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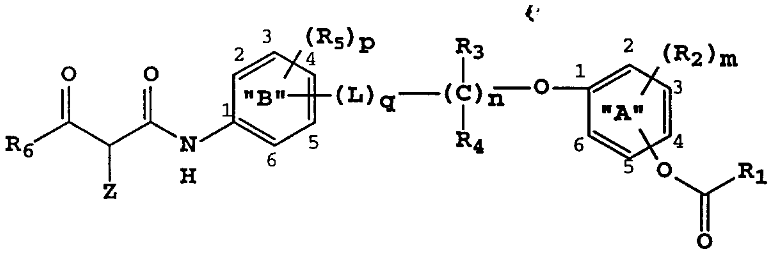
(54) Photographic element containing yellow dye-forming coupler comprising a dye light stability enhancing ballast and process

(57) A photographic element comprises a light sensitive silver halide emulsion layer having associated therewith an open chain α-carbonyl acetanilide yellow dye-forming coupler having the formula:



wherein

R_1 is selected from the group consisting of alkyl, aryl, heterocyclic, and amino groups, provided that R_1 may form a ring bonded to another carbon atom which is a member of Ring "A";
each R_2 is independently selected from the group consisting of those substituents having a Hammett's sigma value of 0 or less, and m is from 0 to 4;
each R_3 and R_4 for each of the n carbon atoms is independently selected from the group consisting of hydrogen, alkoxy, aryl, heterocyclic, aryloxy, and alkyl groups, and n is 0 to 16;
each R_5 is independently selected from the group consisting of halogen, amino, alkyl groups, and groups linked to the "B" ring by oxygen or sulfur, and p is 1 to 3, provided that two R_5 groups may join to form a ring;
each L is independently a divalent linking group and q is 0 to 3; and
Ring "A" is bonded indirectly to the 3-, 4-, or 5-position of Ring "B",
R_6 is selected from the group consisting of alkyl, aryl, and amino groups; and (1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:
(a) an aryloxy or arylthio group;
(b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and
(c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom

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in the triazole group; and

(2) when no R_5 is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent.

Description

Field of the Invention

This invention relates to color photographic materials or elements comprising a yellow dye-forming coupler which forms a dye upon development which exhibits improved stability against dye fade upon exposure to light.

Background of the Invention

A typical photographic element contains multiple layers of light-sensitive photographic silver halide emulsions with one or more of these layers being spectrally sensitized to blue light, green light, and red light, respectively. The blue, green, and red light sensitive layers will typically contain yellow, magenta or cyan dye forming couplers, respectively.

For forming color photographic images, the color photographic material is exposed imagewise and processed in a color developer bath containing an aromatic primary amine color developing agent. Image dyes are formed by the coupling reaction of these couplers with the oxidized product of the color developing agent. Generally, image couplers are selected to provide image dyes with good stability towards heat and light and which desirably have an absorption curve with a suitable peak absorption and low unwanted side absorptions in order to provide color photographic images with good color reproduction.

The present invention is concerned with improving the light stability of yellow image dyes. Couplers that form yellow dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,298,443, 2,407,210, 2,875,057, 3,048,194, 3,265,506, 3,447,928, 4,022,620, 4,443,536, and "Farbkuppler-eine LiteratureUbersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Other examples of yellow dye-forming couplers are detailed in Research Disclosure No. 365, Item 36544, September 1994, Section X-B(6). Such couplers are typically open chain ketomethylene compounds.

The ability of yellow image dyes to resist light fade is important to the longevity of color images, especially those which are destined to be subject to constant daylight exposure such as professional portraits and the like. Yellow images will fade and images formed with yellow dye as a component may change color if the rate of fade for the yellow dye is not sufficiently matched with the other dyes of the photographic element.

