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NONSENSITIZING TRIAZOLOPYRIMIDINE ANTIFOGGANTS FOR SILVER HALIDE EMULSIONS

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4 Claims. (Cl. 96—109)

ABSTRACT OF THE DISCLOSURE

Certain novel tetrazaindene compounds contained within silver halide photographic emulsions are shown, which compounds reduce fog formation in the emulsions but do not cause desensitization thereof.

This invention relates to new organic heterocyclic compounds, their preparation and use. In one aspect this invention is concerned with compounds which can be used in the stabilisation of photographic emulsions or films.

It is well known that light sensitive silver halide emulsions tend to yield, upon development, a deposit of silver in those areas which have not been exposed to light. This deposit, which is commonly termed "chemical fog," impairs the quality of the image and in certain cases may obliterate the image. The tendency of this fog to form is more pronounced when the emulsion is of the highly sensitive type and also when the emulsions are stored under adverse conditions, e.g. high temperatures and high humidity. In order to counteract the tendency of silver halide emulsions to form this fog it is common practice to incorporate various stabilisers into the emulsion. Most of these stabilisers are successful to a high degree in preventing fog formation, but many of them suffer from the disadvantage of reducing the sensitivity of the emulsion and the rate of image development.

It is an object of this invention to provide a new class of heterocyclic chemical compounds suitable for use as stabilisers for silver halide emulsions.

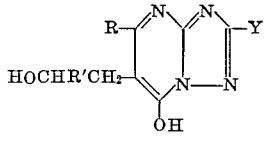
Another object of this invention is to provide stabilised light sensitive emulsions.

A further object of this invention is to provide stabilised silver halide emulsions in which the sensitivity is not significantly reduced by the presence of the stabiliser.

Yet another object of this invention is to provide a method for producing compounds suitable for use as photographic sensitizers.

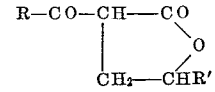
Other objects and advantages will become apparent from the following description of the invention.

The heterocyclic compounds in accordance with this invention are tetraazaindenes of the formula

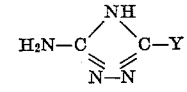


wherein R and R' each independently represent a hydrogen atom, an alkyl group, an aryl group or an aralkyl group, and Y represents a hydrogen atom, alkyl, alkylthio, aryl or amino group. Preferably R and R' each independently represent a hydrogen atom or an alkyl group, and Y preferably represents a hydrogen atom, alkyl group or alkylthio group.

The heterocyclic compounds of this invention are obtainable by the reaction of an alpha-acyl-gamma-lactone of the general formula



and a 3-amino-1,2,4-triazole of the general formula



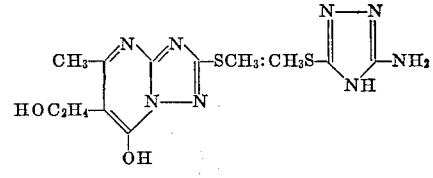
in which R, R' and Y are as defined above. The reaction may be effected under neutral conditions by simply heating the two reactants together at a temperature from about 60° C. to about 160° C., preferably at a temperature of about 100° C. without any added catalyst or diluent. Alternatively the reaction may be effected in the presence of a tertiary organic base at a temperature from about 60° C. to about 150° C., preferably from about 90° C. to 100° C. It is generally desirable that the temperature employed should not exceed the boiling point of the tertiary organic base used. Examples of tertiary organic bases which may be used in the reaction are pyridine and tertiary aliphatic amines, such as triethylamine.

The following examples are presented to illustrate the invention.

Example 1

A mixture of alpha-aceto-gamma-butyrolactone (12.8 g.), 3-amino-5-methylthio-1,2,4-triazole (13.0 g.) and pyridine (5 ml.) was heated on a steam bath for 4 hours. Initially the solid dissolved slowly to give a viscous solution and then as heating continued a solid crystallised out. Water was evolved during the reaction. When the reaction was completed the product was extracted with ether in a Soxhlet Extractor and the residue was recrystallised from a 50% ethanol 50% water mixture (200 ml.) to give colourless needles, M.P. 236 to 238° C. I.R. peaks (cm.$^{-1}$): 1680, 1650, 1580, 1490, 1390, 1280, 1245. U.V. peaks (mμ): 232 (strong), 292 (weak).

