United States Patent Office

3,483,231
Patented Dec. 9, 1969

3,483,231

O-ACETOACETYL OXIMES

Erich Marcus, Charleston, W. Va., and John L. Hughes, Kankakee, Ill., assignors to Union Carbide Corporation, a corporation of New York

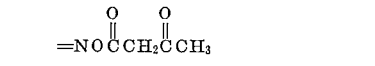
No Drawing. Filed Feb. 23, 1966, Ser. No. 529,217
Int. Cl. C07d 63/2, 3/32; A01n 9/12
U.S. Cl. 260—396 10 Claims

ABSTRACT OF THE DISCLOSURE

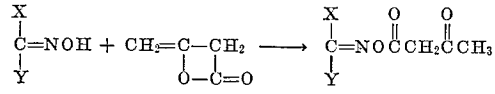
O-acetoacetyl oximes are prdouced by reacting an aldoxime or a ketoxime with diketene. The oximes as a class are known to be useful as agricultural chemicals, as are the compounds of the instant invention.

This invention relates to a new process for producing derivatives of oximes and to the novel compounds produced thereby. More particularly it is concerned with a process for producing O-acetoacetyl derivatives of oximes and to the O-acetoacetyl oxime derivatives per se.

It has been found that oximes react with diketene, either in the absence of or in the presence of a catalyst, to produce the O-acetoacetyl derivatives. The compounds of this invention are characterized by the presence therein of at least one acetoacetyl oximino group of the formula



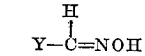
The present invention is based on the discovery that an oxime, either an aldoxime or a ketoxime, can be reacted with diketene to produce compounds containing the group represented by Formula I. The reaction between the oxime and diketene is illustrated by the following equation, wherein a monooxime is represented as the reactant:



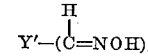
wherein X, when taken singly, can be hydrogen, alkyl containing from 1 to about 6 carbon atoms, cycloalkyl containing from about 5 to about 7 carbon atoms, alkenyl containing from 2 to about 6 carbon atoms, cycloalkenyl containing from about 5 to about 7 carbon atoms, and aryl, aralkyl or alkaryl containing up to about 10 carbon atoms and heterocyclic containing up to about 20 carbon atoms; Y, when taken singly, can be alkyl containing from 1 to about 6 carbon atoms, cycloalkyl containing from about 5 to about 7 carbon atoms, alkenyl containing from 2 to about 6 carbon atoms, cycloalkenyl containing from about 5 to about 7 carbon atoms, and aryl, aralkyl or alkaryl containing up to about 10 carbon atoms and heterocyclic containing up to about 20 carbon atoms; and X and Y, when taken jointly, form a cyclic ring with the carbon atom to which they are attached and can be divalent alkylene of from 3 to about 15 carbon atoms, or divalent alkenylene of from 4 to about 15 carbon atoms. The members X and Y when taken singly or when taken jointly can be substituted with any substituent which will not interfere with the reaction between the isonitroso group of the oxime and the diketene, and the definitions set forth above include such substituted compounds. Thus, for example the oximes may be substituted with halogen, nitro, cyano, alkoxy, aryloxy, alkylthio, etc. groups; also, for example, the cyclic ring can be bicycloalkyl, bicycloalkenyl, tricycloalkyl, tricycloalkenyl, etc.

One can use either a monooxime or a dioxime, and it can be either an aldoxime or a ketoxime. Generally the O-acetoacetyl compounds of the oximes produced in this invention can be readily recovered and they are quite stable. However, it has been observed that the oximes of some aliphatic aldehydes, or the alkyl aldoximes, may not be stable, and while they can be produced in a solvent medium, they tend to decompose when attempts are made to isolate them. In such instances the O-acetoacetyl derivatives of these compounds are not isolated from the solvent.

