil
113	ethyl 2-methyl-3-ketoheptan-oate	37.0	propynylurea	19.6	3-propynyl-5-methyl-6-butyluracil
114	ethyl 2-ethyl-3-ketooctanoate	45.4	benzylthiourea	33.2	3-benzyl-5-ethyl-6-amyl-2-thiouracil
115	ethyl 2-methyl-3-ketohexan-oate	34.2	β-phenethylurea	32.8	3-(β-phenethyl)-5-methyl-6-propyluracil
116	ethyl 2-methyl-3-ketobutyrate	23.8	methylurea	14.8	3,5,6-trimethyluracil
117	ethyl-2-butyl-3-ketovalerate	39.8	2-chlorophenyl-thiourea	37.2	3-(*p*-chlorophenyl)-5-butyl-6-ethyl-2-thiouracil
118	ethyl 2-ethyl-3-ketovalerate	34.2	*m*-tolylurea	30.0	3-(*m*-tolyl)-5,6-diethyluracil
119	ethyl 2-methyl-3-keto-octanoate	39.8	*p*-anisylurea	33.2	3-(*p*-anisyl)-5-methyl-6-amyluracil
120	ethyl 2-ethyl-3-ketobutyrate	31.4	*o*-nitrophenylthio-urea	39.4	3-(*o*-nitrophenyl)-5-ethyl-6-methyl-2-thiouracil
121	ethyl 2-propyl-3-ketohexan-oate	39.8	allylurea	20.0	3-allyl-5,6-dipropyluracil
122	ethyl 2-methyl-3-keto-butyrate	28.8	β-phenethylthiourea	36.0	3-(-phenethyl)-5,6-di-methyl-2-thiouracil

Ex. No.	β Keto Esters	Parts by Weight	Urea or Thiourea	Parts by Weight	Substituted Uracil Product
123	ethyl acetoacetate	95	cyclohexylthiourea	118	3-cyclohexyl-6-methyl-2-thiouracil
124	ethyl acetoacetate	95	cycloheptenylthiourea	127	3-cycloheptenyl-6-methyl-2-thiouracil
125	ethyl acetoacetate	95	cycloheptylthiourea	127	3-cycloheptyl-6-methyl-2-thiouracil
126	ethyl acetoacetate	95	cyclooctylthiourea	138	3-cyclooctyl-6-methyl-2-thiouracil
127	ethyl acetoacetate	95	cyclohexenylurea	107	3-cyclohexenyl-6-methyl-uracil
128	ethyl 3-ketohexanoate	119	cyclooctenylurea	125	3-cyclooctenyl-6-propyl-uracil
129	ethyl acetoacetate	95	cyclopentylthiourea	109	3-cyclopentyl-6-methyl-2-thiouracil
130	ethyl 3-ketoheptanoate	130	cycloheptenylurea	115	3-cycloheptenyl-6-butyl-uracil
131	ethyl acetoacetate	95	cyclooctenylurea	125	3-cyclooctenyl-6-methyl-uracil

EXAMPLE 132

Preparation of 3 - cyclopentenyl - 5,6 - dimethyluracil with no isolation of intermediates

A mixture containing 25.9 parts of cyclopentenylurea, 25.4 parts of methyl 2 - methyl-3 - ketobutyrate, about 2 parts of phosphoric acid, about 100 parts of dioxane, and about 90 parts of benzene is stirred and heated at reflux temperature. The water given off by the reaction is continuously distilled and trapped out of the distillate as the lower layer. The resulting solution is base hydrolyzed *in situ* by adding a solution containing about 14 parts by weight of sodium methoxide and about 40 parts by weight of methanol. The solution is refluxed for 10 minutes and then about 200 parts by weight of water are added. On shaking, the sodium salt of the desired uracil product dissolves in the water. The aqueous solution is separated from the organic layer and acidified. Solid 3 - cyclopentenyl-5,6 - dimethyluracil is separated by filtration and dried.

The following uracils are prepared according to the method of Example 132 by replacing the cyclopentenylurea and methyl 2 - methyl - 3 - ketobutyrate with equivalent amounts of the appropriate ureas, thioureas and β-keto esters.

Ex. No.	β-Keto Ester	Parts by Weight	Urea or Thiourea	Parts by Weight	Substituted Uracil Product
133	methyl 2-ethyl-3-keto-butyrate	28.8	cyclopentylthiourea	29.1	3-cyclopentyl-5-ethyl-6-methyl-2-thiouracil
134	ethyl acetoacetate	25.4	cycloheptylthiourea	33.9	3-cycloheptyl-6-methyl-2-thiouracil
135	ethyl 2-ethoxy-3-keto-butyrate	34.2	cyclopentylthiourea	29.1	3-cyclopentyl-5-ethoxy-6-methyl-2-thiouracil
136	ethyl acetoacetate	25.4	cyclooctylthiourea	36.8	3-cyclooctyl-6-methyl-2-thiouracil
137	methyl-2-butyl-3-keto-heptanoate	42.6	cyclooctylurea	33.9	3-cyclooctyl-5,6-dibutyl-uracil
138	ethyl 2-allyl-3-ketobutyrate	42.2	allylurea	20.6	3-allyl-5-allyl-6-methyl-uracil

EXAMPLE 139

Preparation of 3 - cyclopentenyl - 6 - methyl-uracil, sodium salt

A mixture containing 25.9 parts of cyclopentenylurea, 25.4 parts of ethyl acetoacetate, and about 2 parts of phosphoric acid is gradually added to about 190 parts of benzene which is heated to reflux temperature. The water given off by the reaction is continuously distilled and trapped out of the distillate as the lower layer. The resulting benzene solution is diluted with about 14 parts of sodium methoxide dissolved in about 40 parts of methanol. The solution is refluxed for 10 minutes and then allowed to cool. The solid collected by filtration is essentially pure 3-cyclopentenyl - 6 - methyluracil, sodium salt.

EXAMPLE 140

Preparation of 3 - cyclohexyluracil

A mixture of 56.8 parts of cyclohexylurea, 69 parts of diethyl oxalacetate, and 4 parts of 85% orthophosphoric acid in 400 parts of benzene is heated at reflux for 8 hours, during which time 7.8 parts of water is collected. The solvent is removed and the residual oil taken up in 400 parts of water containing 24 parts of sodium hydroxide. The solution is heated on a steam bath with agitation for 2 hours. Acidification with concentrated hydrochloric acid causes precipitation of 3 - cyclohexyluracil - 6 - carboxylic acid. This is collected by filtration, air-dried, and taken up as a suspension in 100 parts of a eutectic mixture of diphenyl ether and diphenyl. This mixture is stirred and heated at reflux, whereupon CO_2 is evolved. Upon completion of CO_2 evolution, the mixture is cooled, filtered, and the eutectic mixture washed out with benzene, leaving crystalline 3 - cyclohexyluracil on the funnel.

The following compounds are similarly prepared by substituting equivalent amounts of the cycloalkylureas and thioureas set forth below for the cyclohexylurea in Example 140.

Ex. No.	Starting Urea	Parts by Weight	Uracil Product
141	cyclohexylthiourea	63	3-cyclohexyl-2-thiouracil
142	cyclopentenylurea	50	3-cyclopentenyluracil
143	cycloheptylurea	62.5	3-cycloheptyluracil
144	cyclooctylurea	68	3-cyclooctyluracil
145	cyclopentylthiourea	58	3-cyclopentyl-2-thiouracil
146	cyclooctenylurea	67	3-cyclooctenyluracil

EXAMPLE 147

Preparation of 3 - cyclohexyl - 5 - methyluracil

A mixture of 56.8 parts of cyclohexylurea, 73 parts of diethyl - α - methyl oxalacetate, and 4 parts of 85% orthophosphoric acid in 400 parts of benzene is heated at reflux for 8 hours, during which time 7.8 parts of water are collected. The solvent is removed and the residual oil taken up in 400 parts of water containing 24 parts of sodium hydroxide. The solution is heated on a steam bath with agitation for 2 hours. Acidification with concentrated hydrochloric acid causes precipitation of 3 - cyclohexyl - 5 - methyluracil - 6 - carboxylic acid. This is collected by filtration, air-dried, and taken up as a suspension in 100 parts of a eutectic mixture of diphenyl ether and diphenyl. This mixture is stirred and heated at reflux, whereupon CO_2 is evolved. Upon completion of the CO_2 evolution, the mixture is cooled, filtered, and the solvent washed out with benzene. Crystalline 3 - cyclohexyl - 5 - methyluracil remains.

The following compounds are prepared as in Example 147 by substituting equivalent amounts of mono substituted ureas and thioureas and equivalent amounts of oxalacetates set forth in the following table for the cyclohexylurea and diethyl - α - methyl oxalacetate in Example 147.

