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2,317,357

UNITED STATES PATENT OFFICE

2,317,357

DYE INTERMEDIATE

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No Drawing. Application August 21, 1940, Serial No. 353,502

14 Claims. (Cl. 260—283)

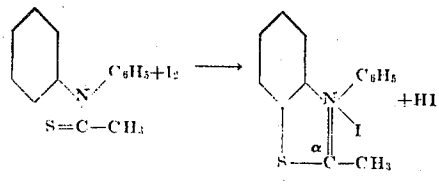
This invention relates to dye intermediates and to a process for the preparation thereof.

A class of intermediates of great value for the preparation of polymethine dyes consists of the cyclammonium alkyl quaternary salts containing a methyl group in the alpha or gamma position, i. e. in one of the so-called reactive positions. Some of these alkyl quaternary salts are, of course, more readily available than others, while the corresponding aryl quaternary salts are almost wholly unavailable. Polynitro aryl pyridinium salts have been prepared by condensing polynitro phenyl halides with pyridine, but the condensation does not take place with quinoline nor with α-picoline. Furthermore, aryl halides devoid of nitro groups will not react even with pyridine to give quaternary salts.

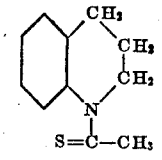
We have now found a new method for preparing cyclammonium quaternary salts containing a methyl group in the alpha position, which method is applicable to the production of both alkyl and aryl quaternary salts. Not only does our new method suffice to produce alkyl and aryl quaternary salts containing a methyl group in the alpha position, but it also suffices to produce alkyl and aryl quaternary salts containing alkyl groups in general, as well as aryl groups, in the alpha position. By means of our new method, many quaternary salts heretofore unknown are made available for the first time.

It is accordingly an object of our invention to provide a new process for preparing quaternary salts. A further object is to provide new quaternary salts. Other objects will appear hereinafter.

In accordance with our invention, we prepare cyclammonium alkyl or aryl quaternary salts containing an alkyl or an aryl group in the alpha position by oxidizing a N-alkyl-N-aryl thioamide, a N,N-diarylthioamide, N-alkyl-N-arylselenoamide, or a N,N-diarylselenoamide with an oxidizing agent which gives rise to an acid radical. The reaction can be illustrated for the benzothiazole series, using halogen as the oxidizing agent, as follows:



As thio- and selenoamides which can be employed in practicing our invention, the N,N-diphenyl-, N-methyl-N-phenyl- and N-methyl-N-naphthyl-compounds are exemplary of the simpler forms. Also a more complex form of N-alkyl-N-aryl derivative can be employed, viz. those in which the alkyl group and the aryl group are joined together as is the case in the thioamide having the following formula:



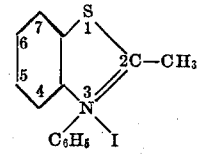
1-thioacetyl-1,2,3,4-tetralydroquinoline

In this case, the nitrogen atom carries two groups—a phenyl and a propyl, the two groups being joined together.

In practicing our invention, we have found it advantageous to employ halogens, especially bromine or iodine, as oxidizing agents. Heat accelerates the oxidation.

The following examples will serve to demonstrate the manner of practicing our invention. These examples are not intended to limit our invention.

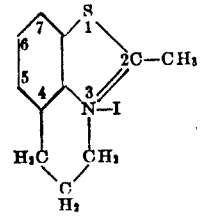
EXAMPLE 1.—*2-Methylbenzothiazole pheniodide*



A mixture of 2.3 g. (1 mol.) of thioacetyldiphenylamine (N,N-diphenylthioacetamide), 5.0 g. (2 mol.) of iodine, and 0.82 g. (1 mol.) of fused sodium acetate and 100 cc. of 90% acetic acid was refluxed gently for about 45 minutes. The hot, dark red solution was decanted from the tarry residue, and the solution was allowed to cool. The crystalline product which formed was collected on a filter, washed with water, ethyl alcohol and diethyl ether and finally allowed to dry in the air. 0.3 g. of material, melting at 128° to 130° C., were thus obtained. This material was 2-methyl-benzothiazole phenyl triiodide. To convert it to the monoiodide, the 0.3 g. of material were suspended in 15 cc. of absolute ethyl alcohol and sulfur dioxide was passed

into the suspension until the triiodide was reduced to the monoiodide. The suspension was then chilled to 0° C. and the monoiodide filtered off and dried in the air. It was obtained as white crystals melting at 135° to 140° C. This salt was probably contaminated with the triiodide.

