Patented May 22, 1945 2,376,380

UNITED STATES PATENT OFFICE

2,376,380

PREPARATION OF AMINO PYRAZOLONES

Henry D. Porter and Arnold Weissberger, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application November 5, 1942, Serial No. 464,650

7 Claims. (Cl. 260—305)

This invention relates to the preparation of amino pyrazolones.

The preparation of 1-phenyl-3-hydroxy-5-pyrazolone imide is described by Conrad & Zart in Berichte, vol. 39 (1906), page 2287. The reaction involves the use of phenyl hydrazine and ethyl cyanoacetate in the presence of sodium ethylate. These intermediates are heated for 20 hours at 120–130° C. according to the Conrad & Zart method.

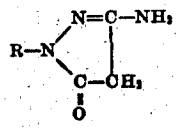
We have found that the Conrad & Zart method does not give 1-phenyl-3-hydroxy-5-pyrazolone imide, but produces 1-phenyl-3-amino-5-pyrazolone (J. Am. Chem. Soc., vol. 64, page 2133 (1942)). This compound, and its derivatives, are valuable couplers for use in the color-forming process of color photography.

It is frequently desirable to prepare amino pyrazolones from hydrazines bearing substituents which will not withstand the long and drastic heat treatment demanded by the Conrad & Zart method, for example, p-nitrophenylhydrazine. Amino pyrazolones formed from p-nitrophenylhydrazine are valuable couplers for color photography and the lack of suitability of the Conrad & Zart method for their preparation necessitated a search for other methods.

It is, therefore, an object of the present invention to provide a new method for the preparation of aminopyrazolones. A further object is to provide a less drastic treatment of aryl hydrazines than that of Conrad & Zart in the preparation of amino pyrazolones. Other objects will appear from the following description of our invention.

These objects are accomplished by condensing the appropriate phenyl hydrazine with ethyl (β-ethoxy-β-imino) propionate.

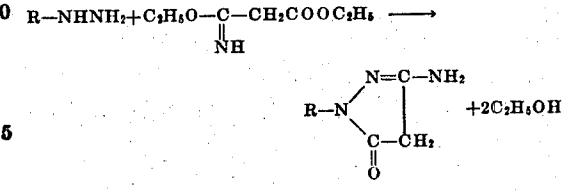
The compounds which we produce with our new method are not all new, but the novelty resides in the provision of an easy method for preparing them. These compounds have the following probable formula:



where R=aryl, alkyl, or a heterocyclic group.

With heterocyclic hydrazines, e. g., 2-benzothiazolyl hydrazine, 2-pyridyl hydrazine and 2-quinolyl hydrazine and cyanacetic ester, the 3-hydroxy-5-pyrazolone imides are obtained while the new method gives the 3-amino-5-pyrazolones, e. g. the 1-(2-benzothiazolyl)-3-amino-5-pyrazolone, a new and hitherto inaccessible compound. In this case the β-(β'-(2-benzothiazolyl) hydrazino)-β-imino-propionic ester is obtained as an intermediate which on treatment with alkali gives the pyrazolone derivative.

The general reaction employed according to our invention is represented as follows, where R—NHNH₂ is an aryl hydrazine:

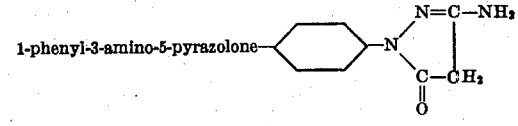


Ethyl (β-ethoxy-β-imino) propionate is described in the literature as the imino ethyl ether of ethyl cyanoacetate (Berichte, vol. 28, page 478, 1895). Our new synthesis is carried out by merely heating the two reactants on the steam both with or without a solvent.

Our method may be used with hydrazine itself, aryl hydrazines such as phenyl hydrazine, tolyl hydrazine, phenoxyphenyl hydrazine, nitrophenyl hydrazine, naphthyl hydrazine, and others, as well as with alkyl hydrazines, such as methyl and ethyl hydrazine, and heterocyclic-substituted hydrazines.

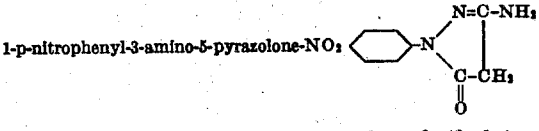
Our invention will now be described by reference to the following specific examples:

Example 1



A mixture of 10 grams (.063 mole) of ethyl (β-ethoxy-β-imino) propionate and 6.8 grams (.063 mole) of phenyl hydrazine was heated on the steam bath for three hours. The resulting mush was slurried with 20 cc. of methyl alcohol, cooled and filtered. The yield was 5.5 grams (50%), M. P. 215–216° C.