Ex. No.	Oxalacetate	Parts by Weight	Urea	Parts by Weight	Substituted Uracil Product
148	diethyl-2-methyloxalacetate	73	cyclooctylurea	68	3-cyclooctyl-5-methyluracil
149	diethyl 2-ethyloxalacetate	78.5	cyclopentylurea	51	3-cyclopentyl-5-ethyluracil
150	diethyl 2-butyloxalacetate	89.5	cyclohexenlyurea	56	3-cyclohexenyl-5-butyl-uracil
151	diethyl 2-methyloxalacetate	73	cyclohexylthiourea	63	3-cyclohexyl-5-methyl-2-thiouracil
152	diethyl 2-cyanooxalacetate	81	cyclohexylurea	57	3-cyclohexyl-5-cyanouracil
153	diethyl 2-cyanooxalacetate	81	isopropylurea	41	3-isopropyl-5-cyanouracil
154	diethyl 2-allyloxalacetate	91	isopropylurea	41	3-isopropyl-5-allyluracil
155	diethyl-2-allyloxalacetate	91	cyclopentylurea	51	3-cyclopentyl-5-allyluracil
156	diethyl 2-methyloxalacetate	73	isopropylurea	41	3-isopropyl-5-methyluracil
157	diethyl 2-methyloxalacetate	73	sec. butylurea	47	3 sec. butyl-5-methyluracil
158	diethyl α-ethyloxalacetate	87	heptylthiourea	69.5	3-heptyl-5-ethyl-2-thiouracil
159	diethyl α-propyloxalacetate	92	allylthiourea	46.4	3-allyl-5-propyl-2-thio-uracil
160	diethyl α-methyloxalacetate	81	benzylurea	60.0	3-benzyl-5-methyluracil
161	diethyl α-butyloxalacetate	97	β-phenethylthiourea	72.0	3-(β-phenethyl)-5-butyl-2-thiouracil
162	diethyl α-ethyloxalacetate	87	3,4-dichlorophenyl-urea	82.0	3-(3,4-dichlorophenyl)-5-ethyluracil
163	diethyl α-propyloxalacetate	92	3-nitro-4-chloro-phenylthiourea	92.3	3-(3-nitro-4-chlorophenyl)-5-propyl-2-thiouracil
164	diethyl α-ethoxyoxalacatete	93	ethylthiourea	41.6	3-ethyl-5-ethoxy-2-thio-uracil
165	diethyl α-methoxyoxalacetate	87	butylurea	46.3	3-butyl-5-methoxyuracil
166	diethyl α-propoxyoxalacetate	98	octylurea	68.7	3-octyl-5-propoxyuracil

Ex. No.	Oxalacetate	Parts by Weight	Urea	Parts by Weight	Substituted Uracil Product
167	diethyl α-methoxyoxalacetate	87	allylthiourea	46.4	3-allyl-5-methoxy-2-thiouracil
168	diethyl α-ethoxyoxalacetate	93	benzylthiourea	66.3	3-benzyl-5-ethoxy-2-thiouracil
169	diethyl α-methoxyoxalacetate	87	*p*-anisylurea	66.3	3-(*p*-anisyl)-5-methoxyuracil
170	diethyl α-methoxyoxalacetate	87	cyclohexylurea	57	3-cyclohexyl-5-methoxyuracil
171	diethyl-2-fluorooxalacetate	74.1	cyclohexylurea	57	3-cyclohexyl-5-fluorouracil
172	diethyl-2-fluorooxalacetate	74.1	cyclopentylurea	51	3-cyclopentyl-5-fluorouracil
173	diethyl-2-fluorooxalacetate	74.1	cyclohexylthiourea	63	3-cyclohexyl-5-fluoro-2-thiouracil
174	diethyl-2-fluorooxalacetate	74.1	cycloheptylurea	62.5	3-cycloheptyl-5-fluorouracil
175	diethyl-2-fluorooxalacetate	74.1	sec. butylurea	47	3-*sec.* butyl-5-fluorouracil
176	diethyl-2-fluorooxalacetate	74.1	allylurea	42	3-allyl-5-fluorouracil
177	diethyl-2-fluorooxalacetate	74.1	isopropylurea	41	3-isopropyl-5-fluorouracil
178	diethyl-2-fluorooxalacetate	74.1	phenylurea	54.4	3-phenyl-5-fluorouracil
179	diethyl-2-fluorooxalacetate	74.1	benzylurea	62	3-benzyl-5-fluorouracil
180	diethyl-2-methyloxalacetate	73	allylurea	42	3-allyl-5-methyluracil

EXAMPLE 181

Preparation of 3 - methyl - 5,6 - trimethyleneuracil

A mixture of 74 parts of methylurea, 162 parts of ethyl 2 - cyclopentanone - 1 - carboxylate and about 10 parts of phosphoric acid was stirred at reflux for 4 hours in a mixture of dioxane and benzene. During this time, the water given off by the reaction was trapped out. The solvent was stripped at reduced pressure and a portion of the resulting solid was recrystallized from cyclohexane to give 2 - (3 - methylureido) - 1 - cyclopentene carboxylic acid, ethyl ester.

The remaining unrecrystallized solid was dissolved in absolute alcohol containing sodium methoxide, and was refluxed for 10 minutes. The solvent was stripped at reduced pressure and the residue dissolved in water, cooled, and acidified. The solid was filtered off, dried, and recrystallized to give the desired 3 - methyl - 5,6 - trimethyleneuracil.

The following uracils are prepared according to the procedure in Example 181 by substituting the ureas or thioureas and the alkyl-2 - cycloalkanone - 1 - carboxylates listed below for the methylurea and the ethyl 2 - cyclopentanone - 1 - carboxylate.

Ex. No.	Substituted Urea	Parts by Weight	Ester of the Cycloalkanone Carboxylate	Parts by Weight	Substituted Uracil Products
182	isooctylurea	172	ethyl 2-cyclopentanone-1-carboxylate	162	3-isooctyl-5,6-trimethyleneuracil
183	cyclohexenylurea	140	methyl 2-cyclopentanone-1-carboxylate	156	3-cyclohexenyl-5,6-trimethyleneuracil
184	methylurea	74	ethyl 2-cyclohexanone-1-carboxylate	187	3-methyl-5,6-tetramethyleneuracil
185	n-octylurea	172	ethyl 2-cyclohexanone-1-carboxylate	187	3-n-octyl-5,6-tetramethyleneuracil
186	cyclopentenylurea	126	methyl 2-cyclopentanone-1-carboxylate	156	3-cyclopentenyl-5,6-trimethyleneuracil
187	allylurea	300	ethyl 2-cyclopentanone-1-carboxylate	468	3-allyl-5,6-trimethyleneuracil
188	cyclopentenylurea	126	methyl 2-cyclohexanone-2-carboyxlate	162	3-cyclopentenyl-5,6-tetraeneuracil
189	cyclooctenylurea	168	methyl 2-cyclohexanone-2-carboxylate	162	3-cyclooctenyl-5,6-tetramethyleneuracil
190	methylurea	74	methyl 2-cycloheptanone-2-carboxylate	162	3-methyl-5,6-pentamethyleneuracil
191	isopropylurea	102	methyl 2-cycloheptanone-2-carboxylate	162	3-isopropyl-5,6-pentamethyleneuracil
192	n-amylurea	130	ethyl 2-cycloheptanone-2-carboxylate	202	3-n-amyl-5,6-pentamethyleneuracil
193	isooctylurea	172	ethyl 2-~~cyclophetanone~~-2-carboxylate	202	3-isooctyl-5,6-pentamethyleneuracil
194	cyclopentylurea	126	ethyl 2-cycloheptanone-2-carboxylate	202	3-cyclopentyl-5,6-pentamethyleneuracil
195	cyclohexylurea	142	ethyl 2-cycloheptanone-2-carboxylate	202	3-cyclohexyl-5,6-pentamethyleneuracil
196	cyclopentenylurea	126	ethyl 2-cycloheptanone-2-carboxylate	202	3-cyclopentenyl-5,6-pentamethyleneuracil
197	cycloheptenylurea	156	ethyl 2-cycloheptanone-2-carboxylate	202	3-cycloheptenyl-5,6-pentamethyleneuracil
198	methylthiourea	90	methyl 2-cyclopentanone-1-carboxylate	156	3-methyl-5,6-trimethylene-2-thiouracil
199	n-butylthiourea	116	methyl 2-cyclopentanone-1-carboxylate	156	3-n-butyl-5,6-trimethylene-2-thiouracil
200	n-decylthiourea	216	methyl 2-cyclopentanone-1-carboxylate	156	3-n-decyl-5,6-trimethylene-2-thiouracil
201	cyclohexylthiourea	154	ethyl 2-cyclopentanone-1-carboxylate	162	3-cyclohexyl-5,6-trimethylene-2-thiouracil