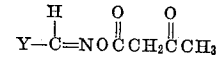
Among the aldoximes which can be used in the process of this invention to produce the O-acetoacetyl oxime derivatives of this invention one can mention acetaldoxime, propionaldoxime, isopropionaldoxime, n-butyraldoxime, isobutyraldoxime, tertiarybutyraldoxime, n-pentaldoxime, isopentaldoxime, n-hexaldoxime, n-heptaldoxime, chloral oxime, bromobutyraldoxime, nitrobutyraldoxime, cyanopentaldoxime, methoxypropionaldoxime, ethoxybutyraldoxime, methylthiobutyraldoxime, cyclopentanecarboxaldoxime, chlorocyclopentanecarboxaldoxime, nitrocyclopentanecarboxaldoxime, cyclohexanecarboxaldoxime, cycloheptanecarboxaldoxime, propanealdoxime, crotonaldoxime, 2,4-pentadienaldoxime, hexenaldoxime, cyclohexenecarboxaldoxime, cyclopentenecarboxaldoxime, benzaldoxime, phenylacetaldoxime, salicylaldoxime, the o, m and p-tolualdoximes, chlorobenzaldoxime, 2,6-dichlorobenzaldoxime, dibromobenzaldoxime, nitrobenzaldoxime, naphthaldoxime, cyanobenzaldoxime, methoxybenzaldoxime, propoxybenzaldoxime, propylbenzaldoxime, dimethylbenzaldoxime, chloronaphthaldoxime, butylnaphthaldoxime, cyanonaphthaldoxime, thiophencarboxaldoxime, furaldoxime, tetrahydrofuraldoxime, glyoxime, phthaldehyde dioxime, adipaldehyde dioxime, 2,7-naphthalenedicarboxaldehyde dioxime, cyclohexanedialdehyde dioxime, suberaldehyde dioxime, 2 - methyl-2-(methyl-thio)-propionaldoxime, pyridinecarboxaldoxime and the like. The monoaldoximes can be represented by the formula



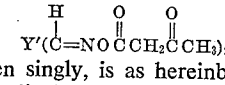
and the di-aldoximes by the formula



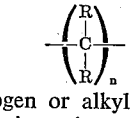
The aldoxime acetylacetates corresponding thereto have, respectively, the formulas



and



wherein Y, taken singly, is as hereinbefore defined, and Y' is a divalent radical of the formula



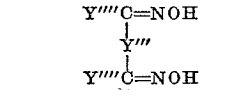
wherein R is hydrogen or alkyl of from 1 to about 4 carbon atoms and *n* is an integer of from 0 to about 6 carbon atoms, cycloalkylene of from about 5 to about 7 carbon atoms, alkenylene of from about 2 to about 6 carbon atoms, cycloalkenylene of from about 5 to about 7 carbon atoms, and arylene, aralkylene, alkarylene, and divalent heterocyclic containing up to about 20 carbon atoms.

Among the suitable ketoximes one can mention acetoxime, methyl ethyl ketoxime, methyl isopropyl

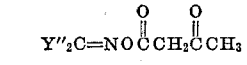
ketoxime, methyl t-butyl ketoxime, methyl n-propyl ketoxime, diethyl ketoxime, methyl secbutyl ketoxime, methyl isobutyl ketoxime, ethyl isopropyl ketoxime, diisopropyl ketoxime, methyl n-butyl ketoxime, ethyl n-propyl ketoxime, methyl n-amyl ketoxime, ethyl n-butyl ketoxime, di-n-propyl ketoxime, di-n-butyl ketoxime, diisobutyl ketoxime, methyl n-hexyl ketoxime, diisoamyl ketoxime, chloroacetoxime, dichloroacetoxime, acetylacetoxime, methyl isobutenyl ketoxime, diisobutenyl ketoxime, dichloroethyl ketoxime, di-nitroamyl ketoxime, di(cyclopentyl)ketoxime, di(cyclohexyl)ketoxime, di(cycloheptyl)-ketoxime, di(chlorocyclopentyl)ketoxime, di(methylcyclopentyl) - ketoxime, di(cyclopentenyl)ketoxime, di(cycloheptenyl)ketoxime, methyl phenyl ketoxime, methyl naphthyl ketoxime, methyl tolyl ketoxime, methyl xylyl ketoxime, phenyl bromomethyl ketoxime, diphenyl ketoxime, phenyl naphthyl ketoxime, ditolyl ketoxime, di(chlorophenyl)ketoxime, di(cyanophenyl)ketoxime, di(butylphenyl)ketoxime, di(methoxyphenyl)ketoxime, phenyl tolyl ketoxime, di(phenethyl)ketoxime, methyl thienyl ketoxime, ethyl furyl ketoxime, cyclohexyl tetrahydrofurfuryl ketoxime, dimethylglyoxime, diphenylglyoxime, 1,4-cyclohexadienedione dioxime, 1,4-cyclohexanedione dioxime, phenyl 1,2-propanedione 2-oxime, benzil monoxime, phenyl pyridyl ketoxime and the like. The mono-ketoximes can be represented by the formula

$$Y''_2C{=}NOH$$

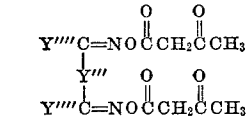
and the di-ketoximes by the formula



The ketoxime acetylacetates corresponding thereto have, respectively, the formulas