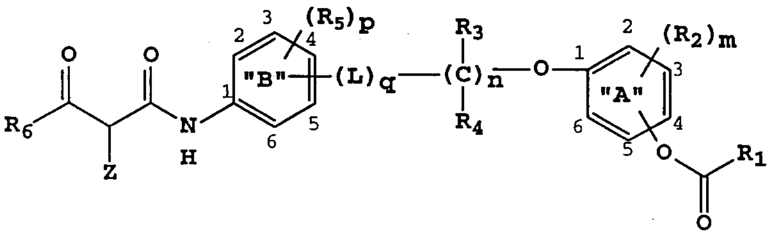
Heretofore, one method of improving the light stability of yellow image dyes has been to add one or more stabilizing addenda to the coupler dispersion. Compounds suitable for this purpose are described more fully in Research Disclosure No. 365, Item 36544, September 1994, Section X-D. Examples of suitable such compounds are shown as Compounds 1, 2, and 3 and P1 in conjunction with Table IV.

U.S. Patent No. 4,248,962 relates to a pyrazolotriazole magenta dye-forming coupler designed to release a photographically useful group upon coupling. The patent proposes a timing group which will undergo an intramolecular nucleophilic displacement reaction to release a photographically useful group. Among the many proposed couplers is one (coupler 44) which contains a ballast having an acetate substituent on a phenoxy group connected through a linking group to a phenyl ring in the ballast. There is no indication that any dye light stability is inferred by the presence of the particular ballast employed in that example.

A problem to be solved is to provide a yellow image dye-forming coupler which forms a dye upon development which exhibits improved stability upon exposure to light. Desirably, the coupler is one for which the dye light stability may be further improved by the addition of a stabilizing addenda.

Summary of the Invention

The invention provides a photographic element comprising a light sensitive silver halide emulsion layer having associated therewith an open chain α-carbonyl acetanilide yellow dye-forming coupler having the formula:



wherein

R_1 is selected from the group consisting of alkyl, aryl, heterocyclic, and amino groups, provided that R_1 may form a ring bonded to another carbon atom which is a member of Ring "A";

each R_2 is independently selected from the group consisting of those substituents having a Hammett's sigma value of 0 or less, and m is from 0 to 4;

each R_3 and R_4 for each of the n carbon atoms is independently selected from the group consisting of hydrogen, alkoxy, aryl, heterocyclic, aryloxy, and alkyl groups, and n is 0 to 16;

each R_5 is independently selected from the group consisting of halogen, amino, alkyl groups, and groups linked to the "B" ring by oxygen or sulfur, and p is 1 to 3, provided that two R_5 groups may join to form a ring;

each L is independently a divalent linking group and q is 0 to 3; and

Ring "A" is bonded indirectly to the 3-, 4-, or 5-position of Ring "B",

R_6 is selected from the group consisting of alkyl, aryl, and amino groups; and

(1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:

(a) an aryloxy or arylthio group;

(b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and

(c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group; and

(2) when no R_5 is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent.

The photographic element of the invention forms a yellow image dye which exhibits an improved stability to light degradation. The invention also encompasses an image-forming process using the coupler and the coupler itself.

Detailed Description of the Invention

The coupler which is the subject of the focus of the present invention is as shown in the Summary of the Invention.

R_1 is the substituent attached to the acyloxy group on the ring "A". It may be an alkyl, aryl, heterocyclic, or an amino group. Also, R_1 may form a ring bonded to another carbon atom which is a member of Ring "A". Particularly suitable are alkyl (including cycloalkyl and branched alkyl), amino, fused alkyl, and aryl groups. Particularly suitable are methyl, isopropyl, fused alkyl, t-butyl, dimethylamino, diethylamino, phenyl, and fused amino.