Ex. No.	Substituted Urea	Parts by Weight	Ester of the Cycloalkanone Carboxylate	Parts by Weight	Substituted Uracil Products
202	cyclooctylthiourea	186	ethyl 2-cyclopentanone-1-carboxylate	162	3-cyclooctyl-5,6-trimethylene-2-thiouracil
203	cyclopentenylthiourea	140	ethyl 2-cyclopentanone-1-carboxylate	162	3-cyclopentenyl-5,6-trimethylene-2-thiouracil
204	cycloheptenylthiourea	156	ethyl 2-cyclopentanone-1-carboxylate	162	3-cycloheptenyl-5,6-trimethylene-2-thiouracil
205	methylthiourea	90	ethyl 2-cyclohexanone-1-carboxylate	187	3-methyl-5,6-tetramethylene-2-thiouracil
206	isoamylthiourea	144	ethyl 2-cyclohexanone-1-carboxylate	187	3-isoamyl-5,6-tetramethylene-2-thiouracil
207	n-heptylthiourea	160	ethyl 2-cyclohexanone-1-carboxylate	187	3-n-heptyl-5,6-tetramethylene-2-thiouracil
208	cyclohexylthiourea	154	ethyl 2-cyclohexanone-1-carboxylate	187	3-cyclohexyl-5,6-tetramethylene-2-thiouracil
209	cyclooctylthiourea	186	ethyl 2-cyclohexanone-1-carboxylate	187	3-cyclooctyl-5,6-tetramethylene-2-thiouracil
210	cyclopentenyl-thiourea	140	ethyl 2-cyclohexanone-1-carboxylate	187	3-cyclopentenyl-5,6-tetramethylene-2-thiouracil
211	1-methyl-2-thiourea	90	ethyl-2-cycloheptanone-1-carboxylate	202	3-methyl-5,6-pentamethylene-2-thiouracil
212	1-ethyl-2-thiourea	104	ethyl 2-cycloheptanone-1-carboxylate	202	3-ethyl-5,6-pentamethylene-2-thiouracil
213	1-tert-butyl-2-thiourea	116	ethyl 2-cycloheptanone-1-carboxylate	202	3-t-butyl-5,6-pentamethylene-2-thiouracil
214	1-cyclohexyl-2-thiourea	154	ethyl 2-cycloheptanone-1-carboxylate	202	3-cyclohexyl-5,6-pentamethylene-2-thiouracil
215	1-cyclooctyl-2-thiourea	186	ethyl 2-cycloheptanone-1-carboxylate	202	3-cyclooctyl-5,6-pentamethylene-2-thiouracil
216	1-cyclopentenyl-2-thiourea	140	ethyl 2-cycloheptanone-1-carboxylate	202	3-cyclopentenyl-5,6-pentamethylene-2-thiouracil
217	1-cyclohexenyl-2-thiourea	152	ethyl 2-cycloheptanone-1-carboxylate	202	3-cyclohexenyl-5,6-pentamethylene-2-thiouracil
218	allylurea	100	ethyl 2-cyclohexanone-1-carboxylate	187	3-allyl-5,6-tetramethyleneuracil
219	allylurea	100	ethyl 2-cycloheptanone-1-carboxylate	202	3-allyl-5,6-pentamethyleneuracil
220	1-allyl-2-thiourea	100	ethyl 2-cyclopentanone-1-carboxylate	162	3-allyl-5,6-trimethylene-2-thiouracil
221	1-allyl-2-thiourea	100	ethyl 2-cyclohexanone-1-carboxylate	187	3-allyl-5,6-tetramethylene-2-thiouracil

Ex. No.	Substituted Urea	Parts by Weight	Ester of the Cycloalkanone Carboxylate	Parts by Weight	Substituted Uracil Products
222	1-allyl-2-thiourea	100	ethyl-2-~~cyclophetanone~~-1-carboxylate	202	3-allyl-5,6-pentamethylene-2-thiouracil
223	benzylurea	150	ethyl 2-cyclopentanone-1-carboxylate	162	3-benzyl-5,6-trimethyleneuracil
224	α-methylbenzylurea	164	ethyl 2-cyclopentanone-1-carboxylate	162	3-(α-methylbenzyl)-5,6-trimethyleneuracil
225	phenethylurea	164	ethyl 2-cyclopentanone-1-carboxylate	162	3-phenethyl-5,6-trimethyleneuracil
226	*p*-methoxybenzylurea	180	ethyl 2-cyclohexanone-1-carboxylate	187	3-*p*-methoxybenzyl-5,6-tetramethyleneuracil
227	*p*-sec.-butylphenethylurea	220	ethyl 2-cyclopentanone-1-carboxylate	162	3-*p*-sec.-butylphenethyl-5,6-trimethyleneuracil
228	*p*-~~nitrophenthyl~~-urea	209	ethyl 2-cyclopentanone-1-carboxylate	162	3-*p*-nitrophenethyl-5,6-trimethyleneuracil
229	*p*-chlorobenzylurea	184.5	ethyl 2-cyclopentanone-1-carboxylate	162	3-*p*-chlorobenzyl-5,6-trimethyleneuracil
230	α,2,4-trichlorobenzylurea	233	ethyl 2-cycloheptanone-1-carboxylate	202	~~(3-α~~,2,4-trichlorobenzyl)-5,6-pentamethyleneuracil
231	α,2,4-trimethylbenzylurea	192	ethyl 2-cyclopentanone-1-carboxylate	162	3-(α,2,4-trimethylbenzyl)-5,6-trimethyleneuracil
232	1-(*p*-chlorobenzyl)-2-thiourea	200.5	ethyl 2-cyclohexanone-1-carboxylate	187	3-*p*-chlorobenzyl-5,6-tetramethylene-2-thoiuracil
233	1-(α-methylbenzyl~~-~~2-thiourea	180	ethyl 2-cyclopentanone-1-carboxylate	162	3-(α-methylbenzyl)-5,6-~~trimethyl~~-2-thiouracil
234	1-(*p*-nitrophenethyl)-2-thiourea	225	ethyl-2-cyclopentanone-1-carboxylate	162	3-*p*-nitrophenethyl-5,6-trimethylene-2-thiouracil
235	cyanourea	85	ethyl 2-cyclopentanone-1-carboxylate	162	3-cyano-5,6-trimethyleneuracil
236	phenylurea	136	ethyl 2-cyclopentanone-1-carboxylate	162	3-phenyl-5,6-trimethyleneuracil
237	*p*-fluorophenylurea	154	ethyl 2-cyclopentanone-1-carboxylate	162	3-(*p*-fluorophenyl)-5,6-trimethyleneuracil
238	3,4-dichlorophenylurea	206	ethyl 2-cyclopentanone-1-carboxylate	162	3-(3,4-dichlorophenyl)-5,6-methyleneuracil
239	*p*-bromophenylurea	215	ethyl 2-cyclopentanone-1-carboxylate	162	3-(*p*-bromophenyl)-5,6-trimethyleneuracil
240	*m*-nitrophenylurea	181	ethyl 2-cyclopentanone-1-carboxylate	162	3-(*m*-nitrophenyl)-5,6-trimethyleneuracil
241	*m*-methylsulphonylphenylurea	214	ethyl 2-cyclopentanone-1-carboxylate	162	3-(3-methylsulphonylphenyl)-5,6-trimethyleneuracil

Ex. No.	Substituted Urea	Parts by Weight	Ester of the Cycloalkanone Carboxylate	Parts by Weight	Substituted Uracil Products
242	*p*-carbethoxyphenyl-urea	208	ethyl 2-cyclopentanone-1-carboxylate	162	3-(4-carbethoxyphenyl)-5,6-trimethyleneuracil
243	*p*-cyanophenylurea	162	ethyl 2-cyclopentanone-1-carboxylate	162	3-(4-cyanophenyl)-5,6-trimethyleneuracil
244	*p*-methoxyphenyl-urea	166	ethyl 2-cyclopentanone-1-carboxylate	162	3-(4-methoxyphenyl)-5,6-trimethyleneuracil
245	*o*-mercaptophenyl-urea	168	ethyl 2-cyclopentanone-1-carboxylate	162	3-(2-mercaptophenyl)-5,6-trimethyleneuracil
246	*p*-dimethylamino-phenylurea	179	ethyl 2-cyclopentanone-1-carboxylate	162	3-(4-dimethylaminophenyl)-5,6-trimethyleneuracil
247	*p*-hydroxyphenyl-urea	152	ethyl 2-cyclopentanone-1-carboxylate	162	3-(4-hydroxyphenyl)-5,6-trimethyleneuracil
248	*p*-sec.-butylphenyl-urea	192	ethyl 2-cyclopentanone-1-carboxylate	162	3-(4-sec.-butylphenyl)-5,6-trimethyleneuracil
249	phenylthiourea	152	ethyl 2-cyclopentanone-1-carboxylate	162	3-phenyl-5,6-trimethylene-2-thiouracil

EXAMPLE 250

Preparation of 3 - isopropyl - 5 - hydroxymethyl - 6 - methyluracil

A mixture of 168 parts of 3 - isopropyl - 6 - methyluracil (which can readily be prepared by the novel β-keto ester route previously described), about 1400 parts of water, about 315 parts of ethyl alcohol, about 66 parts by weight of paraformaldehyde, and about 20 parts by weight of barium hydroxide is heated until the components are completely dissolved. The solution is then cooled and the oil which precipitates is extracted with ether. This ether extract is dried with magnesium sulphate, filtered, and concentrated at reduced pressure to a slightly gummy solid. This solid is recrystallised to give 3 - isopropyl - 5 - hydroxymethyl - 6 - methyluracil.