Analysis.—$C_{12}H_{18}N_8S_2O_2$ requires: C, 38.9; H, 4.9; N, 30.3; S, 17.3. Found: C, 38.9; H, 5.0; N, 30.4; S, 16.9.

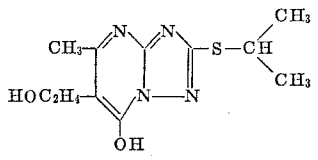


The reaction of this example was repeated without using the pyridine catalyst, the reaction mixture being heated on the steam bath for 16 hours. The product was extracted and recrystallised in a similar manner and a product having identical properties was obtained.

Example 2

A mixture of alpha-aceto-gamma-butyrolactone (12.8 g.), 3-amino-5-isopropylthio-1,2,4-triazole (15.8 g.) and pyridine (5 ml.) was heated on a steam bath for 10 hours. At the end of this period the reaction mixture had set solid. The product was recrystallised from a 20% ethanol 80% water mixture as colourless prisms. M.P. 203 to 205° C. Yield 16.7 g. I.R. peaks (cm.$^{-1}$): 1660, 1640, 1260, 1220, 1040. U.V. peaks (mμ): 245 (strong), 290 (shoulder).

Analysis.—$C_{11}H_{16}N_4O_2S$ requires: C, 49.4; H, 6.0; N, 20.7; S, 12.0. Found: C, 49.4; H, 6.1; N, 20.7; S. 12.2.

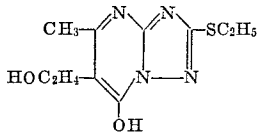


The same product was prepared when the reaction of this example was repeated without using the pyridine catalyst.

Example 3

A mixture of 3-amino-5-ethylthio-1,2,4-triazole (14.4 g.), alpha-aceto-gamma-butyrolactone (12.8 g.) and pyridine (10 ml.) was heated on a steam bath for 7 hours. The mixture became liquid and then crystallised as the reaction proceeded. After cooling the solid mass was broken up and recrystallised from a 20% ethanol 80% water mixture as colourless needles. M.P. 244 to 246° C. Yield 8.9 g. I.R. peaks (cm.$^{-1}$): 1680, 1640, 1580, 1235, 1045. U.V. peaks (mμ): 244 (strong), 278 (weak).

Analysis.—$C_{10}H_{14}N_4O_2S$ requires: C, 47.2; H, 5.5; N, 22.1; S, 12.6. Found: C, 47.4; H, 5.8; N, 22.2; S, 12.5.

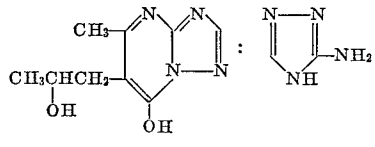


The same product was prepared when the reaction of this example was repeated without using the pyridine catalyst.

Example 4

A mixture of alpha-aceto-gamma-valerolactone (14.2 g.), 3-amino-1,2,4-triazole (8.4 g.) and pyridine (5 ml.) was heated on a steam bath for 16 hours. At the end of this period the reaction mixture had become solid. The solid product was broken up and recrystallised from a 50% ethanol 50% water mixture as colourless needles. M.P. 175 to 178° C. The same compound could have been prepared in the manner given above but without employing the pyridine catalyst. I.R. peaks (cm.$^{-1}$): 1670, 1650, 1560, 1200, 1150, 830, 765.

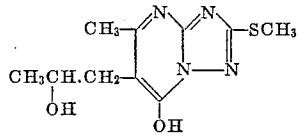
Analysis.—1:1 mixture requires: C, 45.2; H, 5.5; N, 38.4. Found: C, 45.3; H, 5.8; N, 38.7.