Example 2

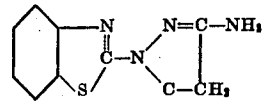


A mixture of 50 grams (.315 mole) of ethyl (β-ethoxy-β-imino) propionate and 48 grams (.315

mole) of p-nitrophenylhydrazine was heated together in 50 cc. of pyridine on the steam bath for two hours. Then 50 cc. of methyl alcohol was added and the mixture cooled, filtered, and washed with methyl alcohol. The yield was 25 grams (36%) M. P. 248–250° C.

Example 3

1(2'-benzothiazolyl)-3-amino-5-pyrazolone



(*a*) Ethyl-β[β'(2 - benzothiazolyl) hydrazino]-β-imino-propionate.

A mixture of 15.9 grams (0.1 mole) of the imino ethyl ether of ethyl cyanoacetate and 16.5 grams (0.1 mole) of 2-benzothiazolylhydrazine in 75 cc. of pyridine was heated on the steam bath for one hour. About 50 cc. of ethyl alcohol was then added and the precipitate filtered off. Further precipitation occurred on adding water to the filtrate. A yield of 21.3 grams (76%) was obtained, M. P. 179–181° C.

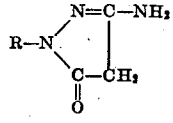
(*b*) A solution of sodium ethylate was prepared from 4.6 grams (0.2 mole) of sodium and 100 cc. of ethyl alcohol. To this was added 27.8 grams (0.1 mole) of ethyl-β[β'(2-benzothiazolyl) hydrazino]-β-iminopropionate. This mixture was refluxed for one hour after which water was added to form a clear solution. Upon making acid, a heavy precipitate formed. A yield of 22.3 grams (96%) was obtained, M. P. 252–4° C.

The compounds produced by our method may be acylated in the usual way to produce acyl derivatives useful in color photography. Treatment of the aryl amino pyrazolone with acetyl chloride or benzoyl chloride produces a monoacetyl or monobenzoyl derivative soluble in alkali which functions as a coupler.

We claim:

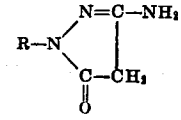
1. The method of producing a pyrazolone derivative, which comprises condensing a hydrazine selected from the class consisting of alkyl hydrazines, aryl hydrazines, and heterocyclic hydrazines, with ethyl (β-ethoxy-β-imino) propionate.

2. The method of producing a pyrazolone derivative of the following probable composition:



where R is selected from the class consisting of alkyl groups, aryl groups, and heterocyclic groups, which comprises condensing a hydrazine selected from the class consisting of alkyl hydrazines, aryl hydrazines, and heterocyclic hydrazines, with ethyl(β-ethoxy-β-imino) propionate.

3. The method of producing a pyrazolone derivative of the following probable composition:



where R is an aryl group, which comprises condensing an aryl hydrazine with ethyl(β-ethoxy-β-imino) propionate.

4. The method of producing a 1-aryl-3-amino-5-pyrazolone, which comprises condensing an aryl hydrazine with ethyl(β-ethoxy-β-imino) propionate by heating the reactants on a steam bath for two to three hours, and separating the resulting product.

5. The method of producing 1 - phenyl - 3 - amino-5-pyrazolone, which comprises condensing phenyl hydrazine with ethyl(β-ethoxy-β-imino) propionate by heating the reactants on a steam bath for two to three hours, and separating the resulting product.

6. The method of producing 1-p-nitrophenyl-3-amino-5-pyrazolone which comprises condensing p-nitrophenyl hydrazine with ethyl(β-ethoxy-β-imino) propionate by heating the reactants on a steam bath for two or three hours, and separating the resulting product.

7. The method of producing 1(2'-benzothiazolyl) - 3 - amino-5-pyrazolone which comprises condensing 2-benzothiazolyl hydrazine with ethyl(β-ethoxy-β-imino) propionate by heating the reactants on a steam bath for about one hour in the presence of pyridine, separating the product, refluxing it with sodium ethylate, acidifying the solution, and separating the resulting product.

HENRY D. PORTER.
ARNOLD WEISSBERGER.