The following compounds are prepared as in Example 250 by substituting equivalent amounts of the appropriate uracil starting reagent for the 3 - isopropyl - 6 - methyluracil.

Ex. No.	5-Hydroxymethyluracil Products
251	3-cyclohexyl-6-ethyl-5-hydroxymethyl-2-thiouracil
252	3-benzyl-5-hydroxymethyl-6-methyluracil
253	3-cyclopentenyl-5-hydroxymethyl-6-propyluracil
254	3-decyl-6-ethyl-5-hydroxymethyluracil
255	3-(*p*-chlorophenyl)-6-butyl-5-hydroxymethyluracil
256	3-allyl-5-hydroxymethyl-6-methyluracil
257	3-isopropyl-5-hydroxymethyluracil
258	3-tert. octyl-5-hydroxymethyluracil
259	3-phenyl-5-hydroxymethyluracil
260	3-decyl-5-hydroxymethyluracil
261	3-cyclopentyl-5-hydroxymethyluracil
262	3-benzyl-5-hydroxymethyluracil
263	3-(3-nitro-4-chlorophenyl)-5-hydroxymethyluracil
264	3-cyclooctyl-5-hydroxymethyluracil
265	3-cyclohexyl-5-hydroxymethyluracil

EXAMPLE 266

Preparation of 3 - isopropyl - 5 - chloro - methyl - 6 - methyluracil

A mixture of 17 parts by weight of 3-isopropyl - 6 - methyluracil and 38 parts by weight of chloromethyl-methyl ether is heated in an autoclave under endogenous pressure at 100°C. for 25 hours. The material is cooled and the excess reagent evaporated under vacuum. The product is extracted from the residue with dry dioxane. The dioxane solution is then evaporated to dryness, leaving essentially pure 5 - chloromethyl - 3 - iso - propyl - 6 - methyluracil as a residue.

The following compounds are prepared as in Example 266 by substituting equivalent amounts of the substituted uracils set forth below for the 3 - isopropyl - 6 - methyluracil in Example 266.

The 5 - chloromethyl uracils, including those listed below, can also be prepared by reaction of the corresponding 5 - hydroxy-methyluracils with thionyl chloride.

Ex. No.	5-Chloromethyluracil Product
267	3-cyclohexyl-5-chloromethyl-6-methyluracil
268	3-(*p*-anisyl)-5-chloromethyl-6-propyl-2-thiouracil
269	3-propynyl-5-chloromethyl-6-ethyluracil
270	3-decyl-5-chloromethyl-6-methyluracil
271	3-(β-phenethyl)-5-chloromethyl-6-methyl-2-thiouracil
272	3-isoamyl-5-chloromethyl-6-butyluracil
273	3-(*m*-nitrophenyl)-5-chloromethyl-6-methyluracil
274	3-cyclohexyl-5-chloromethyluracil
275	3-cyclopentyl-5-chloromethyluracil
276	3-methyl-5-chloromethyluracil
277	3-butynyl-5-chloromethyluracil
278	3-cyclooctyl-5-chloromethyl-2-thiouracil
279	3-isopropyl-5-chloromethyluracil

EXAMPLE 280

Preparation of 3 - isopropyl - 5 - methylthiomethyl - 6 - methyluracil

A suspension of 21.7 parts by weight of 5 - chloromethyl - 3 - isopropyl - 6 - methyluracil and 7.0 parts by weight of sodium methylmercaptide in 100 parts by weight of tetrahydrofuran is heated to reflux for 45 minutes while adding gaseous methylmercaptan at a slow rate. The solvent is then evaporated and the product extracted from the residue with ether. Evaporation of the ether yields the desired 3 - isopropyl - 5 - methylthiomethyl - 6 - methyluracil in a crystalline state.

The following compounds are prepared as in Example 280 by substituting equivalent amounts of the appropriate substituted uracils and equivalent amounts of the appropriate alkoxides or alkylmercaptides for the 5-chloromethyl - 3 - isopropyl - 6 - methyluracil and methylmercaptide in Example 280.

281	3-cyclooctyl-5-methylthiomethyl-6-ethyl-2-thiouracil
281	3-octyl-5-propoxymethyl-6-methyluracil
283	3-phenyl-5-methoxymethyl-6-methyluracil
284	3-(*p*-chlorophenyl)-5-ethoxymethyl-6-propyluracil
285	3-allyl-5-ethoxymethyl-6-ethyl-2-thiouracil
286	3-cyclopentenyl-5-methylthiomethyl-6-methyluracil
287	3-butyl-5-methoxymethyl-6-ethyluracil

EXAMPLE 288

Preparation of 3 - cyclopenten - 2 - yl - 6 - methyluracil

A mixture consisting of 300 parts of xylene, 51.6 parts of ethyl 3 - aminocrotonate, and 43.6 parts of cyclo-penten-2-yl isocyanate was heated under reflux for 1 1/2 hours. The xlyene was removed under reduced pressure and the residual oil taken up in 190 parts of ethanol. The ethanol solution was then added to a boiling solution of 46 parts of sodium hydroxide in 335 parts of water. The resulting mixture was heated at reflux for 10 minutes, cooled to about 60°C., acidified with concentrated hydrochloric acid, and further cooled to 0°C. The solid which separated was collected by filtration and washed well with water. It then was slurried in 250 parts of 2N sodium hydroxide and a small amount of insoluble material filtered off. This filtrate was acidified with concentrated hydrochloric acid and the resulting solid collected by filtration and air-dried to give pure 3 - cyclopenten - 2 - yl - 6 - methyluracil.

The following compounds are similarly prepared by substituting equivalent amounts of the amino esters and equivalent amounts of the isocyanates set forth below for the ethyl 3 - aminocrotonate and ~~cyclopente~~-2-yl isocyanate in Example 288.

Ex. No.	Amino ~~Esters~~	Parts by Weight	Isocyanate	Parts by Weight	Substituted Uracil Product
289	methyl 3-amino-3-ethylacrylate	51.6	cyclopenten-2-yl	43.6	3-cyclopenten-2-yl-6-ethyl-uracil
290	methyl 3-amino-3-propylacrylate	57.2	cyclohexyl	50.0	3-cyclohexyl-6-propyluracil
291	methyl 3-amino-3-propylacrylate	57.2	cyclopentyl	44.4	3-cyclopentyl-6-propyluracil
292	methyl 3-amino-3-propyl-acrylate	57.2	cyclopenten-2-yl	43.6	3-cyclopenten-2-yl-6-propyl-uracil
293	methyl 3-amino-3-butylacrylate	62.8	cyclohexyl	50.0	3-cyclohexyl-6-butyluracil
294	methyl 3-amino-3-butylacrylate	62.8	cyclopentyl	44.4	3-cyclopentyl-6-butyluracil
295	methyl 3-amino-3-butylacrylate	62.8	cyclopenten-2-yl	43.6	3-cyclopenten-2-yl-6-butyl-uracil

The following list contains examples of typical salts.

Ex. No.	Salt
296	3-butyl-5-chloro-6-methyluracil, ½ barium salt
297	3-hexyl-5-chloro-6-ethyluracil, calcium salt
298	3-(*m*-fluorophenyl)-5-bromo-6-methyluracil, magnesium salt
299	3-(*p*-cumyl)-5-chloro-6-propyluracil, potassium salt
300	3-(β-phenethyl)-5-bromo-6-~~butylyracil~~, calcium salt
301	3-allyl-5-chloro-6-methyl-2-thiouracil, sodium salt
302	3-(*p*-chlorophenyl)-5-nitro-6-propyluracil, barium salt
303	3-isopropyl-5,6-dimethyl-2-thiouracil, sodium salt
304	3-propynyl-5-methyl-6-butyluracil, potassium salt
305	3-(*p*-anisyl)-5-methyl-6-amyluracil, sodium salt
306	3-allyl-5,6-dipropyluracil, magnesium salt

Ex. No.	Salt
307	3-benzyl-5-methoxy-6-propyl-2-thiouracil, barium salt
308	3-phenyl-5-methoxy-6-methyluracil, sodium salt
309	3-butyl-6-methyl-5-thiocyanouracil, sodium salt
310	3-phenyl-6-butyl-5-thiocyanouracil, calcium salt
311	3-cyclopentenyl-5,6-dimethyluracil, calcium salt
312	3-cyclopentenyl-5-chloro-6-isobutyluracil, calcium salt
313	3-cyclohexyl-5-fluoro-6-methyluracil, potassium salt
314	3-cyclohexyl-6-methyl-5-nitrouracil, sodium salt
315	3-cycloheptyl-6-hexyl-5-nitro-2-thiouracil, mangesium salt
316	3-cyclohexyl-6-methyl-5-thiocyanouracil, sodium salt
317	3-isopropyl-5-chlorouracil, sodium salt
318	3-isopropyl-5-bromouracil, sodium salt
319	3-cyclohexyl-5-chlorouracil, sodium salt
320	3-cyclohexyl-5-bromouracil, sodium salt
321	3-cycloheptenyl-5-bromouracil, potassium salt
322	3-cyclohexyl-5-methyluracil, 1/3 ferric salt
323	3-cyclohexyl-5-thiocyanouracil, 1/2 barium salt
324	3-cyclohexyl-5-bromouracil, 1/2 zinc salt
325	3-butyl-5-chlorouracil, sodium salt
326	3-cyclopentenyl-6-methyl-2-thiouracil, sodium salt
327	3-cycloheptyl-6-propyl-2-thiouracil, lithium salt
328	3-cyclohexyl-6-methyl-2-thiouracil, calcium salt
329	3-cyclohexenyl-6-methyluracil, sodium salt
330	3-cyclooctyl-6-methyluracil, barium salt
331	3-cycloheptenyl-6-butyluracil, strontium salt
332	3-methyl-5,6-trimethyleneuracil, sodium salt
333	3-*n*-butyl-5,6-trimethylenethiouracil, sodium salt
334	3-methyl-5,6-tetramethyleneuracil, sodium salt
335	3-*n*-propyl-5,6-tetramethylenethiouracil, sodium salt
336	3-ethyl-5,6-pentamethyleneuracil, sodium salt

