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# UNITED STATES PATENT OFFICE

2,307,049

## PROCESS OF PRODUCING AZA-METHINE DYES

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9 Claims. (Cl. 260—240)

This invention relates to the production of dyestuffs.

It is an object of this invention to produce compounds comprising two heterocyclic nitrogen nuclei linked by a chain of atoms including one or more nitrogen atoms. According to the present invention a process for the production of compounds of the above type comprises condensing a quaternary salt of a heterocyclic nitrogen compound containing a reactive thioether or selenoether group in the $\alpha$ or $\gamma$ position to the nitrogen atom with ammonia or an amidine or the salt of one of these compounds.

The heterocyclic nitrogen compound whose quaternary salt is to be employed may consist of any one of the well-known heterocyclic nitrogen compounds such as substituted and unsubstituted thiazoles, thiazolines, oxazoles, oxazolines, selenazoles, selenazolines, pyridines, quinolines, indolenines, diazines e. g. pyrimidines, thiodiazoles and quinazolines, and the corresponding polycyclic compounds such as benzthiazoles, naphthathiazole and anthrathiazole. The compound employed may be the quaternary salt of the thioether or selenoether derivative of the heterocyclic nitrogen compound, or it may be the salt obtained from the corresponding thione or selenone.

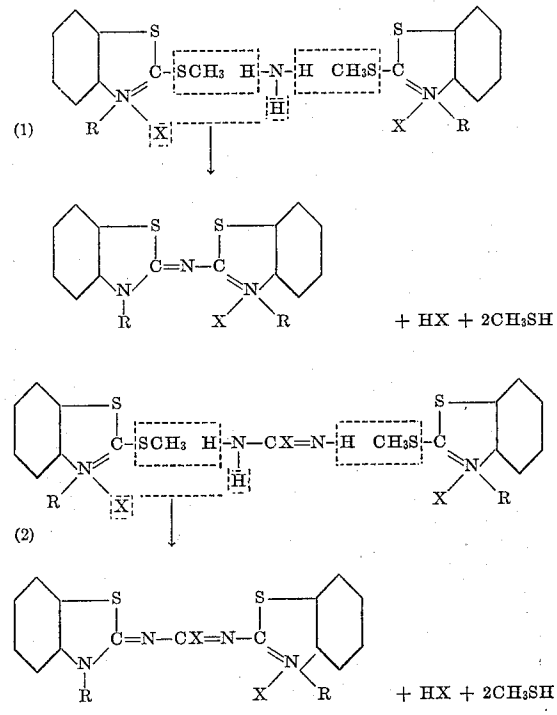
Whilst ammonia and the amidine may be employed as such, generally it is found more convenient to employ salts of these compounds, such as ammonium nitrate and acetamidine hydrochloride and to carry out the reaction in the presence of an acid binding agent; thus the reaction may be carried out in the presence of a solvent such as pyridine which also acts as an acid binding agent, or a neutral solvent such as alcohol may be employed togethehr with a strong acid binding agent such as sodium ethoxide.

Further specific examples of the nitrogen compounds which may be employed are amidines such as formamidine, acetamidine, benzamidine, guanidine, urea, thiourea and O-alkyl pseudo ureas and S-alkyl pseudo thioureas.

The ammonia and amidine compounds which may be employed in accordance with the present invention may be expressed by one of the following general formulae:

$NH_2$—H, or $NH_2$—CX=NH

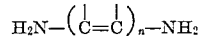
in which X represents any monovalent substituent, such as hydrogen, an alkyl, aryl, or aralkyl group or a hydroxy, alkoxy, thiol, thioether, amino or substituted amino group. It will be observed that these compounds have replaceable hydrogen atoms attached to each of the nitrogen atoms, and when they are condensed with the heterocyclic nitrogen compounds, the replaceable hydrogen atoms react with the reactive groups of the heterocyclic nitrogen compound leaving the nitrogenous residue as the link between the heterocyclic nitrogen nuclei; thus it is believed that the reaction of the present invention may be illustrated by the following equations:




In the case of those amidines which readily break up to give ammonia, it is believed that the reaction may follow the mechanism of the first equation to give a compound in which the linking chain consists only of a single nitrogen atom.

According to a modification of the process of the present invention, dyestuffs are obtained by condensing a quaternary salt of a heterocylic nitrogen compound having a reactive thio-ether or seleno-ether group or a reactive amino-vinyl, acyl-amino-vinyl, aryl-amino-vinyl, or acyl-aryl-amino-vinyl grouping in the $\alpha$ or $\gamma$ position to a nitrogen atom with an organic compound containing two amino groups linked by a single bond or by a conjugate chain of carbon atoms some or all of which form part of one or more aro-

matic carbo-cyclic rings, and which may be represented by the general formula

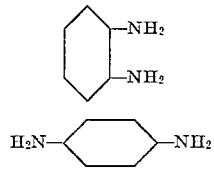


where $n$ is 0 or a positive integer, or salts of such compounds.