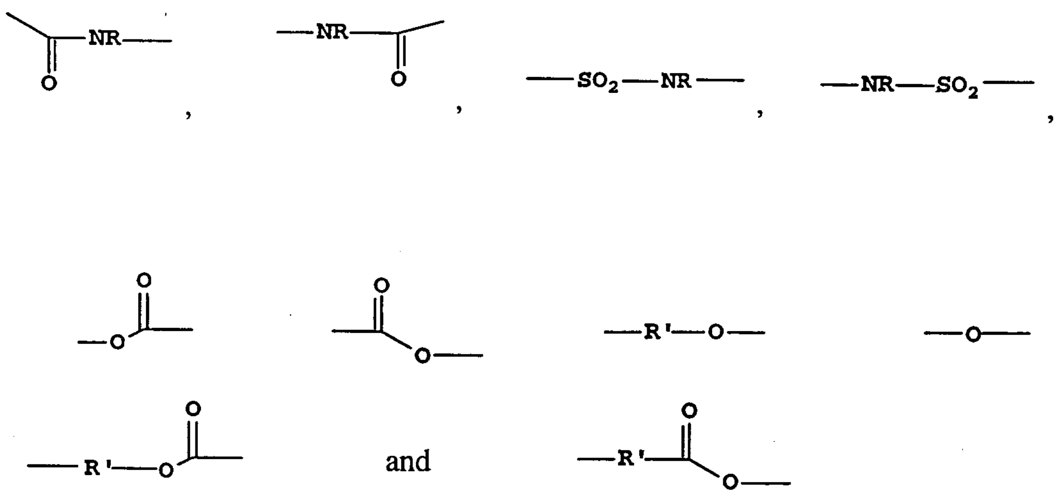
Each R_2 is a substituent on the phenoxy ring "A", and there may be present up to four of these substituents. This substituent may be broadly selected from those substituents which have a Hammett's sigma value of 0 or less. Hammett's sigma values are provided in C. Hansch and A. J. Leo, "Substituent Constants for Correlation Analysis in Chemistry and Biology", Wiley, New York, N.Y., 1979. Generally, values less than 0 indicate that a substituent has an electron donating effect relative to hydrogen. Thus, R_2 is electron donating. It is further provided that at least one R_2 group is located ortho to the acyloxy group containing R_1. Suitably, R_2 is an alkyl, alkoxy or amino compound. Satisfactory compounds include thioalkyl, dialkylamino, and branched alkyl and alkoxy groups. Appropriate examples include t-butyl, t-pentyl, t-octyl, and isopropyl.

Where n>1 the R_3 and R_4 substituents bonded to each of the n carbon atoms may be independently selected. Besides hydrogen, suitable R_3 and R_4 substituents may include alkyl, alkoxy (including polyalkoxy), aryl, aryloxy, heterocyclic, and amino groups. Alkyl or alkoxy groups of 1-18 carbon atoms and hydrogen are satisfactory substituents. If desired, R_3 or R_4 may form a ring with another R_3 or R_4 group.

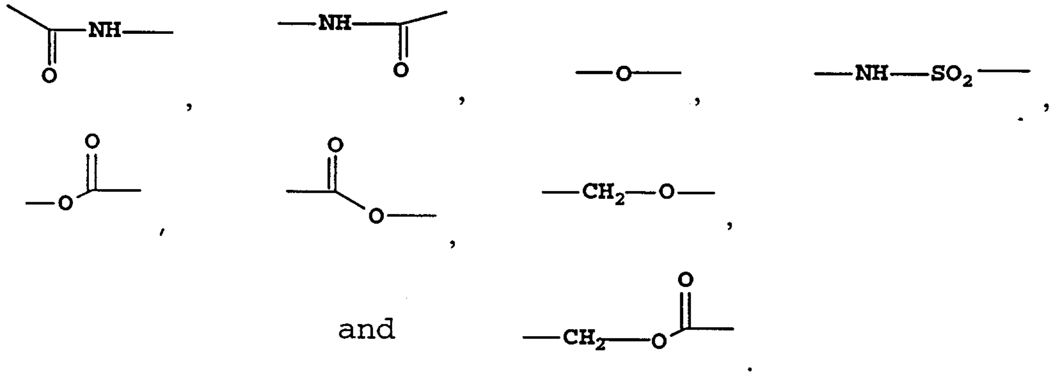
R_5 is a substituent which may or may not be present as indicated by the subscript "p". Each R_5 is a substituent which may be a halogen, an amino group, an alkyl group, or a group linked to the "B" ring by an atom of oxygen or sulfur. Suitably, one or more of the R_5 substituents may occupy the 2-, 4-, or 6- position of the ring "B". Suitably, R_5 may be bonded to the ring "B" by an acyloxy, alkylthio, alkyl, amino, or oxy group. Particularly suitable groups are alkylacyloxy, arylacyloxy, trifluoromethyl, alkylthio, alkoxy, aryloxy, alkyl, or amino groups. The value of "p" may range from 0 to 3.