Ex. No.	Salt
337	3-*n*-butyl-5,6-pentamethyleneuracil, sodium salt
338	3-isopropyl-5,6-pentamethylenethiouracil, sodium salt
339	3-allyl-5,6-trimethyleneuracil, sodium salt
340	3-phenyl-5,6-trimethyleneuracil, sodium salt
341	3-*p*-chlorophenyl-5,6-trimethyleneuracil, sodium salt
342	3-(3,4-dichlorophenyl)-5,6-trimethyleneuracil, sodium salt
343	3-methyl-5,6-trimethylenethiouracil, potassium salt
344	3-isopropyl-5,6-pentamethyleneuracil, potassium salt
345	3-isoamayl-5,6-tetramethylenethiouracil, potassium salt
346	3-allyl-5,6-pentamethyleneuracil, potassium salt
347	3-methyl-5,6-trimethyleneuracil, lithium salt

EXAMPLE 348

The sodium salt of 3 - cyclopentenyl - 5,6 - trimethylene uracil is prepared as follows. A slurry is prepared by suspending 220 parts of 3 - cyclopentenyl - 5,6 - trimethylene uracil in about 700 parts by weight of absolute alcohol. To this well stirred mixture is added about 54 parts of sodium methoxide. The mixture is concentrated under vacumn to a small volume. The residue is stirred with about 1000 parts of acetonitrile, whereupon a granular solid forms. This solid, which is the desired sodium salt, is then filtered off and dried.

The following uracil salts are prepared by the method described in Example 348.

Example	Compound
349	3-cyclohexyl-5,6-trimethylenethiouracil, sodium salt
350	3-cyclopentenyl-5,6-tetramethyleneuracil, sodium salt
351	3-cyclohexyl-5,6-tetramethylenethiouracil, sodium salt
352	3-cycloheptenyl-5,6-pentamethylenethiouracil, sodium salt
353	3-benzyl-5,6-trimethyleneuracil, sodium salt
354	3-α-phenethyl-5,6-trimethyleneuracil, sodium salt
355	3-cyclopentenyl-5,6-tetramethylenethiouracil, potassium salt
356	3-cyclooctenyl-5,6-pentamethyleneuracil, potassium salt
357	3-ethyl-5,6-tetramethyleneuracil, lithium salt

It may sometimes be convenient to prepare salts by the following method:

EXAMPLE 358

Preparation of 3 - isopropyl - 5,6 - trimethyleneuracil barium salt

A mixture of 194 parts by weight of 3-isopropyl - 5,6 - trimethyleneuracil, 600 parts by weight of methyl alcohol, and 54 parts by weight of sodium methoxide is stirred until the components are completely dissolved. To this mixture is added a solution of 224 parts by weight of barium chloride dihydrate in 1000 parts by weight of water. The resulting solution is quickly filtered free of foreign matter. A white solid gradually separates and is filtered off. This is 3 - isopropyl - 5,6 - trimethyleneuracil, barium salt.

The following salts are prepared by the method described in Example 358 by substituting equivalent quantities of the appropriate substituted uracil for the 3 - isopropyl-5,6 - trimethyleneuracil and the corresponding di- and polyvalent metal chlorides for barium chloride.

Example	Compound
359	3-cyclohexyl-5,6-triemthyleneuracil, barium salt
360	3-cyclohexyl-5,6-trimethyleneuracil, magnesium salt
361	3-n-butyl-5,6-trimethyleneuracil, calcium salt
362	3-sec.-butyl-5,6-trimethyleneuracil, ferric salt
363	3-allyl-5,6-trimethyleneuracil, manganous salt
364	3-methyl-5,6-trimethyleneuracil, magnesium salt
365	3-cyclopentenyl-5,6-trimethyleneuracil, ferric salt
366	3-methyl-5,6-tetramethyleneuracil, calcium salt
367	3-sec.-butyl-5,6-tetramethyleneuracil, manganous salt
368	3-isopropyl-5,6-tetramethyleneuracil, barium salt
369	3-methyl-5,6-pentamethyleneuracil, mangesium salt
370	3-cyclohexyl-5,6-pentamethyleneuracil, barium salt

A representative list of the 3-substituted uracils is the following:

3 - ethyl - 5 - bromo - 6 - methyluracil
3 - cyclopentenyl - 5 - bromo - 6 - methyluracil
3 - sec. heptyl - 5 - chloro - 6 - methyluracil
3 - sec. heptyl - 5 - bromo - 6 - methyluracil
3 - sec. octyl - 5 - chloro - 6 - methyluracil
3 - sec. octyl - 5 - bromo - 6 - methyluracil
3 - tert. octyl - 5 - chloro - 6 - methyluracil
3 - tert. octyl - 5,6 - trimethyleneuracil
3 - tert. octyl -5,6 - tetramethyleneuracil
3 - sec. heptyl - 5,6 - trimethyleneuracil
3 - sec. butyl - 5,6 - dichlorouracil
3 - *sec.* butyl - 5 - hydroxymethyl - 6 - methyluracil
3 - cyclohexyl - 5 - fluoro - 6 - methyluracil
3 - cyclohexyl - 5 - allyl - 6 - methyluracil
3 - cyclohexyl - 5 - chloromethyl - 6 - methyluracil
3 - propynyl - 5,6 - dimethyluracil
3 - cyclohexyl - 5 - (2 - hydroxyethyl) - 6 - methyluracil
3 - *sec.* butyl - 5 - fluoro - 6 - methyluracil
3 -isopropyl - 5 - thiocyanato - 6 - methyluracil
3 - isopropyl - 5 - hydroxymethyl - 6 - methyluracil
3 - isopropyl - 5 - chloromethyl - 6 - methyluracil
3 - isopropyl - 5 - methoxymethyl - 6 - methyluracil
3 - cyclohexyl - 5,6 - dimethyl - 2 - thiouracil
3 - isopropyl - 5,6 - dimethyl - 2 - thiouracil
3 - cyclohexyl - 5 - bromo - 6 - methyl - 2 - thiouracil
3 - isopropyl - 5 - bromo - 6 - methyl - 2 - thiouracil
3 - cyclohexyl - 5 - butyluracil
3 - cyclohexyl - 5 - ethyluracil
3 - cyclohexyl - 5 - allyluracil
3 - cyclohexyl - 5 - methoxymethyluracil
3 - β - phenethyl - 5 - bromouracil
3 - (3,4 - dichlorophenyl) - 5 - hydroxymethyluracil

3 - sec. butyl - 5 - bromouracil
3 - sec. butyl - 5 - ethyluracil
3 - cyclohexyl - 5 - methyl - 2 - thiouracil
3 - hexyl - 5 - bromouracil, potassium salt
3 - *sec.* butyl - 5 - bromouracil, sodium salt
3 - phenyl - 5 - fluorouracil
3 - cyclopentyl - 5 - nitrouracil
3 - sec. butyl - 5 - fluoro - 6 - methyluracil
3 - isoamyl - 5 - fluoro - 6 - methyluracil
3 - (*m* - nitrophenyl) - 5 - fluoro - 6 - *n* - propyluracil
3 - cycloheptyl - 5 - fluoro - 6 - ethyluracil

EXAMPLE 371

Emulsifiable oil

3-sec. butyl-5-fluoro-6-methyluracil	20.0%
Alkyl aryl polyether alcohol	2.5%
Oil soluble petroleum sulphonate	2.5%
Methyl isobutyl ketone	75.0%

The emulsifiable oil is prepared by mixing the above components until a homogeneous solution results. It can then be emulsified in water for application.

This emulsifiable oil is useful for weed control on railroad rights-of-way, in railroad yards, and on sidings. When this composition is diluted with 100 gallons of water per acre and sprayed from a railroad spray car at 10 pounds of active ingredient per acre, mixed vegetation such as quackgrass, crab grass, Bermuda grass, brome grass, ragweed, cocklebur, lamb's-quarters, and mare's-tail is controlled for an extended period.

3 - Isopropyl - 5 - bromouracil can also be formulated and used in the manner described in Example 371.

