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2,856,404

MEROCYANINE DYES AND INTERMEDIATES

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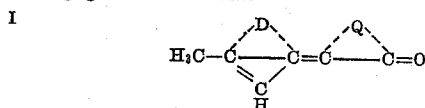
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8 Claims. (Cl. 260—240)

This invention relates to an improved method of making merocyanine dyes, some of which are new compositions of matter, and new intermediates for making these merocyanine dyes. The merocyanine dyes produced according to our invention can be employed in optically sensitizing photographic silver halide emulsions.

It is, therefore, an object of our invention to provide an improved method for making merocyanine dyes. Another object is to provide certain new merocyanine dyes. Still another object is to provide new intermediates for making these merocyanine dyes. A further object is to provide photographic silver halide emulsions sensitized with these merocyanine dyes. Other objects will become apparent from a consideration of the following description and examples.

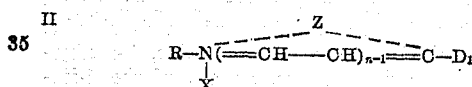
According to our invention, we provide an improved method for making merocyanine dyes by condensing an intermediate selected from those represented by the following general formula:



wherein D represents the atoms necessary to complete a cyclohexene ring and Q represents the non-metallic atoms necessary to complete a nucleus of the indandione series (e. g., 1,3-diketohydrindene, etc.) or a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, such as those of the pyrazolone series (e. g., 3-methyl-1-phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 1-(2-benzothiazolyl)-3-methyl-5-pyrazolone, etc.), those of the isoxazolone series (e. g., 3-phenyl-5(4H)-isoxazolone, 3-methyl-5(4H)-isoxazolone, etc.), those of the oxindole series, (e. g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), those of the 2,4,6-triketodihydropyrimidine series (e. g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e. g., 1-methyl, 1-ethyl, 1-n-propyl, 1-n-heptyl, etc.), or 1,3-dialkyl (e. g., 1,3-dimethyl, 1,3-diethyl, 1,3-di-n-propyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β-methoxyethyl), etc.), or 1,3-diaryl (e. g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.), or 1-aryl (e. g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e. g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives), those of the rhodanine series (i. e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkyl-rhodanines (e. g., 3-ethylrhodanine, 3-allylrhodanine, etc.) or 3-arylrhodanines (e. g., 3-phenylrhodanine, etc.), etc., those of the 2(3H)-imidazo[1,2-a]-pyridone series, those of the 5,7-dioxo-6,7-dihydro-5-thiazolo-[3,2-a]-pyrimidine series (e. g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.), those of the 2-thio-2,4-oxazolidinedione series (i. e., those of the 2-thio-2,4-(3H,5H)-oxazolidinedione series) (e. g., 3-ethyl-2-thio-2,4-oxazolidinedione, etc.), those of the thianaphthenone series (e. g., 3(2H)-thianaphthenone, etc.), those of the 2-thio-2,5-thiazolidinedione series (i. e., the 2-thio-2,5-

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(3H,4H)-thiazolidinedione series) (e. g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.), those of the 2,4-thiazolidinedione series (e. g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3-α-naphthyl-2,4-thiazolidinedione, etc.), those of the thiazolidinedione series (e. g., 4-thiazolidinedione, 3-ethyl-4-thiazolidinedione, 3-phenyl-4-thiazolidinedione, 3-α-naphthyl-4-thiazolidinedione, etc.), those of the 4-thiazolinone series (e. g., 2-ethylmercapto-4-thiazolinone, 2-alkylphenylamino-4-thiazolinones, 2-diphenylamino-4-thiazolinone, etc.), those of the 2-imino-2,4-oxazolinone (i. e., pseudohydantoin) series, those of the 2,4-imidazolidinedione (hydantoin) series (e. g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3-α-naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-α-naphthyl-2,4-imidazolidinedione, 1,3-diphenyl-2,4-imidazolidinedione, etc.), those of the 2-thio-2,4-imidazolidinedione (i. e., 2-thiohydantoin) series (e. g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 3-α-naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-α-naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.), those of the 5-imidazolinone series (e. g., 2-n-propylmercapto-5-imidazolinone, etc.), etc. (especially a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, 3 of said atoms being carbon atoms, 1 of said atoms being a nitrogen atom, and 1 of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom), with a compound selected from those represented by the following general formula:



wherein R represents an alkyl group (e. g., methyl ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, β-methoxyethyl, β-ethoxyethyl, allyl (i. e., methylvinyl), benzyl (phenylmethyl), β-phenylethyl, carboxymethyl, etc.) (especially alkyl groups containing from 1 to 4 carbon atoms), n represents a positive integer of from 1 to 2, X represents an acid radical (e. g., chloride, bromide, iodide, p-toluenesulfonate, benzenesulfonate, ethylsulfate, methylsulfate, etc.), D₁ represents an electronegative radical, such as alkylmercapto (e. g., methylmercapto, ethylmercapto, etc.), arylmercapto (e. g., phenylmercapto, tolylmercapto, etc.), a β-acylanilidovinyl group (e. g., β-acetanilidovinyl, β-benzoylanilidovinyl, etc.), a δ-acylanilido-1,3-butadienyl group (e. g., δ-acetanilido-1,3-butadienyl, δ-benzoylanilido-1,3-butadienyl, etc.), etc., and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 (n is 1) to 6 (n is 2) atoms in the heterocyclic ring, such as those selected from the group consisting of those of the thiazole series (e. g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), those of the benzothiazole series (e. g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxy-methylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.), those of the naphthothiazole series (e. g., naphtho[1,2-]thiazole, naphtho[2,1]thiazole,

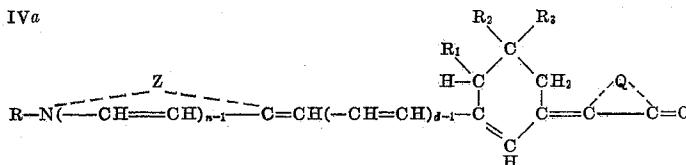
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5-methoxynaphtho[2,1]thiazole, 5-ethoxynaphtho[2,1]thiazole, 8-methoxynaphtho[1,2]thiazole, 7-methoxynaphtho[1,2]thiazole, etc.), those of the thianaphtho-7',6',4,5-thiazole series (e. g., 4'-methoxythianaphtho-7',6',4,5-thiazole, etc.), those of the oxazole series (e. g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-

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wherein R, Z, n, D and Q each have the values given above and d represents a positive integer of from 1 to 3. The dyes produced by condensing an intermediate selected from those represented by Formula III with those of Formula II can be represented by the following general formula:

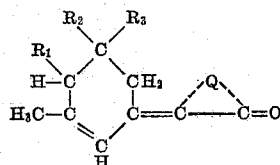
IVa



diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), those of the benzoxazole series (e. g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.), those of the naphthoxazole series (e. g., naphtho[1,2]oxazole, naphtho[2,1]oxazole, etc.), those of the selenazole series (e. g., 4-methylselenazole, 4-phenylselenazole, etc.), those of the benzoselenazole series (e. g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.), those of the naphthoselenazole series (e. g., naphtho[1,2]selenazole, naphtho[2,1]selenazole, etc.), those of the thiazoline series (e. g., thiazoline, 4-methylthiazoline, etc.), those of the 2-quinoline series (e. g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.), those of the 4-quinoline series (e. g., quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, etc.), those of the 1-isoquinoline series (e. g., isoquinoline, 3,4-dihydroisoquinoline, etc.), those of the 3-isoquinoline series (e. g., isoquinoline, etc.), those of the benzimidazole series (e. g., 1,3-diethylbenzimidazole, 1-ethyl-3-phenylbenzimidazole, etc.), those of the 3,3-dialkylindolenine series (e. g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), those of the 2-pyridine series (e. g., pyridine, 5-methylpyridine, etc.), etc.

Particularly useful intermediates selected from those represented by Formula I above include those represented by the following general formula:

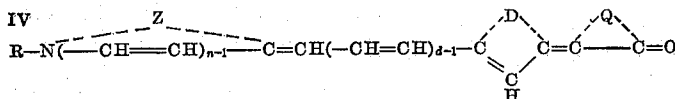
III



wherein R₁ represents a hydrogen atom or a carbalkoxyl group, such as carbomethoxyl, carbethoxyl, etc. (e. g., a carbalkoxyl group containing from 2 to 3 carbon atoms), R₂ and R₃ each represents a hydrogen atom or a lower alkyl group, such as methyl, ethyl, etc., and Q has the values given above.

The dyes produced by condensing an intermediate selected from those represented by Formula I above with those of Formula II can be represented by the following general formula:

IV

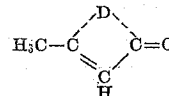


wherein R, Z, n, d, R₁, R₂, R₃ and Q each have the values given above.