EXAMPLE 2.—*2-methyl-3,4-trimethylene-benzothiazolium iodide*



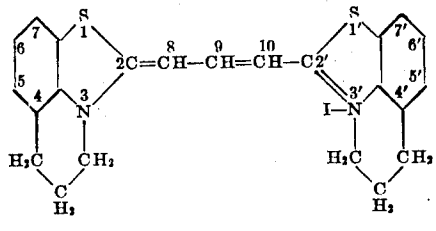
5.73 g. (1 mol.) of 1-thioacetyl-1,2,3,4-tetrahydroquinoline, 15.18 g. (2 mol.) of iodine, 2.46 g. (1 mol.) of fused sodium acetate and 4.47 g. (1 mol.) of sodium iodide dissolved in 50% aqueous acetic acid were mixed together. The mixture was boiled gently, under reflux, for one hour, while agitating the mixture frequently. At the end of this time the hot solution was decanted from the tarry residue. The hot solution was cooled. The triiodide which separated was filtered off, washed with water, ethyl alcohol and finally with diethyl ether. In this manner 7.5 g. of the triiodide were obtained. The triiodide was suspended in 75 cc. of absolute ethyl alcohol and reduced to the monoiodide by slowly bubbling sulfur dioxide through the suspension until the brownish crystals become lemon yellow in color (about one hour). The mixture was chilled to 0° C., the monoiodide filtered off, washed with acetone and dried in the air. In this manner 3.2 g. (34% yield) of the monoiodide was obtained. After three recrystallizations from absolute ethyl alcohol (35 cc. per gram of monoiodide), it was obtained as colorless needles melting at 257° to 260° C. with decomposition.

In a similar manner N-methyl-N-phenylthioacetamide, N-methyl-N-naphthylthioacetamide and N-diphenyl-selenoacetamide can be oxidized to give a quaternary salts containing a reactive methyl group in the alpha position.

The quaternary iodides in the above examples can be converted into the perchlorates by treating an alcoholic solution of the monoiodide with an aqueous solution of sodium perchlorate.

We have found that our new quaternary salts, such as the 2-methyl-3,4-trimethylene benzothiazolium quaternary salts, can be condensed with esters of orthocarboxylic acids, in the presence of pyridine, to give carbocyanine dyes of a new kind, as illustrated in the following example.

EXAMPLE 3.—*3,4; 3',4'-di(trimethylene) thiacarbocyanine iodide*



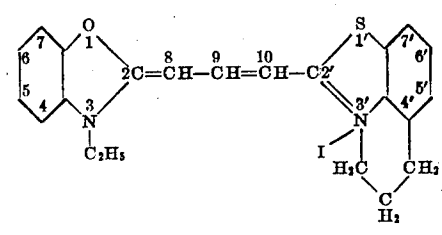
1.1 g. (2 mol.) of 2-methyl-3,4-trimethylene-benzothiazolium iodide and 0.98 g. (1 mol.+300% excess) of ethyl orthoformate were placed in 30 cc. of pyridine. The mixture was refluxed for 45 minutes. The dye separated from the hot reaction mixture. The mixture was cooled and the dye filtered off, washed well with methyl alcohol and dried in the air. In this manner, 0.75 g. (83% yield) of crude dye were obtained. It was recrystallized from methyl alcohol (710 cc. per gram of dye) and obtained, in 50% yield, as a felt of purplish crystals, melting at 308° to 309° C. with decomposition. Its methyl alcoholic solution was bluish red. It sensitized a photographic gelatino-silver-bromiodide emulsion strongly out to 680 mu, with a maximum at about 595 mu.

In a similar manner 2-methyl-3,4-trimetylene-benzothiazolium iodide was condensed with ethyl orthoacetate to give 9-methyl-3,4; 3',4'-di-(trimethylene) thiacarbocyanine iodide in a crude yield of 60%. After two recrystallizations from methyl alcohol (900 cc. per gram of dye), it was obtained, in 40% yield, as dull reddish purple crystals, melting with decomposition at 309° to 310° C. Its methyl alcoholic solution was bluish red. It sensitized a photographic gelatino-silver-bromiodide emulsion strongly out to about 640 mu, with a maximum at about 590 mu.