EXAMPLE 372 — Granules

3-sec. heptyl-5-chloro-6-methyluracil	40%
Anhydrous sodium sulphate	10%
Non-swelling sub-bentonite clay	50%

The components are blended, and micropulverized, then moistened with water and granulated. The granules are then dried and screened.

The granules are applied conveniently by hand for "spot treatment" of undesirable bunch grasses, such as crabgrass and quackgrass, growing in agricultural areas. An application of 20 pounds of active ingredient per acre gives good control.

EXAMPLE 373 — Pellets

3-tert. butyl-5-bromouracil	25%
Anhydrous sodium sulphate	10%
Sodium lignin sulphonate	10%
Ca, Mg bentonite	~~5%~~ 55%

The components are blended and micropulverized, then moistened with 18—20% water and extruded through die holes. The extrusions are cut as formed to give pellets and dried.

These pellets are useful for weed control along highway guard rails, around bridges, cyclone fences, and highway signs. They are applied conveniently by hand methods at 10 to 25 pounds of active ingredient per acre. Excellent control of such woody plants as oak, maple, sweet gum, and willow is obtained.

EXAMPLE 374 — Wettable powder

3 - cyclohexyl - 5 - chloro - 6 - methyluracil, Ca salt	80.0%
Sodium lauryl sulphate	0.6%
Sodium lignin sulphonate	2.0%
Kaolin clay	17.4%

The components are blended and then 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 water gives excellent control of goldenrod, evening primrose, pokeweed, ox-eye daisy, cocklebur, goose grass, crab grass, and love grass.

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

EXAMPLE 375 — Wettable powder

3-sec. octyl-5-bromo-6-methyluracil	80.0%
Sodium lauryl sulphate	0.6%
Partially ~~disulphonated~~ disulphonated sodium lignin sulphonate	1.0%
Calcined, non-swelling montmorillonoid type clay (Pikes Peak clay)	18.4%

The wettable powder is prepared by blending the components 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 water for weed control around oil tank installations and on railroad ballast. Excellent control of weeds such as 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.

The following compounds are formulated and used as above:

3 - (*p* - chlorophenyl) - 5 - chloro - 6 - methyluracil
3 - isopropyl - 5 - thiocyano - 6 - methyluracil

EXAMPLE 376 — Wettable powder

3 - (*β* - phenethyl) - 5 - chloro - 6 - methyluracil	80.00%
Alkyl naphthalene sulphonic acid, Na salt	1.75%
Low viscosity methylcellulose	0.25%
Kaolin	18.00%

This wettable powder is prepared in the same manner as in Example 375. It is used for the control of annual broadleaf and grass weeds growing around telephone poles and highway markers. An application of 15 pounds of active ingredient per acre in 40 gallons water gives excellent control of crab grass, water grass, black-eyed susan, carpetweed, and chickweed.

EXAMPLE 377 — Granules

3 - isopropyl - 5 - chloro - 6 - methyluracil, Ca salt	40%
Anhydrous sodium sulphate	10%
Non-swelling Ca, Mg bentonite	49%
Alkyl naphthalene sulphonate, Na salt	1%

The above components are formulated as 4 to 8 mesh granules by blending and grinding the components, then moist-granulating them, followed by drying and screening.

The granules are broadcast at a level of 10 pounds of active ingredient per acre for the excellent control of oak brush growing on light sandy soil.

EXAMPLE 378 — Aqueous concentrate

3 - propynyl - 5 - bromo - 6 - methyluracil potassium salt	25%
Sodium lauryl sulphate	1%
Water	74%

The concentrate is prepared as a homogeneous solution by agitating the solid components in the water. It can then be readily diluted to use levels with water.

This formulation is used at 2 pounds of active ingredient per acre in 30 gallons of water for the post-emergence control of annual weeds. A directed spray to seedling, crab grass, water grass, pigweed, and lamb's-quarters gives excellent control.

EXAMPLE 379 — Aqueous suspension

3 - tert. octyl - 5 - bromo - 6 - methyluracil	30.00%
Sodium lignin sulphonate	15.00%
Hydrated attapulgite	1.75%
Anhydrous disodium phosphate	0.80%
Sodium pentachlorophenate	0.50%
Water	51.95%

The above components are mixed together and pebble-milled or sand-milled until substantially all the active material is below 5 microns in particle size. The resultant stable aqueous suspension can be readily diluted with water to give a highly dispersed, very slow settling composition which can be sprayed from equipment having no means for agitating the suspension.

This composition is applied at 20 pounds of active ingredient per acre in 100 gallons water for control of annual and perennial broadleaf and grass weeds growing along pipeline rights-of-way. Excellent control of broomsedge, crab grass, seedling Johnson grass, pigweed, goldenrod, and evening primrose is obtained.

EXAMPLE 380 — Emulsifiable Concentrate

3-butyl-5-chlorouracil	20%
Alkyl, aryl polyether alcohol	5%
Dibutyl ketone	75%

The above emulsifiable concentrate is prepared by mixing the three components. It may be extended with water to yield an emulsion.

The above formulation is extended with 30 gallons of water and used in postemergence applications at a level of 1 pound of active ingredient per acre on young germinating annual weeds in established asparagus beds. This formulation is applied in the spring prior to the emergence of the spears of asparagus. Good control of foxtail, Lamb's quarters, pigweed, and cockleburr is obtained.

EXAMPLE 381 — Emulsifiable Oil

An emulsifiable oil is prepared by mixing the components to give a homogeneous solution. This solution can then be emulsified in water for application.

3 - cyclopentenyl - 5,6 - trimethyleneuracil	20.0%
Alkyl aryl polyether alcohol	2.5%
Oil soluble petroleum sulphonate	2.5%
Methyl isobutyl ketone	75.0%

When this emulsifiable oil is applied at 2 pounds of active ingredient per acre in 30 gallons of water, it gives excellent control of germinating annual weeds such as crab grass, cockleburr, and water grass.

EXAMPLE 382 — Wettable Powder

The following powder is prepared by blending the listed components, micropulverising them until substantially all the particles are below 50 microns in size, and ~~them~~ passing the particles through an air attrition mill, such as an air-reductionizer, to reduce the particle size to below 10 microns:

3-cyclopentenyl-6-methyluracil	80.0%
Dioctyl sodium sulphosuccinate concreted with sodium benzoate (Aerosol OTB)	2.0%
Partially desulphonated sodium lignin sulphonate	1.0%
Calcined, non-swelling montmorillonoid type clay (Pikes Peak clay)	17.0%

This composition is used for directed pre-emergence application in established agricultural crops such as sugar cane, asparagus, and safflower. It is dispersed in 40 gallons of water and sprayed with a pressure sprayer. When applied at 0.5 to 2.0 pounds of active ingredient per acre, excellent control of pigweed, lamb's-quarters, purslane, mustard, crab grass, foxtail, and water grass is obtained.

EXAMPLE 383 — Pellets

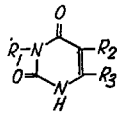
The following composition is blended and micropulverized, then moistened with 18—20% water and extruded through small die holes. The extrusions are cut as formed and dried.

3-cyclohexyluracil	25%
Anhydrous sodium sulphate	10%
Sodium lignin sulphonate	10%
Ca, Mg bentonite	55%

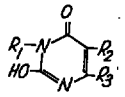
These pellets are useful for weed control along highway guard rails, around bridges, cyclone fences, and highway signs. They are applied by hand methods at 10 to 25 pounds of active ingredient per acre. Excellent control of lamb's-quarters, goldenrod, evening primrose, pokeweed, oxeye daisy, cocklebur, goose grass, crab grass, broom sedge, and love grass is obtained.

Other Examples of the preparation of metal salts of 3-substituted uracils by the novel process of the invention will be found in our Applications Nos. 17,417/64, 17,418/64 and 17,419/60 (Serial Nos. 968,663, 968,664 and 968,665).

Our Application No. 17,417/64 (Serial No. 968,663) discloses certain 3-substituted uracils, herbicidal compositions containing them, and methods of controlling the growth of weeds using them. These 3-substituted uracils are compounds of the general formula



or the corresponding isomeric formula



wherein R_1 represents a cycloalkyl group containing 5 to 8 carbon atoms;

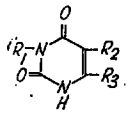
R_2 represents a hydrogen, bromine or chlorine atom or a methyl, ethyl, hydroxymethyl, methoxymethyl or methoxy group; and

R_3 represents a methyl or ethyl group; or

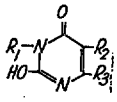
R_2 and R_3 together represent a trimethylene or tetramethylene group,

and sodium, potassium and lithium salts thereof. The subject matter claimed in that application is not claimed here.

Our Application No. 17,418/64 (Serial No. 968,664) discloses certain 3-substituted uracils, herbicidal compositions containing them, and methods of controlling the growth of weeds using them. These 3-substituted uracils are compounds of the general formula



or the corresponding isomeric formula



wherein R_1 represents an alkyl group containing 3 to 6 carbon atoms;

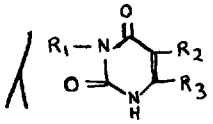
R_2 represents a chlorine or bromine atom or a methyl, ethyl or methoxy group; and

R_3 represents a methyl or ethyl group; or

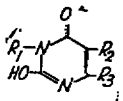
R_2 and R_3 together represent a trimethylene or tetramethylene group,

and sodium, potassium and lithium salts thereof. The subject matter claimed in that application is not claimed here.