Example 5

A mixture of alpha-aceto-gamma-valerolactone (14.2 g.), 3-amino-5-methlythio-1,2,4-triazole (13.0 g.) and pyridine (5 ml.) was heated on a steam bath for 6 hours. Initially the solid slowly dissolved so as to give a viscous solution and then crystallised as heating continued. Water was evolved during the reaction. When the reaction was completed the product was recrystallised from 1:1 mixture of ethanol and water as colourless needles. M.P. 234 to 237° C. I.R. peaks (cm.$^{-1}$): 1640, 1590, 1280, 1260, 760.

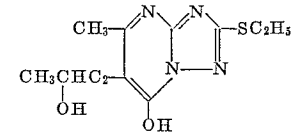
Analysis.—$C_{10}H_{14}N_4O_2S$ requires: C, 47.3; H, 5.5; N, 22.0; S, 12.6. Found: C, 47.5; H, 5.9; N, 22.3; S, 13.1.



Example 6

A mixture of alpha-aceto-gamma-valerolactone (14.2 g.), 3-amino-5-ethylthio-1,2,4-triazole (14.4 g.) and pyridine (5 ml.) was heated on a steam bath for 16 hours. At the end of this period the reaction mixture had set solid. The product was recrystallised from a 1:1 mixture of ethanol and water as colourless needles. M.P. 157 to 159° C. The same compound was prepared when the reaction of this example was repeated without using the pyridine catalyst. I.R. peaks (cm.$^{-1}$): 1640, 1580, 1380, 1330, 930, 760.

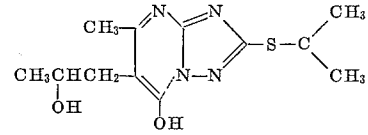
Analysis.—$C_{11}H_{16}N_4O_2S$ requires: C, 49.3; H, 6.0; N, 20.9; S, 11.9. Found: C, 49.6; H, 6.0; N, 21.6; S, 11.4.



Example 7

A mixture of alpha-aceto-gamma-valerolactone (14.2 g.), 3-amino-5-isopropylthio-1,2,4-triazole (15.8 g.) and pyridine (5 ml.) was heated on a steam bath for 16 hours. At the end of this period the reaction mixture had set solid. The product was recrystallised from a 1:1 mixture of ethanol and water as colourless needles. M.P. 214 to 216° C. The same compound was prepared when the reaction of this example was repeated without using the pyridine catalyst. I.R. peaks (cm.$^{-1}$): 1670, 1590, 1380, 1330, 765.

Analysis.—$C_{12}H_{18}N_4O_2S$ requires: C, 51.1; H, 6.4; N, 19.9; S, 11.4. Found: C, 51.0; H, 6.7; N, 20.5; S, 11.4.



Example 8

3-amino-5-ethylthio-1,2,4-triazole (14.4 g.), alpha-formyl-gamma-butyrolactone (11.4 g.) and pyridine (5 ml.) were heated on a steam bath for 4 hours. The reaction mixture first of all melted and then set solid. The solid was recrystallised from ethanol as colourless needles. M.P. 162 to 165° C.

Example 9

3-amino-5-ethylthio-1,2,4-triazole (14.4 g.), alpha-phenylaceto-gamma-butyrolactone (20.4 g.) and pyridine (5 ml.) were heated to a temperature of 120° C. for 3 hours. The mixture melted but did not solidify. The gum so produced was dissolved in hot ethanol and the product crystallised. The product was then recrystallised from ethanol as colourless needles. M.P. 258 to 262° C.

Example 10

3-amino-5-methyl-1,2,4-triazole (9.8 g.), alpha-aceto-gamma-butyrolactone (12.8 g.) and pyridine (5 ml.) were heated on a steam bath for 4 hours. The mixture first melted and then solidified. The solid so produced was recrystallised from ethanol as colourless needles. M.P. 267 to 269° C.

Example 11

A mixture of 3-amino-5-ethylthio-1,2,4-triazole (14.4 g.), alpha - acetyl-gamma-phenyl-gamma-butyrolactone (18.8 g.) and pyridine (5 ml.) were heated to a temperature of 120° C. for 8 hours. The mixture melted and then set to a gum. This gum on crystallisation from ethanol gave a white solid. M.P. >360° C.