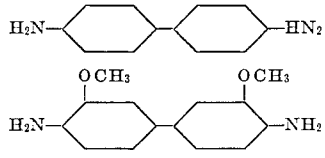
Examples of such compounds are:

hydrazine $H_2N—NH_2$

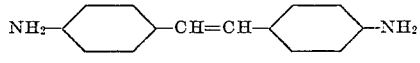
the *o* and *p* arylene diamines such as *o* and *p* phenylenediamines.



benzidine and its homologues such as dianisidine



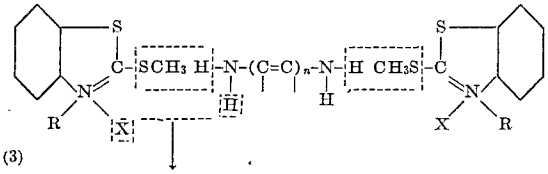
diamino-stilbenes such as 2:2'-, 2:4'-, and 4:4'-diamino-stilbenes, e. g.



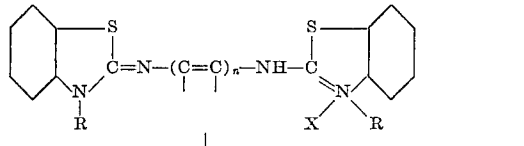
The reaction may be carried out in the presence of a solvent with or without an acid binding agent. When an acid binding agent is required, e. g. when using salts of these compounds, the reaction may be carried out in a neutral solvent such as alcohol together with an acid binding agent such as sodium ethoxide or sodium acetate, or it may be carried out in the presence of a basic solvent such as pyridine which acts as the acid binding agent.

The quaternary salts of the same heterocyclic nitrogen compounds may be employed in this modified process as in the process already described.

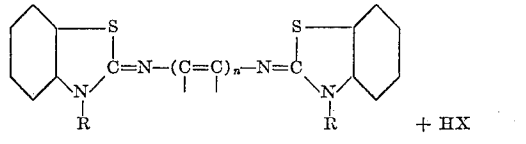
The hydrazine and other compounds are similar to ammonia and the amidines in having replaceable hydrogen atoms attached to the nitrogen atoms and it is believed that the mechanism of the reaction is similar in consequence and possibly may be illustrated by the following equations:



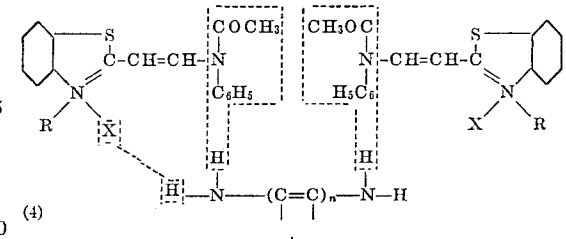
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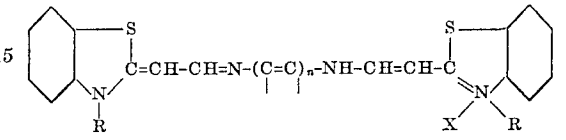
+ HX + $2CH_3SH$



+ HX

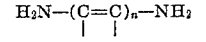


(4)



+HX+$2C_6H_5NHCOCH_3$

Many of the products of the present invention are coloured and are sensitisers for photographic silver halide emulsions. The dyestuffs obtained by the reaction of quaternary salts of heterocylic nitrogen compounds having reactive aminovinyl or substituted aminovinyl groups with organic compounds such as hydrazine which may be represented by the formula



where $n$ is 0 or a positive integer are particularly good sensitisers, and the present invention includes a photographic silver halide emulsion sensitised with such a dyestuff.

One or more of the dyestuffs may be incorporated in the photographic silver halide emulsion before it is coated on a support, or alternatively the support (e. g. a film or plate) coated with the emulsion may be bathed in a solution of one or more of the dyestuffs. The actual quantity incorporated may vary to a certain extent with the individual dyestuff and with the ultimate effect which it is desired to obtain; as an indication, however, of the order of the quantities which may be employed, 100 ccs. of a one in one thousand solution of the dyestuff may be incorporated in six and a half litres of emulsion equivalent to about 250 grams of silver nitrate, or the coated support may be bathed in a one in one thousand solution of the dyestuff; the strength of the solution may vary according to the dyestuff used and may be as low as one in ten thousand.