Our Application No. 17,419/64 (Serial No. 968,665) discloses certain 3-substituted uracils, herbicidal compositions containing them, and methods of controlling the growth of weeds using them. These 3-substituted uracils are compounds of the general formula



or the corresponding isomeric formula

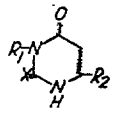


wherein R_1 represents a phenyl or benzyl group;

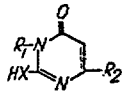
R_2 represents a bromine or chlorine atom or a methyl or ethyl group; and

R_3 represents a methyl or ethyl group, and sodium, potassium and lithium salts thereof. The subject matter claimed in that application is not claimed here.

Our Application No. 32,469/60 (Serial No. 968,662) discloses certain 3-substituted uracils, herbicidal compositions containing them and methods of controlling the growth of weeds using them. These 3-substituted uracils are compounds of the general formula



or the corresponding isomeric formula



wherein R_1 is an alkyl group containing from 3 to 6 carbon atoms;

R_2 is an alkyl group containing 1 to 5 carbon atoms; and

X is oxygen or sulphur;

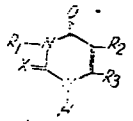
and alkali metal and alkaline earth metal salts thereof. The subject matter claimed in that application is not claimed here.

3-Cyclohexyl-6-methyl uracil is a known compound, and this compound and metal salts thereof do not *per se* form part of the present invention, nor do compositions consisting of (i.e. containing no other ingredients) 3-cyclohexyl-6-methyl uracil or a metal salt thereof and water and/or methanol. This subject matter is not claimed here.

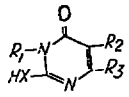
Subject to the foregoing disclaimers,

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising at least one 3-substituted uracil which is a compound of the general formula:



or the corresponding isomeric formula:



wherein R_1 is a covalent organic radical of molecular weight 15 to 250 which is an alkyl group of up to 10 carbon atoms, a substituted alkyl group in which the alkyl group contains up to 3 carbon atoms, a phenyl group, a substituted phenyl group, an aralkyl group of 7 or 8 carbon atoms, a substituted aralkyl group of 7 to 12 carbon atoms, an alkenyl group of 3 to 6 carbon atoms, a propynyl group, a butynyl group, a cycloalkyl group of 5 to 8 carbon atoms, a cycloalkenyl group of 5 to 8 carbon atoms or a cyano group;

R_2 is a hydrogen or halogen atom or an alkyl group of up to 4 carbon atoms, an alkoxy group of up to 3 carbon atoms, a nitro group, an alkoxymethyl group of 2 to 4 carbon atoms, a hydroxymethyl group, a hydroxyethyl group, an allyl group, a thiocyanato group, a cyano group, a halogenomethyl group or a methyl thiomethyl group;

R_3 is a hydrogen or chlorine atom or is an alkyl group of up to 5 carbon atoms, a methoxy group or an ethoxy group;

or R_2 and R_3 together form a divalent alkylene bridge of formula $(CH_2)_n$, wherein n is 3, 4 or 5; and

X is oxygen or sulphur;

with the proviso that if R_2 is a hydrogen atom, then either R_3 is an alkyl group of 1 to 5 carbon atoms and R_1 is an alkyl group of 3 to 6 carbon atoms, an allyl group, a propynyl group or a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms, or R_3 is a hydrogen atom and R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms;

or a metal salt of such a uracil, associated with a diluent which is at least in part an oil.

2. A herbicidal composition comprising a 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a metal salt thereof associated with a diluent which is at least in part a solid.

3. A herbicidal composition according to Claim 1 which contains a surface active agent.

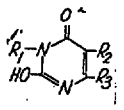
4. A herbicidal composition according to Claim 2 which contains a surface active agent.

5. A herbicidal composition comprising a 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a metal salt thereof associated with a diluent which is a liquid other than an oil and a surface active agent.

6. A herbicidal composition according to Claim 5 wherein the liquid is water.

7. A herbicidal composition comprising a 3-substituted uracil which is a compound of general formula I or II as defined in Claim

or the corresponding isomeric formula

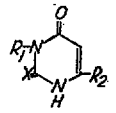


wherein R_1 represents a phenyl or benzyl group;

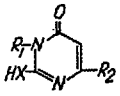
R_2 represents a bromine or chlorine atom or a methyl or ethyl group; and

R_3 represents a methyl or ethyl group, and sodium, potassium and lithium salts thereof. The subject matter claimed in that application is not claimed here.

Our Application No. 32,469/60 (Serial No. 968,662) discloses certain 3-substituted uracils, herbicidal compositions containing them and methods of controlling the growth of weeds using them. These 3-substituted uracils are compounds of the general formula



or the corresponding isomeric formula



wherein R_1 is an alkyl group containing from 3 to 6 carbon atoms;

R_2 is an alkyl group containing 1 to 5 carbon atoms; and

X is oxygen or sulphur;

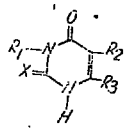
and alkali metal and alkaline earth metal salts thereof. The subject matter claimed in that application is not claimed here.

3-Cyclohexyl-6-methyl uracil is a known compound, and this compound and metal salts thereof do not *per se* form part of the present invention, nor do compositions consisting of (i.e. containing no other ingredients) 3-cyclohexyl-6-methyl uracil or a metal salt thereof and water and/or methanol. This subject matter is not claimed here.

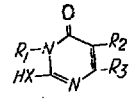
Subject to the foregoing disclaimers,

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising at least one 3-substituted uracil which is a compound of the general formula:



or the corresponding isomeric formula:



wherein R_1 is a covalent organic radical of molecular weight 15 to 250 which is an alkyl group of up to 10 carbon atoms, a substituted alkyl group in which the alkyl group contains up to 3 carbon atoms, a phenyl group, a substituted phenyl group, an aralkyl group of 7 or 8 carbon atoms, a substituted aralkyl group of 7 to 12 carbon atoms, an alkenyl group of 3 to 6 carbon atoms, a propynyl group, a butynyl group, a cycloalkyl group of 5 to 8 carbon atoms, a cycloalkenyl group of 5 to 8 carbon atoms or a cyano group;

R_2 is a hydrogen or halogen atom or an alkyl group of up to 4 carbon atoms, an alkoxy group of up to 3 carbon atoms, a nitro group, an alkoxymethyl group of 2 to 4 carbon atoms, a hydroxymethyl group, a hydroxyethyl group, an allyl group, a thiocyanato group, a cyano group, a halogenomethyl group or a methyl thiomethyl group;

R_3 is a hydrogen or chlorine atom or is an alkyl group of up to 5 carbon atoms, a methoxy group or an ethoxy group;

or R_2 and R_3 together form a divalent alkylene bridge of formula $(CH_2)_n$, wherein n is 3, 4 or 5; and

X is oxygen or sulphur;

with the proviso that if R_2 is a hydrogen atom, then either R_3 is an alkyl group of 1 to 5 carbon atoms and R_1 is an alkyl group of 3 to 6 carbon atoms, an allyl group, a propynyl group or a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms, or R_3 is a hydrogen atom and R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms;

or a metal salt of such a uracil, associated with a diluent which is at least in part an oil.

2. A herbicidal composition comprising a 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a metal salt thereof associated with a diluent which is at least in part a solid.

3. A herbicidal composition according to Claim 1 which contains a surface active agent.

4. A herbicidal composition according to Claim 2 which contains a surface active agent.

5. A herbicidal composition comprising a 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a metal salt thereof associated with a diluent which is a liquid other than an oil and a surface active agent.

6. A herbicidal composition according to Claim 5 wherein the liquid is water.

7. A herbicidal composition comprising a 3-substituted uracil which is a compound of general formula I or II as defined in Claim

* C L M S *

1 or a metal salt thereof associated with a surface active agent.

8. A herbicidal composition according to any one of Claims 3 to 7 which contains 1 to 10% by weight of the surface active agent.

9. A herbicidal composition according to any one of the preceding claims which contains, in addition to the 3-substituted uracil, another compound having herbicidal properties.

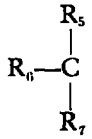
10. A herbicidal composition according to Claim 9 wherein the other compound is one of the known herbicides specifically hereinbefore named.

11. A herbicidal composition according to any one of the preceding claims in the form of a concentrate which requires dilution before use as a herbicide.

12. A herbicidal composition according to any one of the preceding claims wherein X represents an oxygen atom.

13. A herbicidal composition according to any one of the preceding claims wherein if R_1 is a substituted alkyl group it is substituted by an alkoxy group or chlorine atom; if R_1 is a substituted phenyl group it is substituted by one or more alkyl, cyano, hydroxy or alkoxy groups or halogen atoms; and if R_1 is a substituted aralkyl group it is substituted by one or more alkyl, methoxy or nitro groups or chlorine atoms.