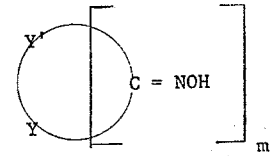


and



wherein Y'', when taken singly, can be alkyl of from 1 to about 6 carbon atoms, cycloalkyl of from about 5 to about 7 carbon atoms, alkenyl of from 2 to about 6 carbon atoms, cycloalkenyl of from about 5 to about 7 carbon atoms, and aryl, aralkyl or alkaryl containing up to about 10 carbon atoms and heterocyclic containing up to about 20 carbon atoms, and, when taken jointly, the two Y'' groups form a saturated or unsaturated hydrocarbyl or heterocyclic ring of from 3 to about 7 ring atoms together with the carbon atom to which said two Y'' groups are attached; and Y''' can be nothing or have the same meanings as defined for Y'; and Y'''', when taken singly, can be alkyl of from 1 to about 6 carbon atoms, cycloalkyl of from 5 to about 7 carbon atoms, alkenyl of from 2 to about 6 carbon atoms, cycloalkenyl of from about 5 to about 7 carbon atoms, and aryl, aralkyl or alkaryl containing up to about 10 carbon atoms and heterocyclic of up to about 20 carbon atoms.

Among the suitable oximes wherein Y and Y', when taken jointly, form a cyclic ring with the carbon atom to which they are attached one can mention cyclopentanone oxime, cyclohexanone oxime, methylcyclohexanone oxime, cyclopentenone oxime, methylcyclopentanone oxime, chlorocyclohexanone oxime, nitrocyclohexanone oxime, propoxycyclohexanone oxime, cyclooctanone oxime, cyclodecanone oxime, 1,4-cyclohexanedione dioxime, p-benzoquinone dioxime, alpha-tetralone oxime, norbornan-2-one oxime, d-camphor oxime, tricyclo [5.2.1.$0^{2,6}$]deca-3,8-dien-5,10-dione-5-oxime, 9-chlorotricyclo[5.2.1.$0^{2,6}$]deca-3-en-8-one oxime, 5-chlorotetracyclo [6.2.1.$1^{3,6}$.$0^{2,7}$]dodecan-4-one oxime, 3-chloro-6-cyanonorborane-2-one oxime, p-benzoquinone dioxime, alpha-tetralone oxime, and the like. These oximes can be represented by the general formula



sented by the general formula

The oximes are well known in the art and the literature discloses several methods for their preparation. One skilled in the art is familiar with the technology required therefor.

In the process of this invention the oxime and diketene are reacted, preferably in the presence of an organic solvent that will not react with the diketene. Among some of the solvents that can be used one can mention acetone, diethyl ether, benzene, ethyl acetate, methylene dichloride, chloroform, carbon tetrachloride, cyclohexane, cyclohexene, heptane, octane, octene, 1,2-dimethoxyethane, and the like. The reaction can be carried out in solution or as a suspension. The oxime and diketene react stoichiometrically and, consequently, equivalent amounts are used. However, a slight excess of diketene, in the order of 5 to 20 mole percent is preferably employed.

The temperature of the reaction can be from —25° C. to about 60° C. or higher. The preferred temperature range is from about 0° C. to about 35° C. in order to minimize formation of dehydroacetic acid, the main by-product of the reaction. Dehydroacetic acid is formed in increased amounts as the temperature is raised and consequently one should carry out the reaction at the lowest temperature suitable. Generally the reaction is carried out with external cooling because of its exothermic nature.

As previously indicated, the reaction can be catalyzed in contact with an amine compound as catalyst if desired. Among the suitable amines one can mention 1,4-diazabicyclo[2.2.1]octane, 1 - azabicyclo[2.2.1]octane, triethylamine, N,N,N',N' - tetramethyl - 1,3 - butanediamine (TMBDA), trimethylamine, N - methylmorpholine, N-ethylmorpholine, N - ethylpiperidine, N - isopropylpyrrolidone, pyridine, quinoline, benzyl dimethylamine, and the like. In general, the amines used for catalytic purposes in the manufacture of polyurethanes can be used; provided, however, that they do not contain groups that will interfere with the reaction between the oxime and the diketene and that they do not react with the starting materials except in a catalytic manner. These amines are well known to the average scientist. It was unexpected and unobvious that these amines would be effective catalysts in the instant invention since it was not heretofore known that they would improve the reaction between the oxime radical with diketene.

The amount of amine catalyst charged can vary from about 0.05 gram to about 5 grams per mole of oxime. Preferably, however, from about 0.1 gram to 2 grams of amine catalyst per mole of oxime is used; it has been found that 1 gram per mole is the most preferred amount. Thus, any catalytic amount, sufficient to catalyze the reaction can be used. In the absence of any catalyst the yield is generally much lower.

The diketene can be used in the pure undiluted form or as a solution in an inert solvent.

In general, the reaction is carried out by slowly adding the diketene to a solution or suspension of the oxime in a solvent, with the catalyst present if desired. The temperature of the reaction is controlled by the rate of addition of diketene, or with a cooling bath, or a combination of both. After all of the diketene has been added, the desired O-acetoacetyl derivative of the oxime is recovered by conventional methods.

Among the O-acetoacetyloxime compounds that can be produced one can mention acetaldehyde O-acetoacetyloxime, butyraldehyde O-acetoacetyloxime, heptaldehyde O - acetoacetyloxime, cyclopentanecarboxaldehyde O-acetoacetyloxime, 2,4 - pentadienal O - acetoacetyloxime, benzaldehyde O - acetoacetyloxime, salicylaldehyde O-acetoacetyloxime, 2,6 - dichlorobenzaldehyde O - acetoacetyloxime, naphthaldehyde O - acetoacetyloxime, cyanobenzaldehyde O - acetoacetyloxime, pyridinecarboxaldehyde O - acetoacetyloxime, bis(O - acetoacetyl)glyoxime, acetone O - acetoacetyloxime, diethylketone O-acetoacetyloxime, methyl butyl ketone O - acetoacetyloxime, dichloroacetone O - acetoacetyloxime, di - (cyclopentenyl)ketone O - acetoacetyloxime, methyl phenyl ketone O - acetoacetyloxime, diphenyl ketone O - acetoacetyloxime, di(chlorophenyl)ketone O - acetoacetyloxime, phenyl tolyl ketone O - acetoacetyloxime, bis(O-acetoacetyl)dimethylglyoxime, p - benzoquinone bis(O-acetoacetyloxime), cyclopentanone O - acetoacetyloxime, phenyl 1,2 - propanedione 2 - (O - acetoacetyloxime), benzyl O - acetoacetyloxime, methylcyclohexanone O-acetoacetyloxime, cyclopentanone O - acetoacetyloxime, cyclododecanone O - acetoacetyloxime, 3 - chloro - 6-cyanonorboran - 2 - one O - acetoacetyloxime, 9 - chlorotricyclo[5.2.1.$0^{2,6}$]dec - 3 - en - 8 - one O - acetoacetyloxime, tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dien-5,10-dione 5-(O-acetoacetyloxime, 5 - chlorotetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodecan-4-one O-acetoacetyloxime, α-tetralone O-acetoacetyloxime, and the like.

The oxime acetylacetates of this invention are useful as intermediates and they are also useful as bactericides and fungicides in agricultural applications. For example, 2,6 - dichlorobenzaldehyde O - acetoacetyloxime and 2-nitrobenzaldehyde O - acetoacetyloxime are quite effective as herbicides, especially in their control of crab grass. 3 - chloro - 6 - cyanobornan - 2 - one O - acetoacetyloxime, as well as phenyl alpha-pyridyl ketone O-acetoacetyloxime, is active on insecticide; formulations of 1000 p.p.m. by weight gave substantially complete control of Southern Army Worms. 2 - methyl - 2 - (methylthio)propionaldehyde O-acetoacetyloxime was effective against the soil fungus Pythium.

The following examples further serve to describe the invention; however, the invention should not be considered limited thereto.

EXAMPLE 1

There were charged to a jacketed flask, equipped with a stirrer, condenser, thermometer and dropping funnel, 107 grams of diethyl ether, 10 grams of 2-methyl-2-(methylthio)propionaloxime (B.P. 67° C. at 2 mm.) and 0.2 gram of triethylenediamine. Over a period of about one hour, 12.5 grams of a 55 weight percent solution of diketene in acetone was added at from 25° C. to 35° C. The reaction mixtures was stirred at room temperature for an additional two hours. The solvent was removed by flash distillation at 25° C. and under reduced pressure. Infrared and NMR analysis established that the produce was 2 - methyl - 2 - (methylthio)propionaldehyde O-acetoacetyloxime of 91 percent purity; yield was 13.2 grams.

In a similar manner acetaldehyde O-acetoacetyloxime, heptaldehyde O-acetoacetyloxime, cyclopentaldehyde O-acetoacetyloxime and 2,4 - pentadienaldehyde O - acetoacetyloxime are produced from their respective oximes.

EXAMPLE 2

In a manner similar to that described in Example 1, 33.6 grams of a 55 weight percent solution of diketene in acetone was added to and reacted with a mixture of 8.8 grams of glyoxime, 143 grams of diethyl ether and 0.2 gram of triethylenediamine. The mixture was stirred for an additional two hours, and then it was extracted with aqueous five percent sodium carbonate to remove the dehydroacetic acid formed as a by-product. The organic phase was washed with water and dried over magnesium sulfate. After removal of the solvents, the solid residue was recrystallized from cyclohexane and 20.2 grams of bis(O - acetoacetyl)glyoxime was recovered having a melting point of 128–130° C.

Microanalysis.—Calculated for $C_{10}H_{12}N_2O_6$: C, 46.9; H, 4.72; N, 10.9. Found: C, 47.3; H, 4.75; N, 10.7.

The bis(O - acetoacetyl)glyoxime is obtained in lower yield in the absence of the amine catalyst.

EXAMPLE 3

In a manner similar to that described in Example 1, 61 grams of the 55 percent diketene solution was added to and reacted with a mixture of 48.4 grams of benzaldoxime, 175 grams of benzene and 0.3 gram of triethylenediamine. After washing and removing the solvent the benzaldehyde O - acetoacetyloxime was purified by recrystallization from a mixture of benzene and cyclohexane. It had a melting point of 60–61° C.; yield was 63.4 grams.

Microanalysis.—Calculated for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.40; N, 6.83. Found: C, 64.5; H, 5.44; N, 6.78.

Benzaldehyde O - acetoacetyloxime is obtained in good yield by replacing triethylenediamine by either triethylamine or pyridine. Lowest yields are obtained in the absence of the amine catalyst.

EXAMPLE 4

In a manner similar to that described in Example 1, 26 grams of the 55 percent diketene solution was added to and reacted with a mixture of 26.8 grams of 2,6-dichlorobenzaldoxime, 132 grams of benzene and 0.3 gram of triethylenediamine. After washing and solvent removal the 2,6-dichlorobenzaldehyde O-acetoacetyloxime was recovered as a liquid having a purity greater than 95 percent as determined by NMR. The structure of the compound was further confirmed by infrared analysis.

EXAMPLE 5

In a manner similar to that described in Example 1, 35 grams of the 55 percent diketene solution was added to and reacted with a mixture of 35 grams of 3,4-dichlorobenzaldoxime, 220 grams of benzene and 0.4 gram of triethylenediamine. After washing and solvent removal the 3,4-dichlorobenzaldehyde O-acetoacetyloxime was purified by recrystallization from aqueous methanol; it had a melting point of 84–86° C.; yield was 40.1 grams.

Microanalysis.—Calculated for $C_{11}H_9NO_3Cl_2$: C, 48.2; H, 3.31; N, 5.11; Cl, 25.9. Found: C, 48.6; H, 3.56; N, 5.14; Cl, 25.8.

3,4-dichlorobenzaldehyde O-acetoacetyloxime is also obtained by using undiluted diketene rather than a solution thereof.

EXAMPLE 6

In a manner similar to that described in Example 1, 18.5 grams of the 55 percent diketene solution was added to and reacted with a mixture of 15.4 grams of 2-nitrobenzaldoxime, 143 grams of diethyl ether and 0.1 gram of triethylenediamine. The 2-nitrobenzaldehyde O-acetoacetyloxime was purified by recrystallization from a mixture of benzene and cyclohexane; it had a melting point of 63–66° C.; yield was 11.1 grams.

Microanalysis.—Calculated for $C_{11}H_{10}N_2O_5$: C, 52.8; H, 4.03; N, 11.2. Found: C, 52.8; H, 3.95; N, 11.3.

EXAMPLE 7

In a manner similar to that described in Example 1, 25 grams of the 55 percent diketene solution was added to and reacted with a mixture of 21.2 grams of isopropenyl t-butyl ketoxime, 175 grams of benzene and 0.3 gram of triethylenediamine. After washing and solvent removal the isopropenyl t-butyl ketone O-acetoacetyloxime was recovered as a liquid having a purity greater than 95 percent as determined by NMR. The structure of the compound was further confirmed by infrared analysis.

EXAMPLE 8

In a manner similar to that described in Example 1, 38 grams of the 55 percent diketene solution was added to and reacted with 27 grams of methyl phenyl ketoxime, 88 grams of benzene and 0.3 gram of triethylenediamine. After washing and solvent removal the methyl phenyl ketone O-acetoacetyloxime was recovered as liquid having a purity greater than 95 percent as determined by NMR. The structure was further confirmed by infrared analysis.