The process of the present invention is illustrated by the following specific examples, several of which give an indication of the sensitising action of the products.

*Example 1*

5.43 gms. of 1-methylmercapto-benzthiazole and 5.58 gms of methyl-p-toluene sulphonate were fused together for four hours at 130–140° C. 1.56 gms. of hydrazine-hydrochloride and 50 ccs. of pyridine were then added and the mixture boiled for half an hour. Crystals formed in the solution even when hot. The solution was poured into cold water, when a heavy precipitate of almost colourless crystals was formed. These were collected and washed and re-crystallised. The purified crystals melted at 257° C. The corresponding ethyl compound was formed in similar manner, using ethyl-p-toluene sulphonate in place of methyl-p-toluene sulphonate and was obtained as colourless crystals melting at 192° C.

*Example 2*

6.03 gms. of 1-ethylmercapto-quinoline, and 5.58 gms. of methyl-p-toluene sulphonate were heated together for four hours at 130–140° C. when the solid quaternary salt was formed. 1.6 gms. of hydrazine-hydrochloride and 30 ccs. of pyridine were then added and the whole maintained at a temperature just below the boiling point for about half-an-hour. The mixture was then poured into water and the red crystals which formed were filtered off, washed with water and spirit and ether and dried and re-crystallised from methyl alcohol as scarlet plates, melting at 258° C. The corresponding ethyl compound, was prepared in a similar manner but using ethyl-p-toluene sulphonate in place of methyl-p-toluene sulphonate and formed scarlet needles and rods melting at 194° C.

*Example 3*

4.95 gms. of 1-methylmercapto-benzoxazole and 5.58 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for four hours. 1.6 gms. of hydrazine-hydrochloride and 30 ccs. of pyridine were then added and the whole mixture boiled for half-an-hour. The mixture was then poured into cold water and a precipitate of fine white crystals was formed. These were collected, washed and dried and the melting point was found to be 277° C.

*Example 4*

1.78 gms. of dimethylthiolthio-($\beta\beta'$)-diazole and 1.88 gms. of methyl-p-toluene sulphonate were heated together for 3½ hours at 120–130° C. After cooling 0.6 gm. of hydrazine hydrochloride and 12 ccs. of pyridine were added and the mixture was gently warmed until solution was effected, after which it was gently boiled under a reflux condenser for half-an-hour. The mixture was then poured into 200 ccs. of water, when light coloured crystals separated out. These were collected and washed and re-crystallised from methyl alcohol to yield light yellow plates melting at 170–172° C.

*Example 5*

1.78 gms. of dimethylthiolthio-($\alpha$ $\beta'$)-diazole and 1.88 gms. of methyl-p-toluene sulphonates were heated together for 3½ hours at 120–130° C. The mixture was allowed to cool and 0.6 gm. of hydrazine hydrochloride and 12 ccs. of pyridine were then added and the whole was gently warmed until solution was effected, after which the mixture was gently boiled under a reflux condenser for half-an-hour. The mixture was then poured into 200 ccs. of water, when whitish crystals separated out. These were collected and washed and re-crystallised from benzene to yield almost colourless plates melting at 282–3° C.

*Example 6*

1.76 gms. of 4-methylthiolquinazoline and 1.86 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for four hours. 0.6 gm. of hydrazine dihydrochloride and 25 ccs. of pyridine were then added and the mixture was gently warmed until the solid was dissolved. The mixture was then gently boiled under a reflux condenser for half-an-hour after which it was poured into water and allowed to stand. The yellow solid which separated out was collected, washed and re-crystallised to give bright yellow crystals melting at over 310° C.

*Example 7*

0.87 gm. of 1-methylquinoline-4-thione and 0.98 gm. of methyl-p-toluene sulphonate were heated together at 130° C. for about 3½ hours. 0.265 gm. of hydrazine dihydrochloride and 15 ccs. of pyridine were then added and the mixture was gently boiled under a reflux condenser for about 30 minutes. The solution became deep orange in colour and solid separated out and the mixture was poured into water. The solid dissolved up in the water, but on allowing the mixture to stand small copper red crystals, melting at 160° C., separated out.

*Example 8*

7.2 gms. of 1-methylmercapto-benzthiazole and 7.5 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for about four hours. 16.16 gms. of thiourea methosulphate and 40 ccs. of pyridine were then added and the mixture warmed on a water bath and finally over a flame. A yellow dye was formed and the mixture was then poured into an aqueous solution of potassium iodide when the product separated out as a light yellow solid. This was re-crystallised from methyl alcohol giving a product melting at 256° C.