14. A herbicidal composition according to any one of claims 1 to 12, wherein R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms or a group of the formula:



wherein R_5 is a hydrogen atom or a methyl group,

R_6 is a methyl or ethyl group, and

R_7 is an alkyl radical of 1 to 5 carbon atoms; R_2 is a chlorine or bromine atom; and R_3 is a methyl group.

15. A herbicidal composition according to any one of Claims 1 to 12 wherein R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms; R_2 is hydrogen; and R_3 is an alkyl group of up to 5 carbon atoms.

16. A herbicidal composition according to Claim 15, wherein R_1 is a cyclopentyl, cyclohexyl or cyclopenten-2-yl group.

17. A herbicidal composition according to any one of Claims 1 to 12, wherein R_2 and R_3 together form a divalent alkylene bridge of formula $(CH_2)_n$, wherein n is 3, 4 or 5.

18. A herbicidal composition according to Claim 17, wherein R_1 is an alkyl or alkenyl group of 1 to 6 carbon atoms, or a cycloalkyl or cycloalkenyl radical of 5 to 8 carbon atoms.

19. A herbicidal composition according to any one of the preceding claims, which contains at least one alkali metal or alkaline earth metal salt of the substituted uracil.

20. A herbicidal composition according to Claim 19, which contains at least one sodium, potassium or lithium salt of the substituted uracil.

21. A herbicidal composition according to any one of Claims 1 to 11 wherein the 3-substituted uracil is one of the compounds specifically hereinbefore named.

22. A herbicidal composition according to Claim 1, 2 or 5 substantially as hereinbefore described.

23. A herbicidal composition according to Claim 1, 2 or 5 substantially as described in any one of the foregoing Examples 371 to 383.

24. A method of controlling the growth of weeds at a locus which comprises applying to the locus a herbicidally effective quantity of at least one 3-substituted uracil which is a compound of general formula I or II as defined in Claim 1 or a metal salt thereof.

25. A method according to Claim 24 wherein the 3-substituted uracil is as defined in any one of Claims 12 to 20.

26. A method according to Claim 24 wherein the 3-substituted uracil is applied in the form of a herbicidal composition as claimed in any one of Claims 1 to 23, where appropriate after dilution.

27. A method of controlling the growth of weeds according to Claim 24 wherein the growth of the weeds specified in any one of Examples 371 to 383 is controlled by the application of the 3-substituted uracil specified in that Example.

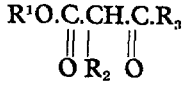
28. A method according to Claim 27 wherein the 3-substituted uracil is applied at the rate specified in the Example.

29. A method of controlling the growth of weeds according to Claim 24 substantially as hereinbefore described.

30. Process for the preparation of a 3-substituted uracil which is a metal salt of a compound of general formula I or II as defined in Claim 1, which comprises
(A) heating a urea of the formula:

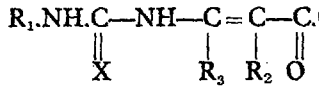


with a β-keto ester of the formula:



[wherein R^1 is an alkyl group of 1 to 6 carbon atoms and X, R_1, R_2 and R_3 are as defined in Claim 1, with the proviso that R_1, R_2 and R_3 are such that they do not interfere with the desired reaction in step (A) or the subsequent

step (B)] in the presence of an acidic compound and under substantially anhydrous reaction conditions, to produce a 3-(3-substituted ureido)-2,3-unsaturated ester of the formula:



and (B) heating the said ester under substantially anhydrous conditions in the presence of a strong base to effect ring closure.

31. Process according to Claim 30, wherein R_2 represents a hydrogen, fluorine, chlorine or bromine atom, an alkoxy group of up to 3 carbon atoms, an allyl group, an alkyl group of up to 4 carbon atoms or a cyano group.

32. Process according to Claim 30 or 31, wherein step (A) is carried out in an inert liquid medium which is liquid above 7°C.

33. Process according to Claim 32, wherein the inert liquid medium boils between 60° and 140°C. under the reaction conditions.

34. Process according to Claim 32 or 33, wherein the ratio by weight of inert liquid medium to reactants is about 1:1.

35. Process according to any one of Claims 32 to 34 wherein the urea, β-keto ester and acid are added gradually to the inert liquid medium as the latter boils under reflux, and the water formed in the reaction is removed as it is formed by azeotropic distillation.

36. Process according to Claim 35 wherein the liquid medium is boiled under reduced pressure.

37. Process according to any one of Claims 30 to 36, wherein there is a slight stoichiometric excess of either the urea or the β-keto ester.

38. Process according to any one of Claims 30 to 37 wherein the acidic compound is a protonic acid.

39. Process according to Claim 38, wherein the acid is sulphuric acid or phosphoric acid.

40. Process according to any one of Claims 30 to 39, wherein the molar ratio of the acid to the urea is from 0.01:1 to 1:1.

41. Process according to any one of Claims 30 to 40, wherein the unsaturated ester obtained in step (A) is separated from the acidic compound before being heated with a strong base in step (B).

42. Process according to any one of Claims 32 to 41, wherein step (A) is carried out in an inert liquid medium which is liquid above 7°C. and the resulting solution of the ester intermediate in the inert liquid medium is heated with a strong base in step (B).

43. Process according to any one of Claims 30 to 42, wherein in step (B) the unsaturated ester and the strong base are heated in an inert liquid medium which is boiled under reflux.

44. Process according to any one of Claims 30 to 43, wherein the salt of a substituted uracil obtained in step (B) is treated with an acid to form the corresponding substituted uracil.

45. Process for the preparation of a salt of a substituted uracil according to Claim 30 substantially as hereinbefore described.

46. Process for the preparation of a salt of a substituted uracil according to Claim 30 substantially as described in any one of Examples 109 to 138.

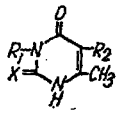
47. 3-substituted uracils and salts of 3-substituted uracils prepared by the process of any one of Claims 30 to 46.

48. A herbicidal composition comprising at least one substituted uracil or salt thereof as claimed in Claim 47, associated with a diluent which is a liquid other than an oil.

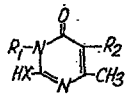
49. A herbicidal composition according to any one of Claims 1 to 22 containing a 3-substituted uracil or salt thereof as claimed in Claim 47.

50. A method of controlling the growth of weeds according to any one of Claims 24 to 29, wherein a 3-substituted uracil or salt thereof as claimed in Claim 47 is applied to the locus.

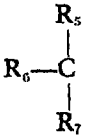
51. A substituted uracil of the general formula:



or the corresponding isomeric formula:



wherein R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms or a group of the formula:



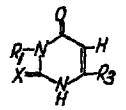
wherein R_5 is a hydrogen atom or a methyl group,

R_6 is a methyl or ethyl group,

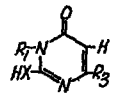
R_7 is an alkyl radical of 1 to 5 carbon atoms; R_2 is a chlorine or bromine atom; and X is oxygen or sulphur.

52. A substituted uracil as claimed in Claim 51 wherein X is oxygen.

53. A substituted uracil of the general formula:



or the corresponding isomeric formula:

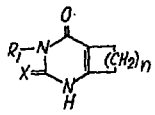


wherein R_1 is a cycloalkyl or cycloalkenyl group of 5 to 8 carbon atoms; R_3 is an alkyl group of up to 5 carbon atoms; and X is an oxygen or sulphur atom.

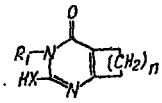
54. A substituted uracil as claimed in Claim 53 wherein R_1 is a cyclopentyl, cyclohexyl or cyclopenten-2-yl group.

55. A substituted uracil as claimed in Claim 53 or 54, wherein X is oxygen.

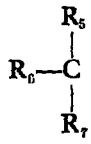
56. A substituted uracil of the general formula:



or the corresponding isomeric formula:



wherein R_1 is a cycloalkyl group of 5 to 8 carbon atoms, a cycloalkenyl group of 5 to 8 carbon atoms or a group of the formula



wherein R_5 is a hydrogen atom or a methyl group,

R_6 is a methyl or ethyl group, and

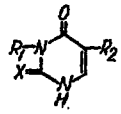
R_7 is an alkyl radical of 1 to 5 carbon atoms;

n is 3, 4 or 5; and

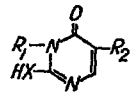
X is oxygen or sulphur.

57. A substituted uracil as claimed in Claim 56 wherein X is oxygen.

58. A substituted uracil of the general formula



or the corresponding isomeric formula



wherein R_1 represents a phenyl group, a substituted phenyl group, a cycloalkyl group containing 5 to 8 carbon atoms or a cycloalkenyl group containing 5 to 8 carbon atoms; R_2 represents a halogen atom or a methyl or nitro group; and X represents oxygen or sulphur.

59. A 3-substituted uracil according to Claim 58 wherein X is oxygen.

60. A metal salt of a 3-substituted uracil as defined in any one of Claims 51 to 59.

61. An alkali metal or alkaline earth metal salt of a 3-substituted uracil as defined in any one of Claims 51 to 59.

62. A sodium, potassium or lithium salt of a 3-substituted uracil as defined in any one of claims 51 to 59.

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