The heterocyclic compounds of the invention although very effective in preventing the formation of fog, do not cause any decrease in the sensitivity of the emulsions, and

indeed, in some cases they may even increase the sensitivity. It is found that particularly good results are obtained when the substituents represented by R, R' and Y in the formulae given above contain not more than 4 carbon atoms.

Best results have been obtained with emulsions containing from 5 mg. to 2.0 g. per gram mole of silver present in the emulsion. The stabilising compounds will normally be added at the completion of chemical ripening or digestion of the emulsion, although it may sometimes be possible for the addition to take place at an earlier stage in the praparation of the emulsion. At whatever stage is chosen the solids may be introduced by themselves or as solutions in inert solvents such as water or ethanol.

The compounds need not necessarily be directly added to the silver halide emulsions in order to give protection to the emulsions against the formation of fog. The compounds have been found effectively to stabilise a layer of silver halide emulsion if that layer is in contact with a layer containing one of the heterocyclic compounds, so that at some time during the manufacture of the photographic film the stabiliser can diffuse into the adjacent emulsion layer. This method of effecting stabilisation may be particularly advantageous for photographic films, such as, colour films, which contain a number of layers of silver halide emulsions.

The following examples illustrate the stabilising effect on a photographic film of heterocyclic compounds of the invention.

Example 12

To a silver chlorobromide photographic emulsion which had been ripened to about 0.2 micron average grain diameter, washed and digested in the presence of sodium thiosulphate until it reached its maximum speed was added 1.25 millimoles of the heterocyclic compound obtained in Example 1 per mole of silver present in the emulsion. The resulting admixture was coated onto a film base and dried.

A sample (sample A) of the coated film was kept for seven days under normal conditions of temperature and humidity, whilst a further sample (sample B) was left for the same period in an incubator at a temperature of 125° F. and a relative humidity of 65% (i.e. under accelerating aging conditions which approximate to a comparatively long shelf life under normal conditions and a somewhat shorter shelf life under tropical conditions). The film was subsequently exposed to light and developed in a standard metol hydroquinone borax developer. The fog which had formed was then measured in each case by determining the density, and also the relative film speeds were measured.

For comparison purposes a photographic film base was coated with an identically prepared emulsion but containing no stabilising compound. Two samples (samples A' and B') of this coated film were subjected to identical conditions of temperature and humidity, and exposed and developed in an identical manner, as the samples A and B, respectively, and the fog formed and their relative speeds were determined.

The results obtained from these experiments are tabulated below in Table I.

TABLE I

Test	Sample A	Sample A'	Sample B	Sample B'
Fog	0.13	0.12	0.27	1.54
Relative log speed	2.33	2.19	2.49	(1)

[1] Too fogged to measure.

From these values it will be observed that the unstabilised emulsion subjected to a period of high temperature and humidity conditions (sample B') was so fogged that its speed could not be measured. The emulsion sample B containing the compound of Example 1 on the other hand had increased fog, but this increase was very much smaller than for sample B' and was in no way detrimental to the commercial use of the film.

It will also be observed that the speeds of the samples containing the stabiliser (samples A and B) were greater than the speed of the unstabilised sample A'.

Example 13

The experiments described in Example 12 were repeated with a photographic film base coated with an emulsion prepared in the same manner as described in Example 12 but containing as the stabilising compound 0.385 millimoles of the compound obtained as described in Example 2, per mole of silver in the emulsion.

The results obtained from the experiments are tabulated below in Table 2. For ease of comparison the results obtained with the unstabilised emulsion coatings are repeated in the table.

TABLE 2

Test	Sample A	Sample A'	Sample B	Sample B'
Fog	0.12	10.12	0.29	1.54
Relative log speed	2.35	2.19	2.49	(1)

[1] Too fogged to measure.

It will be observed that the results obtained correspond to those obtained in Example 12 and confirm the effectiveness of the compounds of the invention is stabilising photographic silver halide emulsions.