This dyestuff is a sensitizer for silver chloride emulsions and extends the sensitivity to about λ4650 Å. with a maximum at about λ4350 Å.

*Example 9*

1.81 gms. of 1-methylthiol benzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for about 3½ hours. 1.52 gms. of crushed thiourea and 30 ccs. of pyridine were then added and the mixture was gently warmed for about 30 minutes. The mixture was then poured into an aqueous solution of potassium iodide and allowed to stand when a thick, oily precipitate was formed. This was allowed to stand for a few days and was then separated from the liquors and treated with benzene when a yellow solid was formed. This was collected and washed and recrystallised from methyl alcohol to yield a bright yellow solid, melting at 245° C.

*Example 10*

1.81 gms. of 1-methylthiol-benzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at about 130–140° C. for about 3½ hours. 1.2 gms. of urea and 30 ccs. of pyridine were then added and the mixture was gently heated for about 40 minutes. The solution became light yellow in colour and was then poured into an aqueous solution of potassium iodide when a light yellow solid separated out. This was filtered off and recrystallised from methyl alcohol in the form of long lemon coloured needles melting at 293° C.

*Example 11*

7.24 gms. of 1-methylmercapto-benzthiazole and 7.50 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for about 3–3½ hours. 7.56 gms. of acetamidine hydrochloride were then added together with 50 ccs. of pyridine, and the mixture was heated on a water bath for two hours. The mixture was poured into an aqueous solution of potassium iodide and a dyestuff was formed which was filtered off, washed and re-crystallised from methyl alcohol to give a product melting at 296° C.

This dye is a sensitizer for silver chloride emul-

sions and extends the sensitivity to about λ4200 Å. with a maximum at about λ4000 Å.

The corresponding 2:2'-diethyl compound was prepared similarly from 1-ethylmercaptobenzthiazole and ethyl-p-toluene sulphonate as small yellow crystals melting at 304° C. with decomposition.

This dye is a sensitizer for silver chloride emulsions and extends the sensitivity to about λ4200 Å. with a sharp maximum at about λ4000 Å.

*Example 12*

1.89 gms. of 2-ethylthiolquinoline and 1.86 gms. of methyl-p-toluene sulphonate were fused together at 130–140° C. for 3½ hours. The mixture was then allowed to cool and 0.5 gm. of acetamidine hydrochloride and 10 ccs. of ethyl alcohol were added and the mixture was warmed on a water bath until the solid dissolved. 0.23 gm. of sodium dissolved in 15 ccs. of methyl alcohol were then added and the mixture boiled on a water bath for 30 minutes. The mixture was then poured into a solution of potassium perchlorate and allowed to stand when orange crystals were deposited. These were collected, washed with hot benzene, and recrystallised from aqueous spirit as orange rhombic crystals melting at 235° C.

This dye is a sensitizer for silver chloride emulsions and extends their sensitivity ranges to about λ4600 Å. with maxima at about λ4100 Å. and λ4400 Å.

*Example 13*

1.65 gms. of 1-methylmercaptobenzoxazole, 1.86 gms. of methyl-p-toluene sulphonate were fused together at 130–140° C. for three hours. 1.89 gms. of acetamidine hydrochloride dried previously in a vacuum desiccator over calcium chloride and 20 ccs. of pyridine were then added and the mixture warmed on a water bath until all the solid dissolved. Methyl mercaptan was evolved and the pyridine solution acquired a light yellow colour. The solution was then boiled gently for thirty minutes and poured into a large bulk of potassium iodide solution and allowed to stand. The solid which separated out was filtered off, washed with benzene and recrystallised from methyl alcohol in the form of small light yellow crystals melting at 274° C. with decomposition.

*Example 14*

2.31 gms. of 1-methylthiol-5:6-benzbenzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were fused together at 160–170° C. for 5½ hours. 1.9 gms. of acetamidine hydrochloride and 20 ccs. of pyridine were then added and the mixture warmed until solution was effected after which it was gently boiled for 40 minutes when the dyestuff was formed and settled out as a light yellow solid. This was collected, extracted with boiling benzene and the residue which was insoluble in benzene was recrystallised from methyl alcohol to yield light yellow crystals melting at 280° C.

This dyestuff is a sensitizer for silver chloride emulsions and extends their sensitivity to about λ4500° Å. with a maximum at about λ4300 Å. The corresponding 3-4-dibenzthiocyadiazine iodide was prepared similarly as yellow crystals melting at 235° C.

This dye is a powerful sensitizer for silver chloride emulsions and extends the sensitivity range to about λ4600 Å. with a sharp maximum at about λ4400 Å.

