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3,171,857

HYDRAZODICARBOXYLIC ACIDDIHYDRAZIDES

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Claims priority, application Switzerland, Sept. 27, 1960, 10,918/60
5 Claims. (Cl. 260—554)

It has been found that hydrazodicarboxylic aciddihydrazides which have been unknown until now are obtained by reaction of a hydrazodicarboxylic acid diester with hydrazine or a substituted hydrazine.

The hydrazidation proceeds according to the following equation:

$$ROCONHNHCOOR + 2HNR'NR''R''' \rightarrow R'''R''NNR'CONHNHCONR'NR''R''' + 2ROH$$

In this formula R has the significance usual in such esters and R', R'' and R''' are hydrogen atoms or hydrocarbon radicals.

When substituted hydrazines of the formula

$$HNR'NR''R'''$$

are used as reactants in the process of the invention, the R', R'' and R''' radicals are hydrogen or hydrocarbon radicals, except of course one must be a hydrocarbon radical to fit the definition of substituted hydrazine. Usually it is preferred that R', R'' and R''' be hydrocarbon radicals of not more than 18 carbon atoms, more preferably not more than 8 carbon atoms. Illustrative of substituted hydrazines usable in the process of the invention are the following: Methyl hydrazine, t-butyl hydrazine, n-dodecyl hydrazine, cyclohexyl hydrazine, benzyl hydrazine, phenyl hydrazine, p-tolyl hydrazine, β-naphthyl hydrazine, N,N'-dimethyl hydrazine, N,N-diphenyl hydrazine, N,N,N'-trimethyl hydrazine, N-phenyl-N'-methyl hydrazine, etc.

The hydrazodicarboxylic acid esters serving as starting material can be prepared in known manner from hydrazine and chloroformic acid esters. In principle, all esters available can be used in this reaction. However, the hydrazidation does not occur equally easily with all esters, as is shown in the following table:

R	Yield, percent
CH_3	70
C_2H_5	15
C_6H_5	91
$pCl-C_6H_5$	90.5

But, these yields which for comparison purposes were obtained with hydrazine by using the working method described in Example 1 do not represent the maximum that can be obtained. Esters wherein R is an araliphatic or cycloaliphatic radical, e.g. the benzyl radical or the cyclohexyl radical, can also be used. Usually it is preferred that R contain not more than 18 carbon atoms, and more preferably not more than 8 carbon atoms. In general, the methyl ester owing to its price and technical availability is preferred in carrying out the invention.

The reaction of an optional hydrazodicarboxylic acid diester is best effected by heating a mixture of hydrazine and ester for some time at higher temperature. Using hydrazine or aliphatically substituted hydrazines, the reaction is complete at about 100° C. in most cases after 30–40 minutes. However, the hydrazidation also occurs at room temperature when the reaction mixture is left standing for a prolonged time. The less basic aromatically substituted hydrazines need more prolonged reaction time and possibly a higher reaction temperature. The process of invention can be carried out with or without a solvent. The lower aliphatic alcohols are especially suitable as solvents. A lower aliphatic alcohol is one having from 1 to 6 carbon atoms. In general, the same or similar working methods are applicable as with the amidation of carboxylic acids by using esters thereof.

To supplement the compound of the invention of the examples the following compounds are named as illustrative of compounds of the invention: hydrazodicarboxylic acid bis-(trimethyl-hydrazide), hydrazodicarboxylic acid bis-(tribenzylhydrazide), hydrazodicarboxylic acid bis - (tricyclohexylhydrazide), hydrazodicarboxylic acid bis-(tri-n-dodecylhydrazide), hydrazodicarboxylic acid bis-(N-phenyl-N-methyl-N'-ethyl-hydrazide), etc.

The hydrazodicarboxylic acid-dihydrazides of the invention are useful as reducing agents. They also have similar uses to hydrazine. Unlike hydrazine the compounds of the invention are solid and more stable. They are useful as solid rocket propellants, since on oxidation large volumes of nitrogen as well as water are formed.

Hydrazodicarboxylic acid-dihydrazides are valuable intermediates. The compound obtained with hydrazine reacts with ketones and aldehydes in the same way as semicarbazide, thereby two molecules of the carbonyl compound can be condensed with one molecule of hydrazodicarboxylic acid-dihydrazide. Derivatives of acetone, benzaldehyde, isobutyraldehyde, etc., are formed very easily and practically quantitatively on mixing the reactants in warm water. The novel compounds, as long as they contain a replaceable hydrogen atom, can be reacted with carboxylic acid chlorides or anhydrides in the normal manner, thus obtaining, the corresponding mono, di or even polyacylderivative. With for example two equivalents of benzenesulfonyl chloride, one obtains the symmetrical dibenzenesulfonylderivative.

Example 1

7.5 g. of hydrazodicarboxylic acid-dimethylester (0.05 mole) and 10 g. of hydrazine hydrate (0.2 mole) are heated at 100° C. for ½ hour. Crystals separate on cooling and standing for some time. These are filtered off, washed with water and methyl alcohol and dried. Recrystallization from hot water gives pure hydrazodicarboxylic acid-dihydrazide.

Yield 70%; M.P. 203–205° C.

Analysis.—$C_2H_8N_6O_2$ (148.1):
Percent C calcd., 16.22; found, 16.34
Percent H calcd., 5.44; found, 5.41
Percent N calcd., 56.74; found, 56.72

Example 2

60.8 g. of hydrazine hydrate (1.2 moles) are dissolved in 130 ml. of ethyl alcohol. 81.6 g. of hydrazodicarboxylic acid-diphenylester (0.3 mole) are slowly added with stirring. The reaction mixture is subsequently refluxed for ½ hour, then cooled and the precipitated crystals filtered off.