The condensations of the intermediates of Formulas I or III with the compounds of Formula II can be accelerated by basic condensing agents, such as the trialkylamines, (triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, etc.), N,N-dialkylanilines (e. g., N,N-dimethylaniline, N,N-diethylaniline, etc.), N-alkylpiperidines (e. g., N-methylpiperidine, N-ethylpiperidine, etc.), etc. The condensations can be carried out in the presence of an inert diluent, such as the lower alcohols (e. g., ethanol, n-propanol, isopropanol, n-butanol, etc.), pyridine, quinoline, 1,4-dioxane, etc. Heat accelerates the condensations, although temperatures varying from ambient (ca. 25° C.) to the reflux temperature of the reaction mixture can be employed.

According to our invention, we provide the intermediates represented by Formula I above by condensing a ketone selected from those represented by the following general formula:

V



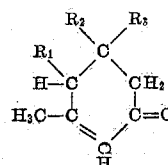
wherein D has the values given above with a ketomethylene compound selected from those represented by the following general formula:

VI



wherein Q has the values given above. Particularly useful ketones selected from those represented by Formula V above include those represented by the following general formula:

VII



wherein R₁, R₂, and R₃ each have the values given above.

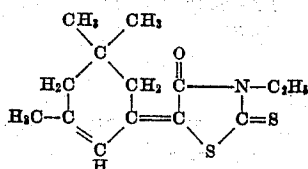
Typical ketone compounds selected from those represented by Formulas V and VII above include isophorone, 3,5-dimethyl-2-cyclohexen-1-one, 3-methyl-2-cyclohexen-1-one, 4-carbethoxy-3-methyl-2-cyclohexen-1-one, etc. The condensations of the compounds of Formula VI with those of Formulas V or VII can be accelerated by strong basic condensing agents, such as piperidine, diethylamine, etc., or by a mixture of ammonium acetate and acetic acid. These condensations can be conveniently carried out in an inert diluent, such as chloroform,

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diethyl ether, etc. Heating accelerates these condensations, temperatures varying from ambient (ca. 25° C.) to the reflux temperature of the reaction mixture being particularly useful.

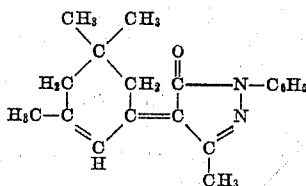
The following examples will serve to illustrate more fully the manner whereby we practice our invention.

Example 1.—3-ethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-rhodanine



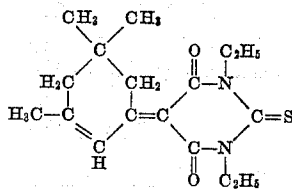
3-ethylrhodanine (32.2 g., 1 mol.), isophorone (27.6 g., 1 mol.) and piperidine (16.0 g., 1 mol.) were mixed and heated for four hours in an oil bath at 135–140° C. The reaction mixture was then poured into high boiling ligroin with stirring and the mixture chilled. The ligroin solution was decanted from the tar and passed through a 2.5 by 25 cm. column packed with equal parts by weight of calcium carbonate and a filter aid. The ligroin solution was concentrated to 50 ml. and chilled overnight. The crude crystalline product was filtered off and recrystallized from methyl alcohol. The yield of purified product was 8.5 g. (15%), M. P. 122–3° C.

Example 2.—3-methyl-1-phenyl-4-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-5-pyrazolone



3-methyl-1-phenyl-5-pyrazolone (17.4 g., 1 mol.), isophorone (15 g., 1 mol.+10%) and two drops of piperidine were mixed and heated in an oil bath at 130–135° C. for four hours. The reaction mixture was then extracted with 400 ml. of 90–120° C. ligroin. The ligroin solution was allowed to cool to room temperature and was then decanted from separated resinous material. After chilling and stirring the desired product separated from the ligroin solution. The crude product was filtered off and recrystallized from ligroin. The yield of purified product was 14.2 g. (48%), M. P. 115–117° C.

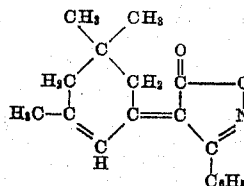
Example 3.—1,3-diethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-2-thiobarbituric acid



1,3-diethyl-2-thiobarbituric acid (40 g., 1 mol.) and isophorone (30.3 g., 1 mol.+10%) were dissolved in chloroform (100 ml.), and ammonium acetate (2.5 g.) and acetic acid (4 ml.) were added. The mixture was heated under reflux for an hour in a system fitted for continuous removal of water. The reaction mixture was then washed with two 100 ml. portions of water and the chloroform removed by distillation. The residue was recrystallized from methyl alcohol and the yield of purified material was 35.2 g. (55%), M. P. 108–9° C.