*Example 15*

2.25 gms. of 1-methylthiol-4:5-methylenedioxybenzthiazole and 1.56 gms. of methyl-p-toluene sulphonate were fused together at about 150° C. 1.9 gms. of acetamidine hydrochloride were then added and the mixture was warmed until solution was effected and then boiled for about 40 minutes when the dyestuff separated out as light yellow crystals. These were collected, extracted with boiling benzene and the residue recrystallised from methyl alcohol to yield a dyestuff melting at 280° C.

This dye is sensitizer for silver chloride emulsions and extends their sensitivity to about λ4500 Å. with an indeterminate maximum at about λ4350 Å.

*Example 16*

2.41 gms. of 1-methylthiol-4:5-dimethoxybenzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at 140° C. for 3½ hours. 1.98 gms. of acetamidine hydrochloride and 20 ccs. of pyridine were then added and the mixture was warmed until solution was effected. The mixture was then gently boiled under a reflux condenser for 40 minutes when a yellow solid separated out. This was collected, extracted with boiling benzene and the residue which was insoluble in benzene was recrystallised from methyl alcohol as small orange crystals melting at 275° C.

This dye is a sensitizer for silver chloride emulsions and extends their sensitivity to about λ4700 Å. with a sharp maximum at about λ4400 Å.

*Example 17*

1.76 gms. of 4-methylthiolquinazoline and 1.86 gms. of methyl-p-toluene sulphonate were fused together at 130–140° C. for 3 hours. 1.9 gms. of acetamidine hydrochloride and 20 ccs. of pyridine were then added and the mixture was gently heated until solution was effected. The mixture was then gently boiled under a reflux condenser for 30 minutes and poured into a large bulk of potassium iodide solution when a solid separated out which was collected and washed.

*Example 18*

3.62 gms. of 1-methylthiolbenzthiazole and 3.72 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for four hours. 3.22 gms. of formamidine hydrochloride and 30 ccs. of pyridine were then added and the mixture was then gently boiled under a reflux condenser for about 30 minutes after which it was poured into 400 ccs. of an aqueous solution containing about 4 gms. of potassium iodide when a light yellow solid separated out. This was filtered off, washed and extracted with hot benzene and the benzene-insoluble residue was recrystallised from methyl alcohol as pale yellow needles, melting at 298° C. with decomposition.

*Example 19*

3.62 gms. of 1-methylthiolbenzthiazole and 3.75 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for 3½ hours. 4.36 gms. of propionamidine hydrochloride and 30 ccs. of pyridine were then added and the mixture was warmed gently until solution was effected. The mixture was then gently boiled under a reflux condenser for 40 minutes and then poured into a large bulk of aqueous potassium iodide solution. The solid which separated out was collected, and extracted with boiling benzene and the benzene-

insoluble residue recrystallised from methyl alcohol as pale yellow needles, melting at 290° C. with decomposition.

This dyestuff is a sensitizer for silver chloride emulsions and extends their sensitivity to about λ4200 Å. with a maximum at about λ4000 Å.

*Example 20*

3.3 gms. of methylthiolbenzoxazole and 3.75 gms. of methyl-p-toluene sulphonate were heated together for 3½ hours at 130–140° C. 4.36 gms. of propionamidine hydrochloride and 30 ccs. of pyridine were then added and the mixture was warmed until solution was effected. The mixture was then boiled gently under a reflux condenser for about 40 minutes after which it was poured into an aqueous solution of potassium iodide and the whitish solid which separated out was collected, extracted with boiling benzene and the benzene-insoluble residue re-crystallised from methyl alcohol as a yellow solid melting at 301° C. with decomposition.

*Example 21*

2.31 gms. of 1-methylthiol-5:6-benzbenzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were fused together at 180–190° C. for 3½–4 hours. 2.18 gms. of propionamidine hydrochloride and 40 ccs. of pyridine were then added and the mixture was gently warmed until solution was effected. The solution was then gently boiled under a reflux condenser for about 40 minutes and the red-orange solution obtained was poured into water. The solid which separated out was collected, washed several times with boiling benzene and the residue was re-crystallised from methyl alcohol as pale orange crystals melting at 273° C. with decomposition.

*Example 22*

2.31 gms. of 1-methylthiol-3:4-benzbenzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at 160–170° C. for four hours. 2.18 gms. of propionamidine hydrochloride and 40 ccs. of pyridine were then added and the mixture was warmed until solution was effected after which it was gently boiled under a reflux condenser for about 40 minutes. The reddish-yellow solution obtained was poured into an aqueous solution of potassium bromide and the solid which separated out was collected washed repeatedly with boiling benzene and the residue was recrystallised from methyl alcohol as pale orange solid melting at 225° C. with decomposition.