In a similar manner, 2-methyl-3,4-trimethyl-enebenzothiazolium iodide was condensed with ethyl orthopropionate to give 9-ethyl-3,4; 3',4'-di(trimethylene) thiacarbocyanine iodide, in a crude yield of 60%. After two recrystallizations from methyl alcohol (320 cc. per gram of dye), it was obtained, in 37% yield, as reddish green needles having a green reflex and melting with decomposition at 296° to 298° C. The methyl alcoholic solution of dye was bluish red. It sensitized a photographic gelatino-silver-bromiodide emulsion moderately strongly out to 625 mu, with a maximum at about 585 mu.

We have also found that our new quaternary salts, such as the 2-methyl-3,4-trimethylene benzothiazolium quaternary salts, can be condensed in the presence of an acid binding agent, with cyclammonium quaternary salts containing an acylated β-arylaminovinyl group in the alpha or gamma position. The following example is illustrative.

EXAMPLE 4.—*3-ethyl-3',4'-trimethylene-oxathiacarbocyanine iodide*



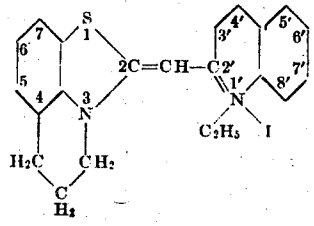
1.0 g. (1 mol.) of 2-methyl-3,4-trimethylene-benzothiazolium triiodide and 1.37 g. (1.8 mol.) of 2-(β-acetanilido-vinyl)-benzoxazole ethiodide were placed in 15 cc. of pyridine. The mixture was boiled, under reflux, for 15 minutes. The reaction mixture was cooled and the dye filtered off. The dye was washed well with methyl alcohol and dried in the air. 0.5 g. of crude dye (58% yield) was thus obtained. To reduce any dye-triiodide present to the monoiodide, the dye was dissolved in hot methyl alcohol and sulfur dioxide was slowly bubbled through the solution. The solution was cooled and the dye filtered off. The dye was thrice recrystallized from methyl alcohol and

obtained, in 12% yield, as reddish needles having a blue reflex and melting at 258° to 259° C. with decomposition. Its methyl alcoholic solution was orange. It sensitized a photographic gelatino-silver-bromiodide emulsion strongly out to 605 mu with a maximum at 550 mu.

In a similar manner, 2-methyl-3,4-trimethylenebenzothiazolium iodide can be condensed with 2-(β-acetanilido-vinyl)-benzothiazole ethiodide, 2-(β-acetanilidovinyl)-thiazoline methiodide or 4-(β-anilinovinyl)-quinoline ethiodide. The condensations can be carried out in the presence of strong organic bases, such as triethylamine, piperidine, N-methylpiperidine or triethanolamine. When using such a strong organic base, the condensations are advantageously effected in the presence of an alcohol solvent, such as ethyl alcohol.

We have also found that our new quaternary salts, such as 2-methyl-3,4-trimethylene benzothiazolium quaternary salts, can be condensed with cyclammonium quaternary salts containing an alkylmercapto or an arylmercapto group in a reactive position, in the presence of an acid-binding agent. The following example is illustrative.

EXAMPLE 5.—*1'-ethyl-3,4-trimethylene-thia-2'-cyanine iodide*

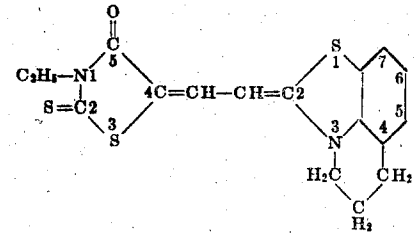


0.9 g. (1 mol.) of 2-methyl-3,4-trimethylenebenzothiazolium triiodide and 2.23 g. (3.6 mol.) of 2-phenylmercaptoquinoline ethiodide were placed in 15 cc. of pyridine. The mixture was boiled, under reflux, for 15 minutes. The resulting brownish solution was chilled to 0° C. The dye was filtered off, washed with water, acetone and then methyl alcohol, and then dried in the air. In this manner 0.5 g. (68% yield) of dye was obtained. After two recrystallizations from methyl alcohol (320 cc. per gram of dye) the dye was obtained, in 40% yield, as orange felted needles, melting at 286° to 287° C. with decomposition. A solution of the dye in methyl alcohol is yellowish brown. The dye sensitized a photographic gelatino-silver-bromiodide emulsion moderately strongly to 555 mu, with a maximum at about 510 mu.

In a similar manner 2-methyl-3,4-trimethylenebenzothiazolium quaternary salts can be condensed with 2-methyl-mercapto-benzothiazole ethiodide, 2-phenylmercaptobenzothiazole ethiodide and 4-phenylmercaptopyridine ethiodide. Instead of a weak organic base, such as pyridine, strong tertiary organic bases, such as triethylamine and N-methylpiperidine, can be used as acid-binding agents. The strong organic base can be used in connection with pyridine or with a solvent, such as ethyl alcohol.

We have also found that our new quaternary salts, such as 2-methyl-3,4- trimethylenebenzothiazolium quaternary salts, can also be condensed, in the presence of an acid-binding agent, with heterocyclic organic compounds containing an acylated arylaminomethylene group adjacent to a carbonyl group, as illustrated in the following example.

EXAMPLE 6.—*3-ethyl-5-[(3,4-trimethylene-2(3)-benzothiazolylidene)-ethylidene]-rhodanine*

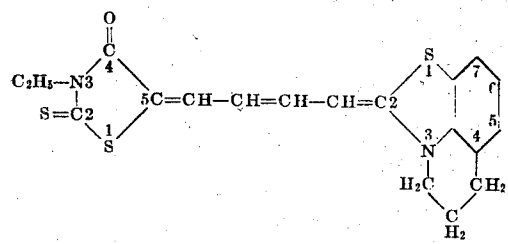


0.3 g. (1 mol.) of 5-acetanilidomethylene-3-ethylrhodanine, 0.32 g. (1 mol.) of 2-methyl-3,4-trimethylenebenzothiazolium iodide and 0.145 cc. (1.05 mol.) of triethylamine were placed in 15 cc. of absolute ethyl alcohol. The mixture was boiled, under reflux, for 20 minutes. The reaction mixture was cooled, the dye filtered off, washed with methyl alcohol and dried in the air. In this manner 0.25 g. (70% yield) of dye were obtained. The dye, after two recrystallizations from a mixture of pyridine and methyl alcohol was obtained in 42% yield, as reddish crystals melting at 288° to 289° C. with decomposition. A solution of the dye in methyl alcohol is pink. The dye sensitized a photographic gelatino-silver-bromiodide emulsion strongly out to 625 mu with a maximum at about 595 mu.

In a similar manner, 2-methyl-3,4-trimethylenebenzothiazolium iodide was condensed with 5-acetanilido - methylene - 3 -ethyl-2-thio-2,4(3,5)-oxazoledione to give 3-ethyl-5-[(3,4-trimethylene-2(3) - benzothiazolylidene) - ethylidene] - 2-thio-2,4(3,5)-oxazoledione, in a yield of 74%. The dye, after two recrystallizations from a pyridine methyl alcohol mixture was obtained as reddish crystals, melting at 287° to 288° C. A solution of the dye in methyl alcohol was orange. The dye sensitized a photographic gelatino-silver-bromiodide emulsion strongly out to 630 mu, with a maximum at about 570 mu.

Our new quaternary salts, such as 2-methyl-3,4-trimethylenebenzothiazolium quaternary salts, can also be condensed, in the presence of an acid-binding agent, with heterocyclic organic compounds containing an acylated arylaminoallylidene group adjacent to a carbonyl group, as illustrated in the following example.

EXAMPLE 7.—*3-ethyl - 5-[(3,4-trimethylene-2(3)-benzothiazolylidene) butenylidene]rhodanine*

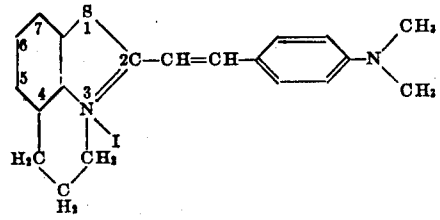


0.4 g. (1 mol.) of 5-(γ-acetanilido-allylidene)-3-ethylrhodanine, 0.76 g. (2 mol.) of 2-methyl-3,4-trimethylenebenzothiazolium iodide and 0.24 g. (2 mol.) of triethylamine were placed in 25 cc. of absolute ethyl alcohol. The mixture was refluxed for 20 minutes. The dye separated from the hot reaction mixture. The reaction mixture was chilled, the dye filtered off, washed well with methyl alcohol and dried in the air. 0.35 g. (73% yield) of crude dye were obtained. The dye was then boiled with 150 cc. of hot methyl alcohol, the alcoholic mixture filtered while hot, and the insoluble residue purified by recrystallization from

pyridine (75 cc. per gram of dye). The dye was thus obtained in 17% yield, as a blue gray powder, melting at 260° to 262° C. with decomposition. A solution of the dye in methyl alcohol was blue. It sensitized a photographic gelatino-silver-bromiodide emulsion strongly out to about 735 mu with a maximum at about 700 mu.

We have also found that our new quaternary salts, such as 2-methyl-3,4-trimethylenebenzothiazolium quaternary salts, can be condensed with dialkylaminobenzaldehydes to give styryl type dyes, as illustrated in the following example.

EXAMPLE 8.—*2-(p-dimethylaminostyryl)-3,4-trimethylenebenzothiazolium iodide*



1.09 g. (1 mol.) of 2-methyl-3,4-trimethylenebenzothiazolium iodide and 0.47 g. (1 mol.) of p-dimethylaminobenzaldehyde were placed in 25 cc. of absolute ethyl alcohol. 3 drops of piperidine were added to the mixture, and the resulting mixture was refluxed for 4½ hours. The dye separated from the bluish red solution. After cooling, the dye was collected on a filter, washed with methyl alcohol and dried in the air. 1.0 g. (71% yield) of dye, was obtained. After three recrystallizations from methyl alcohol (250 cc. per gram of dye), the dye was obtained, in 35% yield, as dull purplish crystals. A solution of the dye in methyl alcohol was bluish red. The dye sensitized a photographic gelatino-silver-bromiodide emulsion weakly out to about 630 mu, with an ill-defined maximum at about 590 mu.

In a similar manner p-diethylamino-benzaldehyde and other dialkylamino-benzaldehydes can be condensed with our new quaternary salts.

In the preparation of photographic emulsions containing our new dyes, it is only necessary to disperse the dyes in the emulsions. The methods of incorporating dyes in emulsions are simple and well known to those skilled in the art. It is convenient to add the dyes from solutions in appropriate solvents. Methanol has proven satisfactory as a solvent for our new dyes. Ethyl alcohol or acetone may also be employed where the solubility of the dyes in methanol is lower than desired.

Sensitization by means of our new dyes is, of course, directed primarily to the ordinarily employed gelatino-silver-halide developing-out emulsions. The dyes are advantageously incorporated in the washed, finished emulsions and should, of course, be uniformly distributed throughout the emulsions.

The concentration of our new dyes in the emulsion can vary widely, i. e. from about 5 to about 100 mgs. per liter of flowable emulsion. The concentration of the dye will vary according to the type of light-sensitive material in the emulsion and according to the effects desired. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art upon making the ordinary tests and observations customarily used in the art of emulsion making.

To prepare a gelatino-silver-halide emulsion sensitized with one of our new dyes, the following procedure is satisfactory: A quantity of the dye is dissolved in methyl alcohol or other suitable solvent and a volume of this solution (which may be diluted with water) containing from 5 to 100 mgs. of dye is slowly added to about 1000 cc. of a gelatino-silver-halide emulsion, with stirring. Stirring is continued until the dye is uniformly distributed throughout the emulsion. With most of our new dyes, 10 to 20 mgs. of dye per liter of emulsion suffices to produce the maximum sensitizing effect with the ordinary gelatino-silver-bromide (including bromiodide) emulsions. With fine-grain emulsions, which includes most of the ordinarily employed gelatino-silver chloride emulsions, somewhat larger concentrations of dye may be necessary to secure the optimum sensitizing effect.

The above statements are only illustrative and are not to be understood as limiting our invention in any sense, as it will be apparent that our new dyes can be incorporated by other methods in many of the photographic silver halide emulsions customarily employed in the art. For instance, the dyes may be incorporated by bathing a plate or film upon which an emulsion has been coated, in the solution of the dye, in an appropriate solvent. Bathing methods, however, are not to be preferred ordinarily.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen, a compound selected from the group consisting of N-alkyl-N-arylthioamides, N,N-diarylthioamides, N-alkyl-N-arylselenoamides and N,N-diarylselenoamides in which the aryl groups contain a hydrogen atom attached to the aryl nucleus in at least one of the positions ortho to the amide nitrogen atom.

2. A process for preparing a cyclammonium quaternary salt compriisng oxidizing, with a halogen selected from the group consisting of bromine and iodine, a compound selected from the group consisting of N-alkyl-N-arylthioamides, N,N-diarylthioamides, N-alkyl-N-arylselenoamides and N,N-diarylselenoamides in which the aryl groups contain a hydrogen atom attached to the aryl nucleus in at least one of the positions ortho to the amide nitrogen atom.

3. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen, a N-alkyl-N-phenylthioamide in which the phenyl group cotnains a hydrogen atom attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

4. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen selected from the group consisting of bromine and iodine, a N-alkyl-N-phenylthioamide in which the phenyl group contains a hydrogen atom attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

5. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen, a N,N-diphenylthioamide in which the phenyl groups contain a hydrogen atom attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

6. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen selected from the group consisting of bromine and iodine, a N,N-diphenylthioamide in which the phenyl groups contain a hydrogen atom

attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

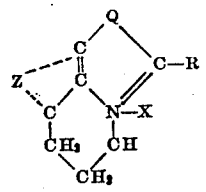
7. A process for preparing a cyclammonium quaternary salt comprising oxidizing, in the presence of a halogen, a N-alkyl-N-phenylthioacetamide in which the phenyl group contains a hydrogen atom attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

8. A process for preparing a cyclammonium quaternary salt comprising oxidizing, in the presence of a halogen selected from the group consisting of bromine and iodine, a N-alkyl-N-phenylthioacetamide in which the phenyl group contains a hydrogen atom attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

9. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen, a N,N-diphenylthioacetamide in which the phenyl groups contain a hydrogen atom attached to the phenyl nucleus in at least one of the positons ortho to the amide nitrogen atom.

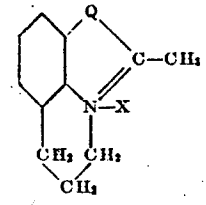
10. A process for preparing a cyclammonium quaternary salt comprising oxidizing, with a halogen selected from the group consisting of bromine and iodine, a N,N-diphenylthioacetamide in which the phenyl groups contain a hydrogen atom attached to the phenyl nucleus in at least one of the positions ortho to the amide nitrogen atom.

11. A cyclammonium quaternary salt of the following general formula:



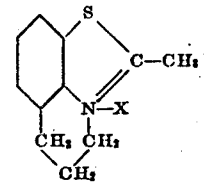
wherein Q represents an atom selected from the group consisting of sulfur and selenium, R represents an organic group selected from the group consisting of alkyl and aryl groups, X represents an acid radical, and Z represents the non-metallicatoms necessary to complete a benzene nucleus.

12. A cyclammonium quaternary salt of the following general formula:



wherein Q represents an atom selected from the group consisting of sulfur and selenium and X represents an acid radical.

13. A cyclammonium quaternary salt of the following general formula:



wherein X represents an acid radical.

14. 2 - methyl - 3,4 - trimethylene - benzothiazolium iodide.

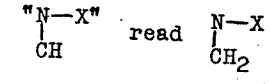
LESLIE G. S. BROOKER.
HOMER W. J. CRESSMAN.

CERTIFICATE OF CORRECTION.

Patent No. 2,317,357. April 27, 1943.

LESLIE G. S. BROOKER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 17, for "tetralydroquinoline" read --tetrahydroquinoline--; page 2, second column, line 16, for "trimetylene" read --trimethylene--; page 4, second column, line 42, for "compriisng" read --comprising--; line 54, for "cotnains" read --contains--; page 5, first column, line 37, for that portion of the formula reading



and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of July, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

Disclaimer

2,317,357.—*Leslie G. S. Brooker* and *Homer W. J. Cressman*, Rochester, N. Y. DYE INTERMEDIATE. Patent dated Apr. 27, 1943. Disclaimer filed Jan. 17 1948, by the assignee, *Eastman Kodak Company*.

Hereby enters this disclaimer to claims 5 and 9 of said patent.

[*Official Gazette February 24, 1948.*]