Yield 40.4 g. (=91% of the theory); M.P. 203–205° C.

Hydrazodicarboxylic acid-dihydrazide is insoluble in most common solvents but soluble in hot water. The aqueous solution is weakly alkaline (pH 7–8). Two base-equivalents can be titrated with perchloric acid in acetic acid solution. The aqueous solution displays strong reducing properties.

Example 3

To a 10% solution of hydrazide in warm water a corresponding amount of acetone is added. Crystallization begins at once. The reaction mixture is kept at 50° C. for 15 minutes, then cooled and filtered.

Yield 95%. Recrystallization from acetonitrile, M.P. 234–235° C.

Analysis.—$C_8H_{16}N_6O_2$ (228.3):
Percent C calcd., 42.09; found, 42.16
Percent H calcd., 7.07; found, 7.31
Percent N calcd., 36.82; found, 36.97

Example 4

Isobutyraldehyde is used instead of acetone and one then preceeds as in Example 3.

Yield (crude) 100%. Recrystallization from DMF/water, M.P. 199–200° C.

Analysis.—$C_{10}H_{20}N_6O_2$ (256.3):
Percent C calcd., 46.82; found, 46.91
Percent H calcd., 7.87; found, 7.98
Percent N calcd., 32.79; found, 32.61

Example 5

Benzaldehyde is used instead of acetone and one then proceeds as in Example 3.

Yield 52.4% from pyridine/water. Recrystallization from DMF, M.P. 234–235° C.

Analysis.—$C_{16}H_{16}N_6O_2$ (324.3):
Percent N calcd., 25.91; found, 25.23.

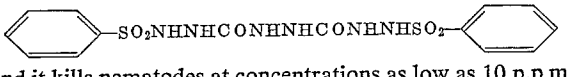
Example 6

0.88 g. of sodium hydroxide (0.022 mole) and 1.48 g. of hydrazodicarboxylic acid-dihydrazide (0.01 mole) are successively dissolved in 10 ml. of water. Then, 2.56 g. of benzenesulfonylchloride (0.02 mole) are added and the mixture is shaken vigorously. The reaction is started by immersing the flask briefly in hot water; it then proceeds exothermally. After 15 minutes' shaking it is left standing for 3 hours. The crystals are filtered off and washed with water. Recrystallization from 50% ethyl alcohol.

Yield 0.65 g. (=15% of the theory); M.P. 234–236° C.

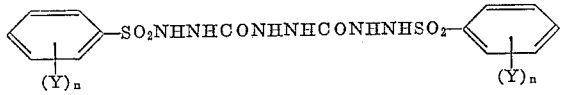
Analysis.—$C_{14}H_{16}N_6O_6S_2$ (428.5):
Percent C calcd., 39.25; found, 39.14
Percent H calcd., 3.76; found, 3.98
Percent N calcd., 19.62; found, 19.41
Percent S calcd., 14.97; found, 14.88

This compound of the invention has the structure



and it kills nematodes at concentrations as low as 10 p.p.m.

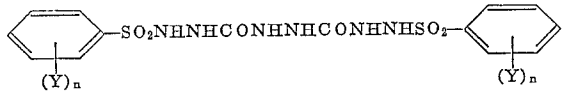
If, in Example 6, instead of benzenesulfonylchloride, an equimolar amount of p-toluene-sulfonylchloride, 2,4-xylenesulfonylchloride, m-chlorophenylsulfonylchloride, pentachlorophenylsulfonylchloride, o-bromophenylsulfonylchloride or similar compound were used, the corresponding bis substituted-phenyl sulfonyl derivate of hydrazodicarboxylic acid-dihydrazide would result rather than the bis benzene sulfonyl derivative of Example 6. Sulfonyl bromides are also usable to make these derivatives. Compounds closely related to the above compound of the invention of Example 6, which related compounds are also biological toxicants, especially nematocides are compounds of the following formula:



wherein Y is a halogen atom, preferably chlorine, or a methyl group, and n is an integer from 0 to 5 inclusive. Y, if there is more than one Y on a phenyl radical, can be a mixture of halogens and methyl groups.

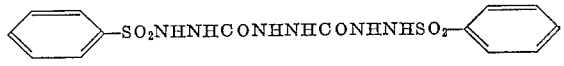
What is claimed is:

1. A compound of the formula



wherein Y is selected from the class consisting of halogen atoms and the methyl radical, and n is an integer from 0 to 5, inclusive.

2.



3. A compound of the formula

$$R(R')C{=}NNHCONHNHCONHN{=}C(R')R$$

wherein R is alkyl having not more than 8 carbon atoms and R′ is selected from the class consisting of hydrogen atoms and the methyl radical.

4. $(CH_3)_2C{=}NNHCONHNHCONHN{=}C(CH_3)_2$.

5.

$$(CH_3)_2CHCH{=}NNHCONHNHCONHN{=}CHCH(CH_3)_2$$

References Cited in the file of this patent

Stolle: Chem. Berichte, volume 43 (1910), pages 2468–70.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,171,857

March 2, 1965

Erhard P. Benzing

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 33, beginning with "3. A compound of" strike out all to and including "=CHCH$(CH_3)_2$", in line 43, same column 4; in the heading to the printed specification, line 8, for "5 Claims." read -- 2 Claims. --.

Signed and sealed this 24th day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

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