*Example 23*

2.41 gms. of methylthiol-4:5-dimethoxybenzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at about 140° C. for 3½ hours. 2.18 gms. of propionamidine hydrochloride and 30 ccs. of pyridine were added and the mixture was gently warmed until solution was effected. The solution was then gently boiled under a reflux condenser for about 40 minutes after which it was poured into an aqueous solution of potassium iodide. The lemon yellow solid was separated out, and extracted with boiling benzene and the benzene-insoluble residue was recrystallised from methyl alcohol to yield lemon yellow crystals melting at 289° C. with decomposition.

*Example 24*

7.2 gms. of 1-methylmercapto-benzthiazole and 7.5 gms. of methyl-p-toluene sulphonate were heated together for about 2½ hours. 15.4 gms. of benzamidine hydrochloride and 50 ccs. of pyridine were then added. The mixture was warmed on a water bath and then heated very strongly for thirty minutes. The mixture was then poured into an aqueous solution of potassium iodide when a yellow solid was formed, which was recrystallised to give a product melting at 294° C.

This dyestuff is a sensitizer for silver chloride emulsions and extends their sensitivity ranges to about λ4200 Å. with a maximum at about λ4000 Å.

*Example 25*

2.31 gms. of 1-methylthiol-5:6-benzbenzthiazole and 1.83 gms. of methyl-p-toluene sulphonate were heated together for 3½ hours at 130–140° C. 3.88 gms. of benzamidine hydrochloride and 40 ccs. of pyridine were added and the mixture was gently warmed until the solid dissolved after which it was gently boiled under a reflux condenser for ½ hour. The solution was then poured into an aqueous solution of potassium bromide and allowed to stand for a time when a light yellow solid settled out. This was collected washed and extracted with benzene, leaving a light yellow residue melting at 264° C.

*Example 26*

2.31 gms. of 1-methylthiol-3:4-benzbenzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at 160–170° C. for about 3½ hours. 3.85 gms. of benzamidine hydrochloride and 40 ccs. of pyridine were added and the mixture was gently warmed until the solid was dissolved and was then gently boiled under a reflux condenser for about ½ hour. The solution was then poured into an aqueous solution of potassium bromide and allowed to stand for a short time. A light yellow solid was formed which was filtered off, washed and extracted with hot benzene leaving a residue comprising a light yellow solid melting at 287° C. in a brown liquid.

*Example 27*

7.24 gms. of 1-methylmercapto-benzthiazole and 7.46 gms. of methyl-p-toluene sulphonate were mixed and heated together at 130°–140° C. for 3 hours. The mixture was then allowed to cool and 12.8 gms. of powdered ammonium nitrate and 50 ccs. of pyridine were added and the mixture heated on a water bath for thirty minutes and the gently boiled under a reflux condenser for a further thirty minutes. The mixture was then poured into an aqueous solution of potassium iodide and a pale yellow solid which precipitated out was filtered off and recrystallised from methyl alcohol to give pale yellow needles melting at 294° C.

This dye is a sensitizer for silver chloride emulsions and extends their sensitivity ranges to about λ4200 Å. with a maximum at about λ4000 Å.

*Example 28*

1.78 gms. of dimethylthiol- (α β′)-thiodiazole and 1.88 gms. of methyl-p-toluene sulphonate were heated together for 3½ hours at 130–140° C. 0.5 gm. of ammonium nitrate and 15 ccs. of pyridine were then added and the mixture was gently boiled under a reflux condenser for about 30 minutes. The mixture was then poured into an aqueous solution of potassium iodide and allowed to stand when an oil separated out. This was separated off, and washed with benzene leaving a pale yellow coloured solid, melting at 205° C.

*Example 29*

1.78 gms. of dimethylthiol thio-($\beta\beta'$)-diazole and 1.88 gms. of methyl-p-toluene sulphonate were heated together at 120–130° C. for 3½ hours. 0.5 gm. of ammonium nitrate and 15 ccs. of pyridine were then added and the mixture was gently boiled under a reflux condenser for ½ hour. It was then poured into an aqueous solution of potassium iodide when an oil settled out. This was separated off and washed with benzene leaving yellow brown crystals melting at 213° C.

*Example 30*

1.89 gms. of 2-ethylthiol-quinoline and 1.88 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for 3½ hours. After allowing the product of this fusion to cool, 50 ccs. of a cold saturated solution of ammonia in ethyl alcohol were added and the mixture was gently warmed until the solid was dissolved ammonia being continuously bubbled through the liquid. 0.28 gm. of sodium dissolved in 10 ccs. of ethyl alcohol were then added and the mixture was gently boiled under a reflux condenser and ammonia bubbled through the liquid for a further half hour. The liquor was then poured into an aqueous solution of potassium perchlorate and acidified with hydrochloric acid. After standing for some time crystals were formed, which were separated off, washed with hot benzene and recrystallised to yield brown needle shaped crystals melting at 225° C.

*Example 31*

3.62 gms. of 1-methylthiol benzthiazole and 3.72 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for about 3½ hours. 1.08 gms. of o-phenylene-diamine and 40 ccs. of pyridine were then added and the mixture was gently heated until the solid was dissolved and then gently boiled under a reflux condenser for about 30 minutes. It was then poured into water and allowed to stand when an oil separated out. This was separated off and extracted with boiling benzene. The benzene extract was cooled and a grey solid was precipitated from it, which was recrystallised from boiling benzene to yield an almost colourless solid, melting at 278° C.

*Example 32*

3.62 gms. of 1-methylthiol-benzthiazole and 3.72 gms. of methyl-p-toluene sulphonate were heated together at 130°–140° C. for about 8½ hours. 1.45 gms. of p-phenylene-diamine dihydrochloride and 40 ccs. of pyridine were then added and the mixture was gently warmed until all the solid was dissolved and was then gently boiled under a reflux condenser for about ½ hour. A pale yellow solid began to form and the mixture was poured into water when a light yellow precipitate was formed. This was filtered off, collected and washed and extracted with hot benzene. The extract was cooled and the solid which formed was recrystallised to give almost colourless crystals melting at 275° C.

*Example 33*

1.81 gms. of 1-methylthiol-benzthiazole and 1.86 gms. of methyl-p-toluene sulphonate were heated together at 130–140° C. for 8½ hours. 1.8 gms. of guanidine carbonate and 60 ccs. of pyridine were then added and the mixture gently boiled for 30 minutes. A yellow flocculent precipitate was formed. The mixture was then poured into an aqueous solution of potassium iodide and allowed to stand when a light yellow solid separated out. This was collected, washed and recrystallised from hot methyl alcohol to give yellow crystals melting at 310° C.

*Example 34*

2.23 grams of 1:3:3-trimethyl-2-ω-acetanilido-vinyl-indolenium iodide and 1.05 grams of hydrazine hydrochloride were mixed with 20 ccs. of pyridine and the whole warmed on a water bath for about half an hour when an orange dye formed. The mixture was then gently boiled under a reflux condenser for about twenty minutes. The liquid obtained was then poured into aqueous potassium iodide solution when the dyestuff was precipitated out as a crimson solid and recrystallised from methyl alcohol to give a dye which decomposed at about 250° C. This dye is a very powerful sensitiser for silver chloride emulsions and extends their sensitivity ranges to about λ5900 Å. with a flat sensitising curve over the range from about λ4600 Å. to about λ5400 Å.

*Example 35*

22.3 grams of 1:3:3-trimethyl-2-ω-acetanilido-vinyl indolenium iodide and 9.05 grams of p-phenylenediamine hydrochloride and 200 ccs. of pyridine were mixed and heated together on a water bath for twenty-five minutes and then gently boiled under a reflux condenser for a further ten minutes. The orange solution obtained was then poured into water when small brick-red crystals quickly settled out. These were filtered off, washed with spirit and ether and dried and melted at 272° C.

*Example 36*

11.2 grams of 1-ω-acetanilido-vinyl-benzthiazole ethiodide, 4.5 grams of p-phenylenediamine hydrochloride were mixed together with 300 ccs. of pyridine. The solids dissolved up and the solution became yellow in colour. The solution was then heated on a water bath for forty minutes, after which it was gently boiled under a reflux condenser for ten minutes, when a crimson solid separated out. The mixture was then poured into water and the crimson crystals which separated out were filtered off, washed and dried. They melted at 285° C.

*Example 37*

21 grams of 1-ω-acetanilido-vinyl-benzoxazole methiodide and 9.05 grams of paraphenylenediamine hydrochloride were mixed with 100 ccs. of pyridine and gently boiled together. A deep yellow solution was obtained and orange coloured crystals were deposited from the hot solution. After allowing this solution to stand until cool the crystals were filtered off, washed and dried. They had a melting point higher than 305° C.