EXAMPLE 9

In a manner similar to that described in Example 1, 17 grams of the 55 percent diketene solution was added to and reacted with 16.3 grams of phenyl 1,2-propanedione 2-oxime, 107 grams of diethyl ether and 0.3 gram of triethylenediamine. After washing and solvent removal the phenyl 1,2-propanedione 2-(O-acetoacetyloxime) was recovered as liquid having a purity greater than 95 percent as determined by NMR. The structure of the produce was further confirmed by infrared analysis.

EXAMPLE 13

In a manner similar to that described in Example 1, 13 grams of the 55 percent diketene solution was added to and reacted with a mixture of 14 grams of 3-chloro-7-cyanonorbornan-2-one oxime, 175 grams of benzene and 0.2 gram of triethylenediamine. After washing and solvent removal the O-acetoacetyloxime of the above oxime was purified by recrystallization from aqueous methanol; it had a melting point of 87–89° C.; yield was 12.3 grams.

Microanalysis.—Calculated for $C_{12}H_{13}N_2ClO_3$: C, 53.6; H, 4.87; N, 10.4; Cl, 13.2. Found: C, 54.4; H, 4.93; N, 10.0; Cl, 13.3.

In the following table examples showing the production of additional O-acetoacetyloximes are set forth; these, also, were carried out under reaction conditions similar to those described in Example 1.

Ex.	Oxime	Catalyst	O-acetoacetyloxime
14	Isobutyraldehyde oxime	None	Isobutyraldehyde O-acetoacetyloxime.
15	Butyraldehyde oxime	Triethylamine	Butyraldehyde O-acetoacetyloxime.
16	Chlorocyclopentaldehyde oxime	Triethylenediamine	Chlorocyclopentaldehyde O-acetoacetyloxime.
17	3,4-dimethoxybenzaldehyde oxime	do	3,4-dimethoxybenzaldehyde O-acetoacetyloxime.
18	Naphthaldehyde oxime	N-methylmorpholine	Naphthaldehyde O-acetoacetyloxime
19	Furaldehyde oxime	TMBDA	Furaldehyde O-acetoacetyloxime
20	Pyridine carbaldoxime	None	Pyridine aldehyde O-acetoacetyloxime
21	Phthalaldehyde oxime	Pyridine	Phthalaldehyde O-acetoacetyloxime.
22	Diisopropylketone oxime	Triethylamine	Diisopropylketone O-acetoacetyloxime.
23	Dichloroacetone oxime	TMBDA	Dichloroacetone O-acetoacetyloxime.
24	Di(methylcyclopentyl)ketone oxime	Triethylenediamine	Di(methylcyclopentyl)ketone O-acetoacetyloxime.
25	Ditolyl ketone oxime	do	Ditolyl ketone O-acetoacetyloxime.
26	Benzil anti-monoxime	do	Benzil anti-(O-acetoacetyloxime).
27	Phenyl α-pyridyl ketoxime	do	Phenyl α-pyridyl O-acetoacetyloxime.
28	p-benzoquinone dioxime	do	p-Benzoquinone bis(O-acetoacetyloxime).
29	Salicylaldoxime	do	Salicyladehyde O-acetoacetyloxime.
30	Cyclododecanone oxime	do	Cyclododecanone O-acetoacetyloxime.
31	Piperonal oxime	do	Piperonal O-ocetoacetyloxime.
32	Methyl 2-thienyl ketoxime	do	Methyl 2-thienyl ketone.
33	9-chlorotricyclo[5.2.1.$0^{2,6}$]-dec-3-en-8-one oxime	do	9-chlorotricyclo[5.2.1.$0]^{2,6}$]dec-3-en-8-one O-acetoacetyloxime.
34	Norbornan-2-one-oxime	do	Norbornane 2-(O-acetoacetyloxime).
35	Cyclohexanone oxime	do	Cyclohexanone O-acetoacetyloxime.
36	Alpha-tetralone oxime	do	Alpha-tetralone O-acetoacetyloxime.
37	Beta-resorcylaldoxime	do	Beta-resorcylaldehyde O-acetoacetyloxime.
38	2-chloro-3,5,5-trimethyl-2-cyclohexenone oxime	do	2-chloro-3,5,5-trimethyl-2-cyclohexenone O-acetoacetyloxime.

as determined by NMR. The structure was further confirmed by infrared analysis.

EXAMPLE 10

In a manner similar to that described in Example 1, 18.5 grams of the 55 percent diketene solution was added to 19.7 grams of diphenyl ketoxime, 14.3 grams of diethyl ether and 0.1 gram of triethylenediamine. After washing and solvent removal the diphenyl ketone O-acetoacetyloxime was purified by recrystallization from a mixture of benzene and cyclohexane; it had a melting point of 68–70° C.; yield was 16.2 grams.

Microanalysis.—Calculated for $C_{17}H_{15}NO_3$: C, 72.6; H, 5.38; N, 4.98. Found: C, 72.5; H, 5.35; N, 5.10.

EXAMPLE 11

In a manner similar to that described in Example 1, 12.5 grams of 99.7 percent diketene was added to and reacted with 11 grams of acetone oxime, 50 grams of diethyl ether, and 0.15 gram of triethylenediamine. After removal of solvent, acetone O-acetoacetyloxime was recovered as a liquid. The structure of the produce was confirmed by infrared analysis. NMR established a purity greater than 85 percent. Attempts to further purify the product were unsuccessful; however, the impure reaction product can be used as recovered.

EXAMPLE 12

In a manner similar to that described in Example 1, 26 grams of the 55 percent diketene solution was added to and reacted with a mixture of 24 grams of 3-chloronorbornan-2-one oxime, 175 grams of benzene and 0.3 gram of triethylenediamine. After washing and removal of solvent the O-acetoacetyloxime of the above oxime was recovered as liquid having a purity greater than 95 percent

A number of the O-acetoacetyloximes have exhibited interesting biological properties. For example, benzaldehyde O-acetoacetyloxime and 3,4 - dichlorobenzaldehyde O-acetoacetyloxime were evaluated with regard to bactericidal activity. Benzaldoxime acetylacetate was observed as exhibiting an analgesic action on mice and also found to possess activity against cucumber anthracnose, a plant virus disease. 3,4-dichlorobenzaldehyde O-acetoacetyloxime showed bactericidal activity against the test organisms *Staphylococcus aureus, Eschirichia coli, Erwinia amylovora,* and *Xanthomonas melvaclarum.*

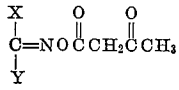
The test formulations were prepared by dissolving one gram of the O-acetoacetyloxime compound in 50 ml. of acetone in which had been dissolved 0.1 gram of "Triton X–155", an alkylphenoxy polyethoxyethanol surfactant, as an emulsifying or dispersing agent. The prepared solution was mixed with 200 ml. of water to give a base stock containing 0.4 weight percent of the compound. This stock was further diluted with water to give a test compound formulation containing 250 parts of test compound million parts of formulation.

The organisms used in the tests were cultured on potato dextrose agar nutrient media. An 18 ml. portion of the nutrient media was placed in a series of 50 ml. Erlenmeyer flasks, plugged with cotton, and autoclaved for 20 minutes. The flasks were cooled to 50° C. to 60° C. in a water bath and 2 ml. of the selected test solution was placed in each flask and agitated to insure uniform mixing; the contents of the flasks were immediately poured into sterile Petri dishes and permitted to solidify before inoculation. The agar dishes were inoculated by streaking with toxicant mixture and then incubated for two days at 30° C. at which time it was observed that there was no growth of bacteria in the tubes containing the

3,4-dichlorobenzaldehyde O-acetoacetyloxime and only a slight growth in the tubes containing the benzaldehyde O-acetoacetyloxime. A control test showed severe growth of bacteria.

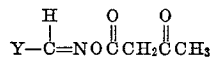
What is claimed is:

1. A compound of the formula:

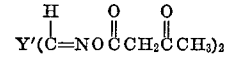


wherein X, when taken singly, is a member selected from the group consisting of hydrogen, alkyl containing from 1 to about 6 carbon atoms, cycloalkyl containing from about 5 to about 7 carbon atoms, alkenyl containing from 2 to about 6 carbon atoms, cycloalkenyl containing from about 5 to about 7 carbon atoms, and aryl, aralkyl, or alkaryl containing up to about 10 carbon atoms, thienyl, furyl, tetrahydrofurfuryl and pyridyl; Y, when taken singly, is a monovalent member selected from the group consisting of alkyl containing from 1 to about 6 carbon atoms, cycloalkyl containing from about 5 to about 7 carbon atoms, alkenyl containing from 2 to about 6 carbon atoms, cycloalkenyl containing from about 5 to about 7 carbon atoms, and aryl, aralkyl, or alkaryl containing up to about 10 carbon atoms, thienyl, furyl, tetrahydrofurfuryl and pyridyl; and X and Y when taken jointly, form a cyclic ring with the carbon atom to which they are attached and are selected from the group consisting of divalent alkylene of from 3 to about 15 carbon atoms, and divalent alkenylene of from 4 to 15 carbon atoms.

2. A compound selected from the group consisting of aldoxime acetylacetates of the formulas:



and

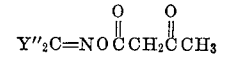


wherein Y, taken singly, is a monovalent member selected from the group consisting of alkyl containing from 1 to about 6 carbon atoms, cycloalkyl containing from about 5 to about 7 carbon atoms, alkenyl containing from 2 to about 6 carbon atoms, cycloalkenyl containing from about 5 to about 7 carbon atoms, and aryl, aralkyl, or alkaryl containing up to about 10 carbon atoms, thienyl, furyl, tetrahydrofurfuryl and pyridyl; and Y′ is a divalent member selected from the group consisting of the radical of the formula

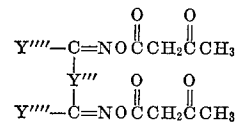


wherein R is a member selected from the group consisting of hydrogen and alkyl of from 1 to about 4 carbon atoms and *n* is an integer of from 0 to about 6 carbon atoms, cycloalkylene containing from 5 to about 7 carbon atoms, alkenylene containing from 2 to about 6 carbon atoms, cycloalkenylene containing from about 5 to about 7 carbon atoms, and arylene, aralkylene, or alkarylene containing up to about 10 carbon atoms, thienylene, furylene, tetrahydrofurfurylene and pyridylene.

3. A compound selected from the group consisting of ketoxime acetylacetates of the formulas:



and



wherein Y″, when taken singly, is a member of the group consisting of alkyl of from 1 to about 6 carbon atoms, cycloalkyl of from about 5 to about 7 carbon atoms, alkenyl of from 2 to about 6 carbon atoms, cycloalkenyl of from about 5 to about 7 carbon atoms, and aryl, aralkyl, or alkaryl containing up to about 10 carbon atoms, thienyl, furyl, tetrahydrofurfuryl and pyridyl; and, when taken jointly, the two Y″ groups form a member of the group consisting of saturated and unsaturated hydrocarbyl and heterocyclic rings of from 3 to about 7 ring atoms together with the carbon atom to which said two Y″ groups are attached; Y‴ is a member selected from the group consisting of nothing, a divalent radical selected from the group consisting of



in which R is a member of the group consisting of hydrogen and alkyl of from 1 to about 4 carbon atoms and *n* is an integer of from 0 to about 6 carbon atoms, cycloalkylene of from about 5 to about 7 carbon atoms, alkenylene of from about 2 to about 6 carbon atoms, cycloalkenylene of from about 5 to about 7 carbon atoms, and arylene, aralkylene, or alkarylene consisting up to about 10 carbon atoms and divalent thienyl, furyl, tetrahydrofurfuryl or pyridyl; and Y⁗, when taken singly, is a member of the group consisting of alkyl of from 1 to about 6 carbon atoms, cycloalkyl of from 5 to about 7 carbon atoms, alkenyl of from 2 to about 6 carbon atoms, cycloalkenyl of from about 5 to about 7 carbon atoms, and aryl, aralkyl, or alkaryl consisting up to about 10 carbon atoms thienyl, furyl, tetrahydrofurfuryl or pyridyl.

4. The aldoxime acetylacetate of claim 2, 2,6-dichlorobenzaldehyde O-acetoacetyloxime.

5. The ketoxime acetylacetate of claim 3, acetone O-acetoacetyloxime.

6. The ketoxime acetylacetate of claim 3, alphatetralone O-acetoacetyloxime.

7. The ketoxime acetylacetate of claim 3, p-benzoquinone bis(O-acetoacetyloxime).

8. The ketoxime acetylacetate of claim 3, 1-phenyl-1,2-propanedione-2(O-acetoacetyloxime).

9. The ketoxime acetylacetate of claim 3, methyl phenyl ketone O-acetoacetyloxime.

10. The aldoxime acetylacetate of claim 2, 3,4-dimethoxy benzaldehyde O-acetoacetyloxime.

References Cited

UNITED STATES PATENTS

3,165,392 1/1965 Koopman ---------- 71—106

DANIEL D. HORWITZ, Primary Examiner

U.S. Cl. X.R.

71—121; 260—294.8, 295, 332.2, 347.2, 347.3, 464, 465, 465.4, 566; 424—263, 275, 285, 304, 327