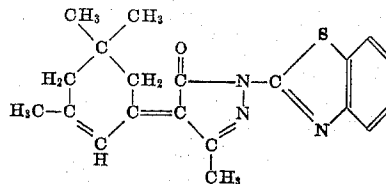
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Example 4.—3-phenyl-4-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-5-(4H)-isoxazolone



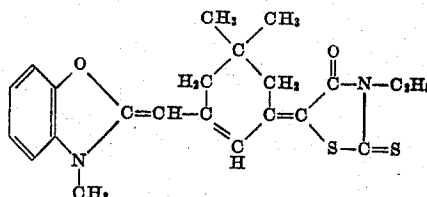
3-phenyl-5-(4H)-isoxazolone (16.1 g., 1 mol.) and isophorone (15.2 g., 1 mol.+10%) were dissolved in chloroform (40 ml.) and ammonium acetate (2 g.) and acetic acid (4 ml.) were added. The reaction mixture was then heated under reflux for eighteen hours in an apparatus designed for the continuous removal of water. The chloroform solution was then washed with two 100 ml. portions of water. The chloroform was removed by distillation and the residue recrystallized from methyl alcohol. The yield of purified product was 9.6 g. (35%), M. P. 174–5° C.

Example 5.—1-(2-benzothiazolyl)-3-methyl-4-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-5-pyrazolone



1-(2-benzothiazolyl)-3-methyl-5-pyrazolone (7.7 g., 1 mol.) and isophorone (5.1 g., 1 mol.+10%) were dissolved in chloroform (40 ml.), and ammonium acetate (2 g.) and acetic acid (4 ml.) were added. The mixture was heated under reflux for twenty-four hours in an apparatus designed for the continuous removal of water. The chloroform solution was washed with two 20 ml. portions of water and the solvent removed under reduced pressure. The residue was stirred with methyl alcohol (50 ml.) and filtered, the solid being discarded. The methyl alcoholic solution was treated with water (200 ml.) and the precipitated product filtered off. After recrystallization from methyl alcohol, the yield of purified material was 2.8 g. (24%), M. P. 204–5° C. dec.

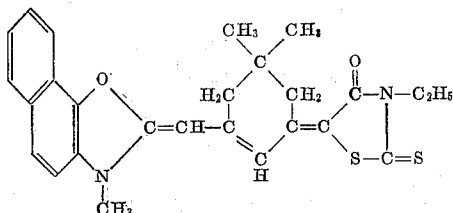
Example 6.—3-ethyl-5-[4-(3-methyl-2(3H)-benzoxazolylidene)-1-3-neopentylene-2-butenylidene]rhodanine



2-methylmercaptobenzoxazole (1.65 g., 1 mol.+300%) and methyl p-toluenesulfonate (1.86 g., 1 mol.+300%) were mixed and heated on the steam bath overnight. To the crude quaternary salt was added 3-ethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)rhodanine (0.70 g., 1 mol.), the mixture dissolved in pyridine (15 ml.) and triethylamine (1.4 ml., 1 mol.+300%) added. The reaction mixture was then heated under reflux for one-half hour and poured into methyl alcohol (100 ml.). After chilling overnight, the crude dye was filtered off, washed with water and methyl alcohol and dried. The yield of purified dye after two recrystallizations from pyridine and methyl alcohol was 0.42 g. (41%), M. P. 217–18° C. dec.

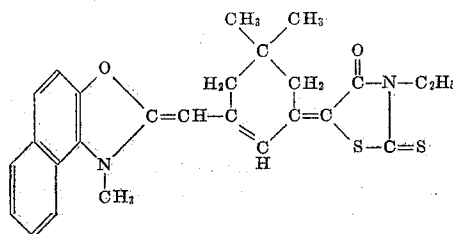
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Example 7.—3-ethyl-5-[4-(3-methyl-2(3H)-naphtho[2,1]oxazolylidene)-1,3-neopentylene-2-butenylidene]rhodanine



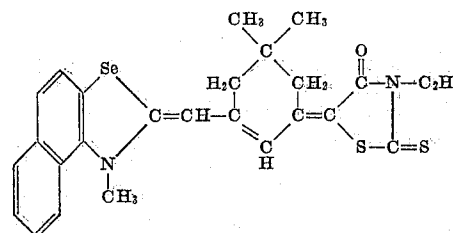
2-methylmercapto- α -naphthoxazole (2.15 g., 1 mol.+100%) and methyl p-toluenesulfonate (2.05 g., 1 mol.+120%) were mixed and heated overnight in an oil bath at 100–105° C. The crude quaternary salt and 3-ethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)rhodanine (1.40 g., 1 mol.) were dissolved in pyridine and triethylamine (1.4 ml., 1 mol.+100%) was added. After heating under reflux for a half-hour, the reaction mixture was poured with stirring into methyl alcohol (150 ml.) and chilled overnight. The crude dye was filtered off, washed with methyl alcohol and dried. The crude dye was purified by boiling with three 100 ml. portions of methyl alcohol and filtering hot each time. After two recrystallizations from pyridine and methyl alcohol, the yield of purified dye was 0.73 g. (31%), M. P. 251–2° C. dec.

Example 8.—3-ethyl-5-[4-(1-methyl-2(1H)-naphtho[1,2]oxazolylidene)-1,3-neopentylene-2-butenylidene]rhodanine



2-methylmercapto- β -naphthoxazole (2.15 g., 1 mol.+100%) and methyl p-toluenesulfonate (2.05 g., 1 mol.+120%) were mixed and heated on the oil bath at 100–105° C. overnight. The crude quaternary salt and 3-ethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)rhodanine (1.40 g., 1 mol.) were dissolved in pyridine (15 ml.) and triethylamine (1.4 ml., 1 mol.+100%) was added. After the reaction mixture was heated under reflux for a half-hour, it was poured into methyl alcohol (150 ml.) with stirring. After chilling overnight, the crude dye was filtered off, boiled with three 100 ml. portions of methyl alcohol, filtered and dried. After two recrystallizations from pyridine and methyl alcohol, the yield of purified dye was 0.37 g. (16%), M. P. 264–5° C. dec.

Example 9.—3-ethyl-5-[4-(1-methyl-2(1H)-naphtho[1,2]selenazolylidene)-1,3-neopentylene-2-butenylidene]rhodanine

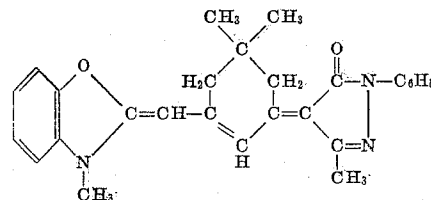


3-ethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)rhodanine (0.70 g., 1 mol.) and 1-methyl-2-methylmercaptanaphtho[1,2]selenazolium p-toluenesulfonate (1.20 g., 1 mol.+10%) were dissolved in pyridine (15 ml.), and triethylamine (0.7 ml., 1 mol.+100%) was added.

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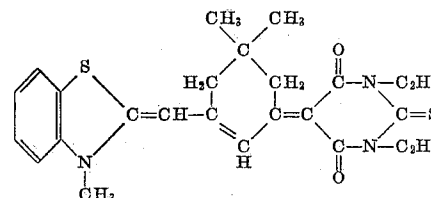
The reaction mixture was heated under reflux for a half-hour and was then poured into methyl alcohol (150 ml.). After chilling overnight, the crude dye was filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol the yield of purified dye was 0.65 g. (49%), M. P. 234–5° C. dec.

Example 10.—3-methyl-4-[4-(3-methyl-2(3H)-benzoxazolylidene)-1,3-neopentylene-2-butenylidene]-1-phenyl-5-pyrazolone



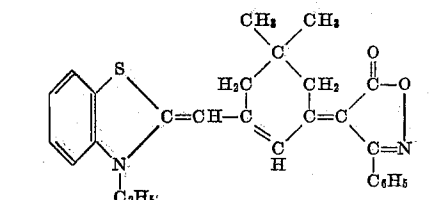
3-methyl-1-phenyl-4-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-5-pyrazolone (1.47 g., 1 mol.), 3-methyl-2-methylmercaptobenzoxazolium p-toluenesulfonate (5.26 g., 1 mol.+200%) and triethylamine (2.1 ml., 1 mol.+200%) were dissolved in pyridine (15 ml.) and the mixture heated under reflux for ten minutes. The crude dye was precipitated by the addition with stirring of water (100 ml.) and after chilling, the aqueous solution was decanted. The residue was stirred with methyl alcohol until crystalline and then chilled overnight. The crude dye was then filtered off, dried and twice recrystallized from ethyl alcohol. The yield of purified dye was 1.01 g. (48%), M. P. 176–8° C.

Example 11.—1,3-diethyl-5-[4-(3-methyl-2(3H)-benzothiazolylidene)-1,3-neopentylene-2-butenylidene]-2-thiobarbituric acid



1,3-diethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-2-thiobarbituric acid (1.54 g., 1 mol.) and 3-methyl-2-methylmercaptobenzothiazolium p-toluenesulfonate (3.67 g., 1 mol.+100%) were dissolved in pyridine (15 ml.) and triethylamine (1.4 ml., 1 mol.+100%) was added. The reaction mixture was heated under reflux for ten minutes and the crude dye was then precipitated by the addition of methyl alcohol (100 ml.). After chilling overnight, the dye was filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol, the yield of purified dye was 1.82 g. (80%), M. P. 237–8° C.

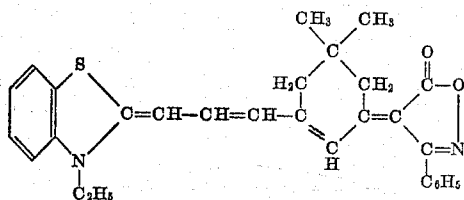
Example 12.—4-[4-(3-ethyl-2(3H)-benzothiazolylidene)-1,3-neopentylene-2-butenylidene]-3-phenyl-5(4H)-isoxazolone



3-phenyl-4-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-5(4H)-isoxazolone (1.41 g., 1 mol.), 3-ethyl-2-ethylmercaptobenzothiazolium ethylsulfate (3.32 g., 1 mol.+100%) and triethylamine (1.4 ml., 1 mol.+100%) were dissolved in pyridine (10 ml.) and heated under reflux for ten minutes. The crude dye was then precip-

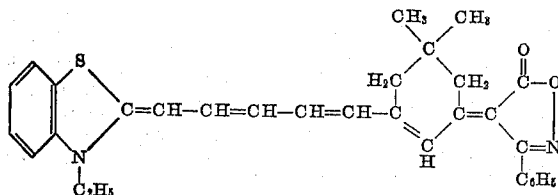
itated by the addition with stirring of water (50 ml.). After chilling, the crude dye was filtered off, washed with water and methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol, the yield of purified dye was 1.48 g. (67%), M. P. 235-6° C. dec.

Example 13.—4 - [6 - (3 - ethyl - 2 - (3H) - benzothiazolylidene) - 1,3 - neopentylene - 2,4 - hexadienylidene] - 3 - phenyl-5(4H)-isoxazolone



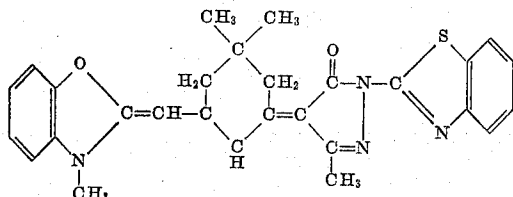
3-phenyl-4-(3,5,5-trimethyl-2-cyclohexene-1-ylidene)-5(4H)-isoxazolone (1.41 g., 1 mol.), 2-β-acetanilido-vinyl-3-ethylbenzothiazolium iodide (2.25 g., 1 mol.) and triethylamine (1.4 ml., 1 mol.+100%) were dissolved in pyridine (10 ml.) and heated under reflux for ten minutes. The reaction mixture was poured into a beaker, 100 ml. of methyl alcohol added with stirring and the mixture chilled overnight. The crude dye was then filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol, the yield of purified dye was 1.59 g. (68%), M. P. 232-3° C. dec.

Example 14.—4-[8-3-ethyl-2(3H)-benzothiazolylidene]-1,3-neopentylene-2,4,6-octatrienylidene]-3-phenyl-5(4H)-isoxazolone



3-phenyl-4-(3,5,5-trimethyl-2-cyclohexene-1-ylidene)-5(4H)-isoxazolone (1.41 g., 1 mol.), 2-β-acetanilido-1,3-butadienyl-3-ethylbenzothiazolium iodide (2.38 g., 1 mol.) and triethylamine (0.7 ml., 1 mol.) were dissolved in pyridine (15 ml.) and heated under reflux for two minutes. The crude dye was precipitated from the reaction mixture by the addition of water (100 ml.). The crude product was filtered off, thoroughly washed with methyl alcohol and ether and dried. After a recrystallization from pyridine and methyl alcohol and a second recrystallization from benzene, the yield of purified dye was 0.12 g. (5%), M. P. 179-80° C. dec.

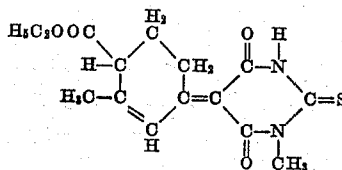
Example 15.—1-(2-benzothiazolyl)-3-methyl-4-[4-(3-methyl-2(3H)-benzoxazolylidene)-1,3-neopentylene-2-butenylidene]-5-pyrazolone



2-methylmercaptobenzoxazole (1.65 g., 1 mol.+400%) and methyl p-toluenesulfonate (1.86 g., 1 mol.+400%) were mixed and heated to reflux over a free flame and then allowed to cool slowly to room temperature. 1-(2-benzothiazolyl)-3-methyl-4-(3,5,5-trimethyl-2-cyclohexene-1-ylidene)-5-pyrazolone (0.71 g., 1 mol.), triethylamine (1.4 ml., 1 mol.+400%) and pyridine (10 ml.) were then added and the reaction mixture heated

under reflux for ten minutes. The crude dye was precipitated by the addition of methyl alcohol (100 ml.), filtered from the reaction mixture, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol, the yield of purified dye was 0.24 g. (25%), M. P. 310-11° C. dec.

In a manner similar to that illustrated in the above examples, other new intermediates and merocyanine dyes can be prepared. For example, the intermediate represented by the following formula:



can be prepared by condensing 1-methyl-2-thiobarbituric acid with 4-carbethoxy-3-methyl-2-cyclohexen-1-one.

All the dyes of our invention are particularly useful in manufacturing photographic, silver halide emulsions, serving to alter the sensitivity thereof. 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 emulsion and should, of course, be uniformly distributed throughout the emulsion. 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 emulsion are simple and well known to those skilled in the art of emulsion making. It is convenient to add the dyes from solutions in appropriate solvents. The solvent must, of course, be compatible with the emulsion and substantially free from any deleterious effect on the light-sensitive materials. Pyridine has proven satisfactory as a solvent for the majority of our new dyes.

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 pyridine or other suitable solvent and a volume of this solution (which may be diluted with methanol) 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 bromide) emulsions. With fine-grain emulsions, which include 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 can 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.

Photographic silver halide emulsions which can advantageously be sensitized by means of the new dyes of our invention comprise the customarily employed gelatino-silver-chloride, gelatino-silver-chlorobromide, gelatino-silver-bromide, and gelatino-silver-bromiodide developing-out emulsions.

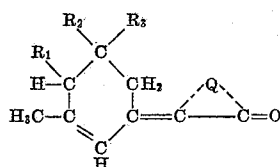
Photographic silver halide emulsions, such as those listed above, containing the sensitizing dyes of our invention can also contain such addenda as chemical sensitizers, e. g., sulfur sensitizers (e. g., allyl thiocarbamide, thio-urea, allylisothiocyanate, cystine, etc.), various gold compounds (e. g., potassium chloroaurate, auric trichloride, etc.) (see U. S. Patents 2,540,085; 2,597,856 and 2,597,915, various palladium compounds, such as palladium chloride (U. S. 2,540,086), potassium chloropalladate (U. S. 2,598,079), etc., or mixtures of such sensitizers; anti-foggants, such as ammonium chloroplatinate (U. S. 2,566,245), ammonium chloroplatinite (U. S. 2,566,263), benzotriazole, nitrobenzimidazole, 5-nitroindazole, benzidine, mercaptans, etc. (see Mees—"The Theory of the Photographic Process," MacMillan Pub., 1942, page 460), or mixtures thereof; hardeners, such as formaldehyde (U. S. 1,763,533), chrome alum (U. S. 1,763,533), glyoxal (U. S. 1,870,354), dibrom-acrolein (Br. 406,750), etc.; color couplers, such as those described in U. S. Patent 2,423,730, Spence and Carroll U. S. Patent 2,640,776, etc.; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in U. S. Patents 2,322,027 and 2,304,940, can also be employed in the above-described emulsions.

In the manner described above, a number of the dyes of our invention represented by Formulas IV or IVa above were separately incorporated in an ordinary gelatino-silver-bromiodide emulsion, the dyes being thoroughly incorporated in the emulsions by stirring. After a short digestion, the emulsions were coated onto ordinary cellulose acetate film supports and the coatings exposed in a spectrograph and sensitometer and then developed in the usual way. The sensitizing range and maximum absorption for each of the dyes are indicated in the following table.

Dye of Example	Sensitizing Range in mμ	Maximum in mμ
6	540-700	670
7	560-700	675
8	570-700	670
9	650-720	700
10	to 630	595
11	520-675	630
12	to 630	605
13	580-740	680
15	to 640	620

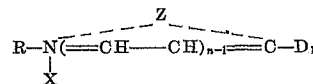
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A process for making polymethine dyes comprising condensing in the presence of a basic condensing agent an intermediate selected from those represented by the following general formula:



wherein R₁ represents a member selected from the group consisting of a hydrogen atom and a carbalkoxyl group containing from 2 to 3 carbon atoms, R₂ and R₃ each represents a member selected from the group consisting of a hydrogen atom and a lower alkyl group, and Q represents the non-metallic atoms necessary to complete

a nucleus selected from the group consisting of an indandione nucleus, a pyrazolone nucleus, an isoxazolone nucleus, an oxindole nucleus, a 2,4,6-triketohexahydropyrimidine nucleus, a 2-thio-2,4,6-triketohexahydropyrimidine nucleus, a rhodanine nucleus, a 2(3H)-imidazo[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a thianaphthenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a 4-thiazolinone nucleus, a 2-imino-2,4-oxazolinone nucleus, a 2,4-imidazolidinedione nucleus, a 2-thio-2,4-imidazolidinedione nucleus, and a 5-imidazolinone nucleus, with a compound selected from those represented by the following general formula:

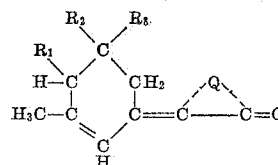


wherein R represents an alkyl group containing from 1 to 8 carbon atoms, n represents a positive integer of from 1 to 2, X represents an acid radical, D₁ represents a member selected from the group consisting of an alkylmercapto group containing from 1 to 2 carbon atoms, an arylmercapto group containing from 6 to 7 carbon atoms, a β-acylanilidovinyl group wherein the acyl radical contains from 2 to 7 carbon atoms, and a δ-acylanilido-1,3-butadienyl group wherein the acyl radical contains from 2 to 7 atoms, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thianaphtheno-7',6',4,5-thiazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a thiazoline nucleus, a 2-quinoline nucleus, a 4-quinoline nucleus, a 1-isoquinoline nucleus, a benzimidazole nucleus, a 3,3-dialkylindolenine nucleus, a 2-pyridine nucleus, and a 4-pyridine nucleus.

2. A process as defined in claim 1 wherein the basic condensing agent is a trialkylamine.

3. A process as defined in claim 2 wherein the trialkylamine is triethylamine.

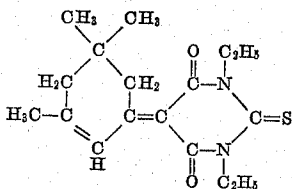
4. An intermediate useful in the preparation of polymethine dyes selected from those represented by the following general formula:



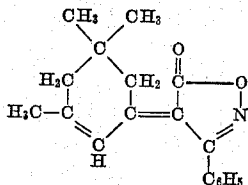
wherein R₁ represents a member selected from the group consisting of a hydrogen atom and a carbalkoxyl group containing from 2 to 3 carbon atoms, R₂ and R₃ each represents a member selected from the group consisting of a hydrogen atom and a lower alkyl group, and Q represents the non-metallic atoms necessary to complete a nucleus selected from the group consisting of an indandione nucleus, a pyrazolone nucleus, an isoxazolone nucleus, an oxindole nucleus, a 2,4,6-triketohexahydropyrimidine nucleus, a 2-thio-2,4,6-triketohexahydropyrimidine nucleus, a rhodanine nucleus, a 2(3H)-imidazo[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a thianaphthenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a 4-thiazolinone nucleus, a 2-imino-2,4-oxazolinone nucleus, a 2,4-imidazolidinedione nucleus, a 2-thio-2,4-imidazolidinedione nucleus, and a 5-imidazolinone nucleus.

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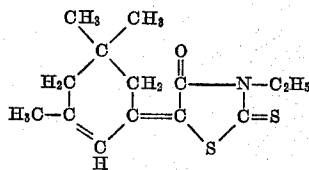
5. The compound represented by the following formula:



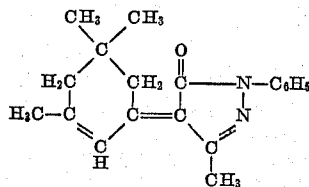
6. A compound represented by the following formula:



7. The compound represented by the following formula:

14

8. The compound represented by the following formula:



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