*Example 38*

11.2 grams of 1-ω-acetanilido-vinyl-benzthiazole ethiodide and 2.7 grams of hydrazine dihydrochloride were mixed together with 100 ccs. of spirit and 4.1 grams of anhydrous sodium acetate. On gently warming the mixture, a deep orange solution with a faint red tinge was obtained. This was diluted with water and brown crystals with a green reflex were deposited. These crystals were filtered off, washed and recrystallised from methyl alcohol and were found to melt at 226° C. with decomposition.

*Example 39*

22.3 grams of 1:3:3-trimethyl-2-ω-acetanilido-

vinyl-indolenium iodide, 9.2 grams of benzidine and 150 ccs. of dry spirit were gently boiled together under a reflux condenser for 30 minutes. The substances dissolved in the spirit and then orange crystals with a bluish reflex separated from the hot solution. After cooling the solid was filtered off from the liquors and well washed with spirit and ether. The crystals melted above 300° C.

A further experiment showed that this reaction could be carried out equally well using pyridine in place of the alcohol.

*Example 40*

22.5 grams of 1-ω-acetanilido-vinyl-benzthiazole ethiodide and 9.2 grams of benzidine were mixed together with 200 ccs. of dry spirit and the whole gently boiled for 30 minutes. A brown crystalline solid separated out, which was filtered off, washed and dried and obtained as dark brown crystals melting at 260° C.

*Example 41*

21 grams of 1-ω-acetanilido-vinyl-benzoxazole methiodide and 9.2 grams of benzidine were mixed together with 100 ccs. of alcohol and the whole gently heated for a few minutes. An intense yellow solution was obtained from which small orange crystals separated out. These were filtered off and washed and dried and obtained as orange yellow powder having a melting point above 300° C.

*Example 42*

18.1 grams of 1-methylthiol benzthiazole were heated together with 18.6 grams of methyl-p-toluene sulphonate for three and a half hours at 130–140° C. 18.4 grams of benzidine and 200 ccs. of spirit were added and the mixture was gently warmed for twenty minutes when a light yellow solid was deposited and mercaptan evolved. The solid was filtered off, well washed with benzene spirit and ether and obtained as almost colourless powder melting above 300° C.

*Example 43*

22.3 grams of 1:3:3-trimethyl-2-ω-acetanilido-vinyl indolenium iodide, 12.2 grams of di-anisidine (2:2'-dimethoxy benzidine) and 100 ccs. of pyridine were mixed together and gently boiled under a reflux condenser for thirty minutes. A deep orange solution was obtained from which a brick red solid was deposited on cooling. This solid was filtered off, well washed and obtained as small brick red crystals, melting at 282° C. with decomposition.

I claim:

1. A process for the production of dyestuffs which comprises reacting in the presence of an acid binding agent a compound selected from the group consisting of thioethers and selenoethers of quaternary salts of heterocyclic nitrogen compounds having a nucleus of the type contained in cyanine dyes in which the quaternary nitrogen atom is a heterocyclic nitrogen atom and the ether groups are in a position taken from the group consisting of alpha and gamma positions to the quaternary nitrogen atom with a second nitrogenous compound selected from the group consisting of ammonia, amidines, hydrazine, ortho- and para-arylene diamines, benzidines, 2:2'-, 2:4'- and 4:4'-diamino stilbenes and the salts of such compounds.

2. The process of claim 1 wherein the quaternary salt of the heterocyclic nitrogen compound is reacted with a salt of the other nitrogenous compound in the presence of an acid binding substance.

3. The process of claim 1 wherein the quaternary salt of the heterocyclic nitrogen compound is reacted with a salt of the other nitrogenous compound in the presence of a substance which acts both as a solvent and as an acid binding substance.

4. The process of claim 1 wherein the quaternary salt of the heterocyclic nitrogen compound is reacted with a salt of the other nitrogenous compound in the presence of pyridine.

5. The process of claim 1 wherein the quaternary salt of a heterocyclic nitrogen compound is reacted with a salt of the other nitrogenous compound in the presence of a neutral solvent and a strong acid binding substance.

6. The process of claim 1 wherein the quaternary salt of the heterocyclic nitrogen compound is reacted with a salt of the other nitrogenous compound in the presence of alcohol as a solvent and sodium ethoxide as an acid binding substance.

7. A process for the production of a dyestuff comprising reacting an alkylthiol azole alkyl salt with an amidine.

8. A process for the production of a dyestuff comprising reacting 1-methylthiol-3:4-benzthiazole-methyl para-toluene sulphonate with acetamidine hydrochloride in the presence of pyridine.

9. A process for the production of a dyestuff comprising reacting 1-ethylthiol-benzthiazole-ethyl-para-toluene sulphonate with acetamidine hydrochloride in the presence of pyridine.

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