Example 14

The experiments described in the preceding Examples 12 and 13 were repeated on

(a) a photographic film base coated with an emulsion containing 1.285 millimoles of the compound obtained in Example 3 per mole of silver in the emulsion;
(b) a photographic film base coated with an emulsion containing 1.285 millimoles of the compopnd obtained in Example 3 per mole of silver in the emulsion; and
(c) a photographic film base coated with an emulsion containing no stabiliser.

In each case the method of preparation of the emulsions and their subsequent treatment was identical to that described in Example 12.

The results obtained of measurement of the density for each sample are tabulated below in Table 3, in which columns A and B give the results for the emulsion samples subjected to normal conditions and high temperature/high humidity conditions, respectively.

TABLE 3

Stabiliser	Fog	
	A	B
None	0.10	>2.0
Compound of Example 3: 0.513 millimoles per mole of Ag	0.14	0.42
Compound of Example 3: 1.285 millimoles per mole of Ag	0.20	0.29

It will be observed that the results obtained correspond to those obtained in Example 12 and confirm the effectiveness of the heterocyclic compounds of the invention in stabilising photographic silver halide emulsions.

Example 15

To a sulphur and gold sensitized silver iodobromide photographic emulsion which had been ripened to about 1.4 micron average grain diameter, washed and digested in the presence of sodium thiosulphate until it reached its maximum speed was added 1.25 millimoles of the heterocyclic compound obtained in Example 1 per mole of silver present in the emulsion. The resulting admixture was coated on to a film base and dried.

One sample (sample A) of the coated film was kept for seven days under normal conditions of temperature and humidity, whilst a further sample (sample B) was left for the same period in an incubator at a temperature of

125° F. and a relative humidity of 65% (i.e. under accelerating aging conditions which approximate to a comparatively long shelf life under normal conditions and a somewhat shorter shelf life under tropical conditions). The film was subsequently exposed to light and developed in a standard metal hydroquinone carbonate developer. The fog which had formed was then measured in each case by determining the density, and also the relative film speeds were measured.

For comparison purposes a photographic film base was coated with an identically prepared emulsion but containing no stabilising compound. Two samples (samples A' and B') of this coated film were subjected to identical conditions of temperature and humidity, and exposed and developed in an identical manner, as the samples A and B, respectively, and the fog formed and their relative speeds were determined.

The results obtained from these experiments are tabulated below in Table 4.

TABLE 4

Test	Sample A	Sample A'	Sample B	Sample B'
Fog	0.27	0.28	0.2	0.8
Relative log speed	4.35	4.33	4.02	(1)

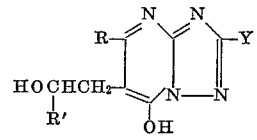
[1] Too fogged to measure.

From these values it will be observed that the unstabilised emulsion subjected to a period of high temperature and humidity conditions (sample B') was so fogged that its speed could not be measured. The emulsion, sample B, containing the compound of Example 1 on the other hand had increased fog, but this increase was very much smaller than for sample B' and was in no way detrimental to the commercial use of the film. The stabilisers of this invention are particularly useful in silver iodobromide and silver chlorobromide photographic emulsions.

Various other modifications and embodiments will be apparent to those skilled in the art without departing from the spirit or scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A silver halide emulsion containing as the stabiliser a compound of the formula:



in which R and R' each are selected from the group consisting of hydrogen, alkyl, aryl and aralkyl and Y is selected from the group consisting of hydrogen, alkyl, alkylthio, aryl and amino.

2. The silver halide emulsion of claim **1** in which said stabiliser compound is present in an amount from 5 mg. to 2.0 grams per gram mole of silver.

3. The silver halide emulsion of claim **2** in which the silver halide is silver chlorobromide.

4. The silver halide emulsion of claim **2** in which the silver halide is silver iodobromide.

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U.S. Cl. X.R.

96—107

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

December 24, 1968

Patent No. 3,418,130

John Stevens et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the title, "NONSENSITIZING" should read -- NON-DESENSITIZING --. Column 6, TABLE 2, third column, line 1 thereof, "10.12" should read -- 0.12 --. Column 7, line 6, "metal" should read -- metol --.

Signed and sealed this 17th day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents