United States Patent Office

2,969,359

Patented Jan. 24, 1961

2,969,359

AMINOKETONES

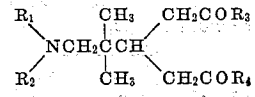
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No Drawing. Filed Mar. 24, 1958, Ser. No. 723,101

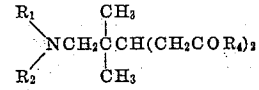
8 Claims. (Cl. 260—247.7)

This invention concerns specific aminoketones as new compositions of matter.

The compounds of this invention may be represented by the following formulas:

I 

and

II 

in which R_1 and R_2, taken individually, represent alkyl groups of not over four carbon atoms and, taken collectively, represent a divalent saturated aliphatic chain of four to five atoms which jointly with the amino nitrogen forms a five- to six-membered heterocyclic monoamine.

The symbol R_3 represents an alkyl group of not over seventeen carbon atoms, an alkenyl group of three to seventeen carbon atoms, or an aryl or substituted aryl of six to about twenty carbon atoms. Alkyl in this sense is to be construed as including cycloalkyl. Actually, R_3 may also be an alkynyl group of three to seventeen carbon atoms provided that neither of the carbon atoms connected by the triple bond bears a hydrogen atom. However, the alkyl and alkenyl representations of R_3 are preferred.

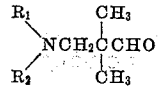
The symbol R_4 stands for an aryl or substituted aryl group of six to about twenty carbon atoms. Typical groups that R_4 may represent include phenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, dibromophenyl, tolyl, xylyl, trimethylphenyl, ethylphenyl, diethylphenyl, triethylphenyl, methylethylphenyl, butylphenyl, tributylphenyl, butenylphenyl, pentylphenyl, dipentylphenyl, dihexylphenyl, hexenylphenyl, butylhexylphenyl, diheptylphenyl, octylphenyl, octenylphenyl, nonylphenyl, ethylnonylphenyl, decylphenyl, dodecylphenyl, dodecenylphenyl, methyldodecenylphenyl, tetradecylphenyl, butoxyphenyl, octoxyphenyl, decoxyphenyl, butoxybutylphenyl, octoxyethylphenyl, naphthyl, methylnaphthyl, ethylnaphthyl, butylnaphthyl, butenylnaphthyl, octylnaphthyl, decylnaphthyl, decenylnaphthyl, chloronaphthyl, dichloronaphthyl, and bromonaphthyl.

Typical groups that R_3 may represent, in addition to those listed as typical of R_4, include methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, heptyl, octyl, decyl, dodecyl, tetradecyl, heptadecyl, allyl, butenyl, hexenyl, octenyl, nonenyl, decenyl, dodecenyl, and heptenyl.

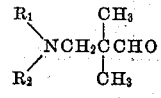
R_1 and R_2, taken singly, may represent alkyl groups of no more than four carbon atoms, that is, methyl, ethyl, propyl, or butyl groups, in which case R_1 and R_2 may be the same or different. R_1 and R_2, taken together and in conjunction with the amino nitrogen, may stand for a morpholino, thiamorpholino, pyrrolidinyl, or piperidino group, and these groups having one or more lower alkyl substituents, such as methyl and ethyl groups.

The alkyl groups of R_1, R_2, R_3, and R_4 and the alkenyl groups of R_3 and R_4 may be straight or branched chains in any of the known spatial configurations. The substituents on the aryl groups, in R_3 and R_4, may be at any of the possible ring positions. While, of course, some spatial configurations and ring positions are preferred over others, all possible configurations and positions are satisfactory for the present purposes.

The compounds of this invention of the type Formula II are prepared by reacting

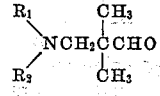


with CH_3COR_3 in equimolecular proportions and then with CH_3COR_4 in equimolecular proportions. To obtain a Formula II compound, there is reacted on a one for two molar basis

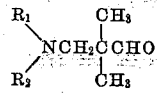


with CH_3COR_4.

The reactants of this invention,



CH_3COR_3, and CH_3COR_4, are those in which R_1, R_2, R_3, and R_4 have already been defined. These illustratively and typically include α-(dimethylaminomethyl)isobutyraldehyde, α-(diethylaminomethyl)isobutyraldehyde, α-(morpholinomethyl)isobutyraldehyde, or α-(pyrrolidinylmethyl)isobutyraldehyde, acetone, methyl cyclohexyl ketone, methyl octyl ketone, methyl tetradecyl ketone, methyl butenyl ketone, or methyl dodecenyl ketone, acetophenone, methyl trimethylphenyl ketone, methyl chlorophenyl ketone, methyl dodecenylphenyl ketone, methyl octoxyphenyl ketone, methyl naphthylketone, and methyl decylnaphthyl ketone. The reactants CH_3COR_3 and CH_3COR_4 are all known or can be made by conventional methods. The reactants



are known or can be readily made by the reaction of the appropriate secondary amine hydrochloride with formaldehyde and isobutyraldehyde according to known methods.

The present compounds whether of the type of Formula I or II are prepared by bringing together at a reacting temperature the selected reactants, depending on the formula type product desired, as discussed heretofore. Temperatures in the range of about 0° C. to the reflux temperature of the reaction mixture may be used. Generally, temperatures between about 20° to 125° C. are employed, with 25° to 80° C. preferred.

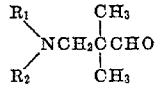
A strongly basic catalyst is required for the consummation of the instant reaction. Suitable for this purpose are alkali metals, such as sodium, potassium, or lithium, alkali metal lower alkoxides, such as sodium methoxide, potassium ethoxide, lithium methoxide, sodium isopropoxide, quaternary ammonium bases, such as trimethylbenzylammonium hydroxide, and the like.

An insert volatile organic solvent is preferably employed such as benzene, toluene, ethanol, isopropanol, tert-butanol, ethyl ether, isopropyl ether, dioxane, and the like. At the conclusion of the reaction, the solvent may be removed, when desired, by distillation, prefer-

ably under reduced pressure, or by evaporation, such as on a steam bath.

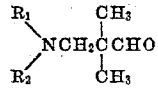
The time of reaction is not especially critical. Reaction times in the range of two to ten hours have been found satisfactory. Shorter or longer times may be employed as desired. Generally, of course, the shorter reaction times sometimes have a tendency to reduce the yield of product and the longer reaction times tend to maximize that result. This will all be clear to one skilled in the art from the teachings of this invention.

If the product of the type of Formula I is desired, there is reacted the formula



with CH_3COR_3 on an equimolecular basis and then with CH_3COR_4 on an equimolecular basis. By carefully employing equimolecular amounts of reactants, a product of high purity is obtained. If the Formula I product is a liquid, which is usually the case, it may be isolated from the reaction mixture by first adding an excess of a strong mineral acid, such as hydrochloric, sulfuric, or phosphoric, in any convenient concentrations, such as aqueous 5 to 10% solutions. The acid destroys the catalyst and at the same time forms an acid salt of the amine product. If small amounts of extraneous substances are present in the acidulated mixture, an extraction may be performed using chloroform, benzene, ethyl ether, or the like. The mixture is made basic to free the amine product and then the product is extracted with the same solvents as mentioned before or with similar ones. The solvent is removed, preferably on a steam bath, leaving the product. In some instances, particularly where the lower molecular weight products are concerned, it may be advantageous to strip off the solvent and distill the product, preferably at reduced pressure. Distillation of the higher molecular weight products is not recommended because some of them have a tendency to decompose at the higher temperatures. If the Formula II product is a solid, it may be filtered off, washed and then recrystallized from a suitable solvent, including lower alkanols, such as ethanol, isopropanol, or the like, and dried, such as over anhydrous sodium sulfate or on a steam bath. The Formula II products are generally yellow to tan in color.

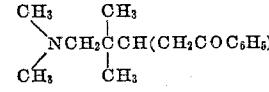
To make a product of the type of Formula II, there are reacted



and CH_3COR_4 in a one-to-two molecular ratio. These products are generally solids that may be isolated in a manner similar to the solid products of Formula I.

Whether a Formula I or II type product is being prepared, the yields consistently exceed 90% and frequently are substantially quantitative. The compounds of this invention are valuable as highly selective plant growth regulators. As indicated by the standard Lanolin Ring Method, in which a lanolin paste containing 1% of a compound of this invention is employed, and Coated Sand Method, in which 32 mg. of a present compound is used to coat 20 g. of quartz sand in which the test seeds are planted, the present compounds are excellent herbicides for dicotyledonous plants while not substantially interfering with the growth of monocotyledonous plants. In many instances the present compounds completely inhibit dicotyledonous plants and in all other cases cause considerable damage on the dicotyledonous plant life whose inhibition is desired. While all of the present compounds are valuable as selective herbicides,

a particularly outstanding performance is observed with



This unusual selctive herbicidal activity permits the use of the present compounds in many situations not available to many known commercial preparations.

The compounds of this invention may be used as herbicides in any of the usual ways of distribution. They may be employed in dusts, wettable powders, self-dispersible concentrates, solutions, or suspensions. Compositions suitable as dusts are prepared from a compound or compounds of the present invention dispersed in a solid carrier such as talc, clays, pyrophillite, diatomaceous earths, or mixtures thereof by grinding the components together or by depositing the subject compound on the solid carrier from a volatile solvent and evaporating the solvent, if desired. The subject compound is preferably present in the range of one-half to 25%, which is the most effective herbicidal range, when used in a dusting composition. A small amount of a suitable wetting and/or sticking agent may be employed, if desired, such as a condensate of polyglycerol and a long chain fatty acid, with or without reaction with phthalic anhydride.

Compositions suitable as wettable powders are prepared from a compound or compounds of the instant invention, usually present in the range of about 25 to 90%, mixed with about 1 to 5% of a suitable wetting agent such as a water-soluble, surface-active alkylphenoxypolyethoxyethanol, a condensate of ethylene oxide and oleic acid or tall oil fatty acid or rosin acid, a condensate of ethylene oxide and long-chained mercaptans, sodium dodecyl sulfate, or sodium alkylbenzenesulfonates and about one-half to 3% of a suitable dispersing agent, such as a soluble salt of a copolymer of maleic anhydride and an unsaturated hydrocarbon such as styrene or octene, a formaldehyde-condensed naphthalene sulfonate, or a lignin sulfonate. This mixture is then formulated with a sufficient amount of a solid carrier, of the kinds set forth above, to make 100%. Such a wettable powder may be suspended in an aqueous medium and applied in a spray. The active compound is preferably present in the final formulation in the range of about 0.02 to 0.5%, which is the most effective herbicidal range.

Compositions suitable as self-emulsifiable or self-dispersible concentrates are prepared from a compound or compounds of this invention, usually present in a range of about 25 to 98%, mixed with about 1 to 25% of a suitable emulsifying agent, such as a water-soluble, surface-active addition product of ethylene oxide and methylene bisdiamylphenol, octylphenoxypolyethoxyethanol, polyglycerol toleic acid condensates, or sorbitan laurate or mixtures thereof. If desired, a suitable dispersing agent, such as a soluble salt of a copolymer of maleic anhydride and an unsaturated hydrocarbon such as styrene or nonene, a formaldehyde-condensed naphthalene sulfonate, or a lignin sulfonate, may be employed in an amount of about one-half to 3%. Also, if desired, an inert organic solvent for the instant compound, the wetting agent, and the emulsifying agent, such as an aromatic naphtha, xylene, solvent esters, etc., may be employed usually in the amount of about 3 to 70%. There may similarly be used water-miscible solvent such as acetone or methyl ethyl ketone or dioxane. This concentrate is then added to a suitable medium, such as water, where it becomes emulsified or suspended without the necessity of the inclusion of additional agents. The instant compound is preferably present in the final formulation in the range of about 0.01 to 0.5% which is the most practical herbicidal range.

For greatest ease of application and maximum dis-

tribution effects, it is desirable that the present compounds be used in an aqueous spray. Another method of preparing a spray includes adding the desired amount of one of the present compounds, taken up in about 5% of a suitable solvent such as acetone, to water containing about 2% of a suitable wetting agent such as those previously listed. Sufficient compound should be added to assure the application of about one-eighth to one pound of the compound in a sufficient quantity by aqueous solution for application to one acre. Conveniently, spray is applied to about 40 gallons per acre, so the proper amount of compound to be added can be easily calculated.

Specific formulations that have been found to be highly satisfactory include the following, in which parts by weight are shown.

DUST

22.79 parts—clays.
2.21 parts—a compound of this invention,

WETTABLE POWDER

84.3 parts—a compound of this invention,
2 parts—water-soluble, surface-active alkylphenoxypolyethoxyethanol,
1 part—soluble salt of a copolymer of maleic anhydride and octene,
12.7 parts—clays.

This wettable powder, in the amount of 1.33 pounds, is added to 40 gallons of water for a one-acre application.

CONCENTRATE

97 parts—a compound of this invention,
2 parts—water-soluble, surface-active alkylphenoxypolyethoxyethanol,
1 part—soluble salt of a copolymer of maleic anhydride and octene.

This concentrate, in the amount of 1.16 pounds, is then added to 40 gallons of water for a one-acre application.

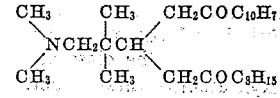
The compounds of this invention are useful herbicides when employed in either a pre-emergence or post-emergence application, as desired. The post-emergence application produces somewhat better control and is, therefore, the recommended procedure.

The compounds of this invention as well as their method of preparation may be more fully understood from the following examples which are offered by way of illustration and not by way of limitation and in which parts by weight are used throughout.

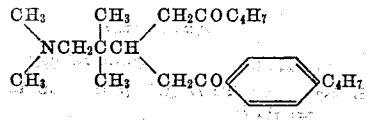
Example 1

There are introduced into a reaction vessel 1.5 parts of metallic sodium in 18 parts of anhydrous ethanol and then 60 parts of methyl octenyl ketone. There is added dropwise 50 parts of α-(dimethylaminomethyl) isobutyraldehyde. The mixture is heated to reflux for six hours and then added, with cooling, to 50 parts of aqueous 37% hydrochloric acid in 75 parts of water. The resulting mixture is extracted with ether to remove any acid insoluble material. To the aqueous solution, there is added 55 parts of an aqueous 50% solution of sodium hydroxide. The product is extracted with ether and the ether extract is dried over anhydrous sodium sulfonate and the ether removed on a steam bath. To this there is added 200 parts of absolute ethanol in which there is dissolved 5 parts of sodium. To the resulting mixture, there is introduced 17 parts of methyl naphthyl ketone. The mixture is allowed to stand at room temperature (22° to 28° C.) for five days and is then neutralized with an aqueous 10% hydrochloric acid solution and filtered to remove precipitated salts. The filtrate is freed of solvent by evaporation leaving a dark

oily product which gives an analysis for the compound having the formula



In like manner, from α-(dimethylaminomethyl)isobutyraldehyde, methyl butenyl ketone, and methyl butenylphenyl ketone, there is made the product having the formula



Example 2

There are added to a solution of 15 parts of sodium in 150 parts of absolute ethanol, 75 parts of α-(piperidinomethyl)isobutyraldehyde, and 109 parts of p-ethoxyacetophenone. The reaction mixture is allowed to stand at 25° to 28° C. for seven days, then neutralized with aqueous 10% hydrochloric acid, and filtered. The filtrate is stripped leaving a low-melting yellow solid product which is identified by elemental analysis to be 1,1-di(p - ethoxybenzoylmethyl) - 2,2-dimethyl-3-piperidinopropane.

In a similar way, from p-butylacetophenone and α-(pyrrolidinylmethyl)isobutyraldehyde, there is made 1,1-di(p - butylbenzoylmethyl) - 2,2-dimethyl-3-pyrrolidinylpropane.

Example 3

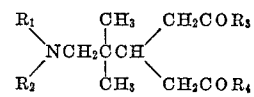
To a solution of 6.9 parts of sodium in 75 parts of absolute ethanol, there are added 40 parts of acetophenone and 30 parts of α-(dimethylaminomethyl)isobutyraldehyde. The mixture is held at 22° to 26° C. for ten days and then filtered. There is obtained a crystalline product which melts at 101°–102.5° C. and is identified as 1,1 - di(benzoylmethyl) - 2-(dimethylaminoethyl)-2-methylpropane. The product contains 3.82% nitrogen, 78.9% carbon, and 8.36% hydrogen.

In a like way, from methyl octylphenyl ketone and α-(morpholinomethyl)isobutyraldehyde, there is prepared 1,1 - di(octylbenzoylmethyl)-2-(morpholinomethyl)-2-methylpropane in the presence of trimethylbenzylammonium hydroxide, using reacting temperatures of 48° to 55° C. for 16 hours.

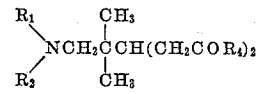
This case is a continuation-in-part of United States Serial No. 561,340, filed January 25, 1956, now abandoned.

I claim:

1. As a composition of matter, a compound from the group consisting of



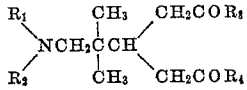
and



in which R_1 and R_2 taken singly represent alkyl groups of one to four carbon atoms and taken collectively with the amino nitrogen atom to which they are attached form a heterocyclic group selected from the class consisting of morpholino, thiamorpholino, piperidino and pyrrolidinyl, R_3 is a member from the class consisting of alkyl groups of one to seventeen carbon atoms, alkenyl groups of three to seventeen carbon atoms, and aryl and substituted aryl groups of six to twenty carbon atoms, and R_4 is a member of the group consisting of aryl and substituted aryl groups of six to twenty carbon atoms, said substituted aryl groups being free from in-

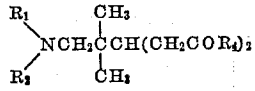
terfering substituents within the symbols R_3 and R_4, said aryl groups are selected from the class consisting of phenyl and naphthyl and the substituents on said aryl groups being selected from the class consisting of chlorine, bromine, alkyl, alkenyl, alkoxy, and alkoxyalkyl.

2. As a new composition of matter, the compound having the formula



in which R_1 and R_2 are alkyl groups of one to four carbon atoms, R_3 is an alkyl group of one to seventeen carbon atoms and R_4 is a phenyl group.

3. As a new composition of matter, the compound having the formula



in which R_1 and R_2 are alkyl groups of one to four carbon atoms and R_4 is a phenyl group.

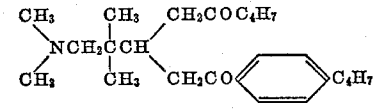
4. As a new composition of matter, 1-(dimethylamino) - 2,2 - dimethyl - 3-(naphthylcarbonylmethyl)-3-(octenylcarbonylmethyl)-propane.

5. As a new composition of matter, 1,1-di(benzoylmethyl)-2-(dimethylaminoethyl)-2-methylpropane.

6. As a new composition of matter, 1,1-di(octylbenzoylmethyl)-2-(morpholinomethyl)-2-methylpropane.

7. As a new composition of matter, 1,1-di(p-butylbenzoylmethyl)-2,2-dimethyl-3-pyrrolidinylpropane.

8. As a new composition of matter, the compound having the formula



No references cited.