R_6 may comprise an aliphatic or aromatic group. Suitably, R_6 may be an amino group, an alkyl group, a carbocyclic group, or heterocyclic group having an atom of nitrogen, sulfur, oxygen, or phosphorus in the ring. More suitably, R_6 may be a secondary or tertiary alkyl group, a phenyl group, a phenyl amino group, or an alkyl amino group. Typically, the secondary alkyl group may be an isopropyl group, the tertiary alkyl group may be t-butyl, t-pentyl, t-octyl, or 1-methyl-1-cyclopropyl. The phenyl group may be phenyl or phenyl substituted, for example, with alkoxy, alkyl or amido groups. The heterocyclic ring may be a pyrolidino or indolino group and the amino may be a phenylamino or alkylamino group.

The group L is optionally present. As indicated by the value of q of up to three, there may be present as many as three L groups. Each of the L groups may be independently selected to provide a linkage between the ring "B" and the remainder of the coupler. In the broadest sense, L may be any divalent group linking the ballast directly or indirectly with a noncoupling position of the rest of the coupler. Each L may be represented, for example, by one of the groups:



wherein R is hydrogen or an alkyl group and R' is an alkylene group. Specifically useful are:



With regard to Z, (1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:

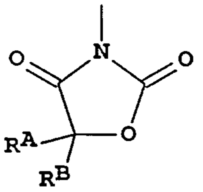
(a) an aryloxy or arylthio group;

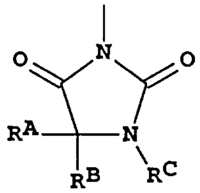
(b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and

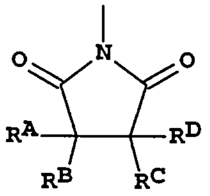
(c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group; and

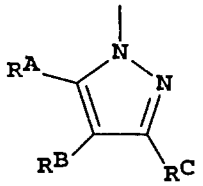
(2) when no R_5 is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent. In the latter case, any suitable coupling-off group of the art may be employed as described more fully hereafter. Typical such group include aryloxy, arylthio and nitrogen heterocyclic groups. If desired, the coupling-off group may include a so-called timing group together with a photographically useful group ("PUG") which can permit the PUG to diffuse away from the coupler's initial location to perform a function such as inhibiting development, assisting bleaching etc. Such groups are more fully described hereafter.

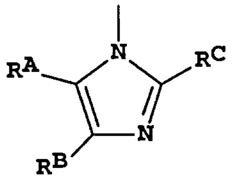
It is suitable that the group Z represents a heterocyclic group containing, a nitrogen atom in a five or six membered ring, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring. Examples of such a heterocyclic group contain one or more nitrogen atoms in the ring and possibly an oxygen atom. The use of dione formulas is convenient. Examples of suitable groups are pyrazole, imidazole, hydantoin, urazole, and oxazole groups such as the following:

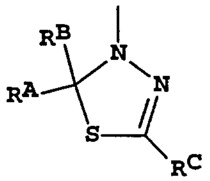


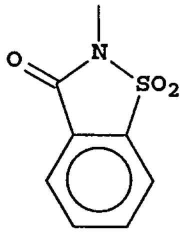


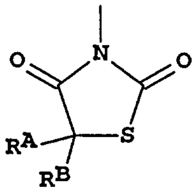


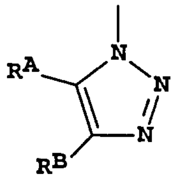


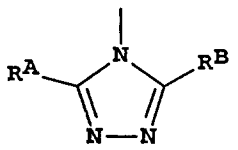












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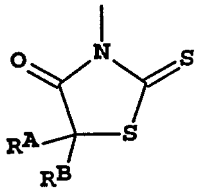
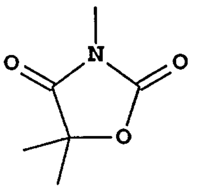
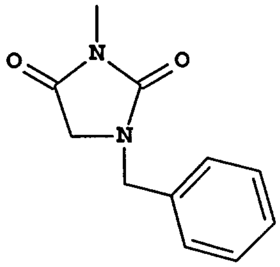
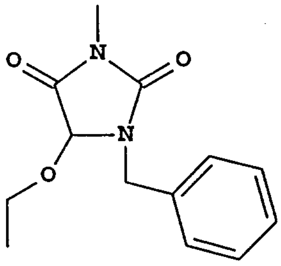
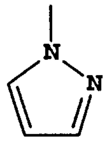


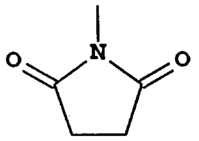
wherein each R^A, R^B,R^C and R^D is an independently selected group such as hydrogen, or an alkyl (e.g. methyl, ethyl ,propyl, phenylmethyl, sulfonamidoalkyl), aryl, or alkoxy (e.g. methoxy, ethoxy) group. Particularly useful as Z are the following:

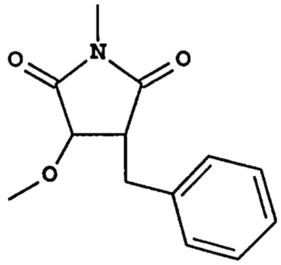


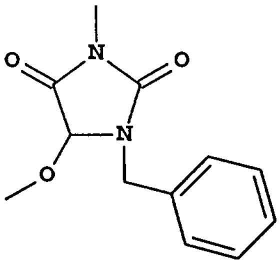












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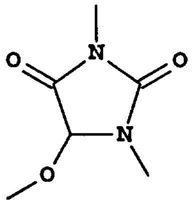

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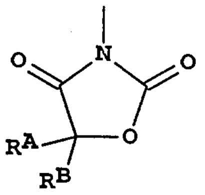
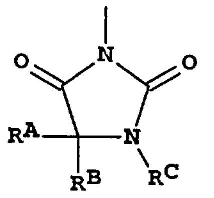
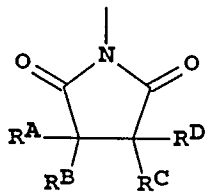
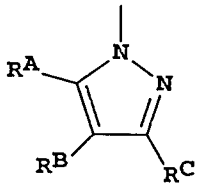
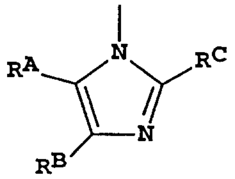
When an R_5 is halogen, group Z may represent a heterocyclic group containing in a five or six membered ring one or two nitrogen atoms and possibly an oxygen atom, where the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring. The use of dione formulas is convenient. Examples of suitable groups are pyrazole, imidazole, hydantoin, succinimide, thiazole, thiazolidino, thiadiazole, saccharin, rhodanine, and oxazole groups such as the following:

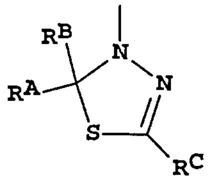


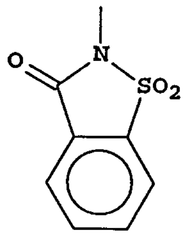


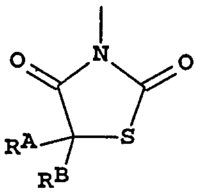












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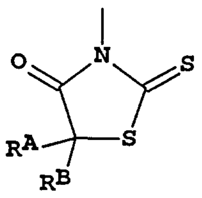


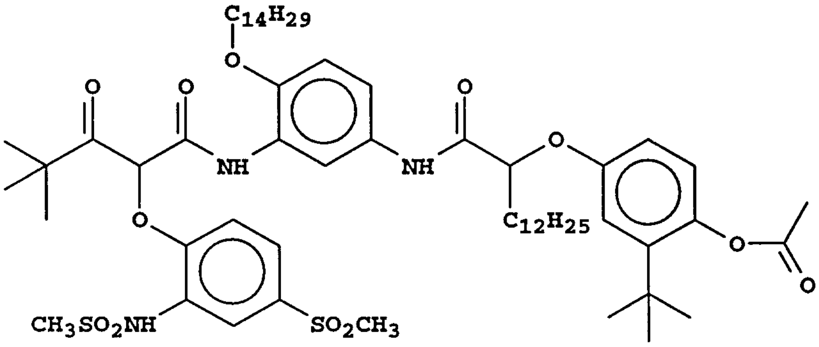
wherein each R^A, R^B,R^C and R^D is an independently selected group such as hydrogen, or an alkyl (e.g. methyl, ethyl ,propyl, phenylmethyl, sulfonamidoalkyl), aryl, or alkoxy (e.g. methoxy, ethoxy) group.

When it is desired to release a development inhibitor group, a benzotriazole group is useful as Z.

Other useful coupling-off groups are arylthio such as phenylthio groups and aryloxy such as phenoxy groups.

Examples of suitable couplers of the invention are as follows:

Y-1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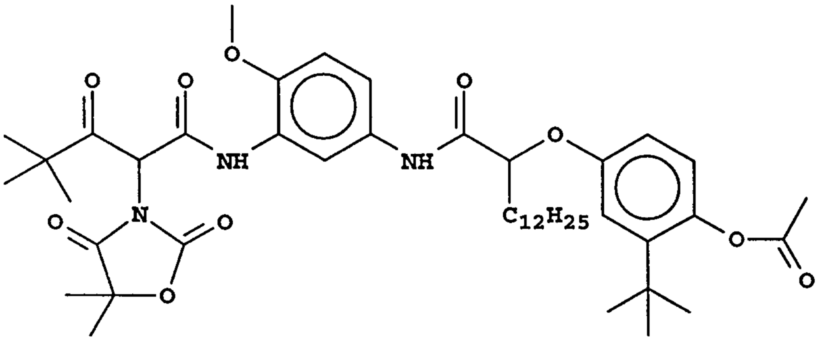
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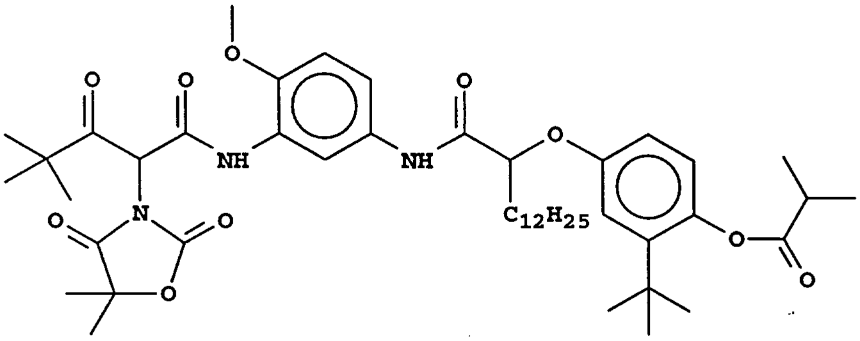
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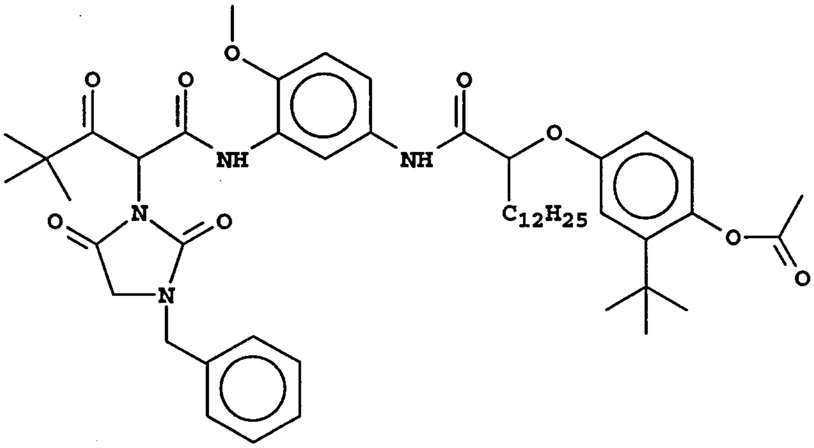
Y-4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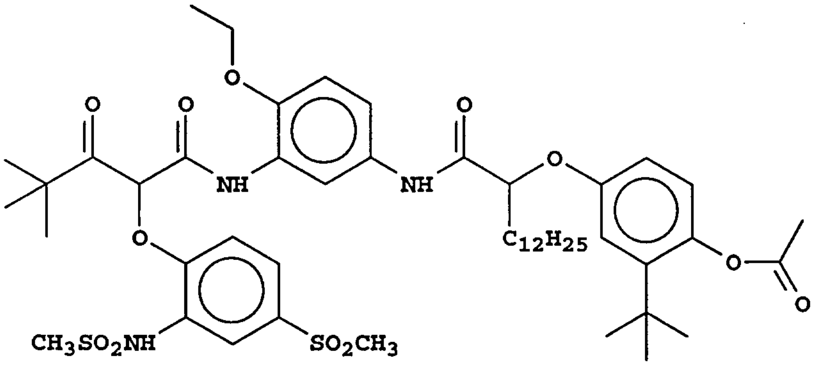
Y-5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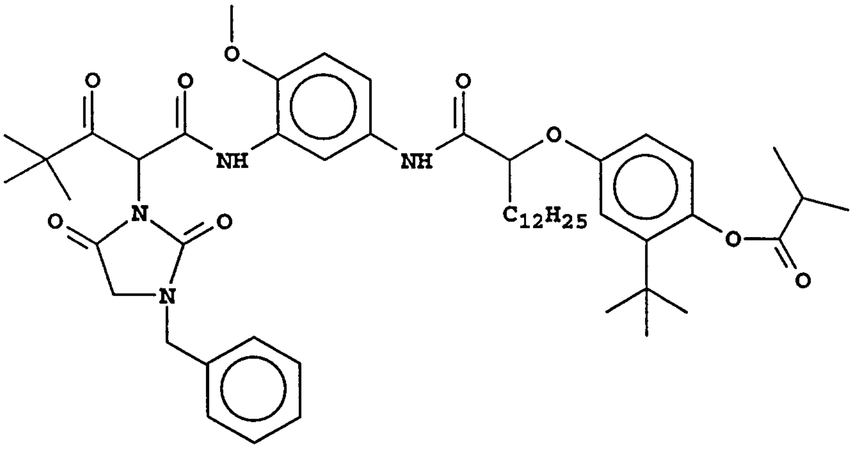
Y-6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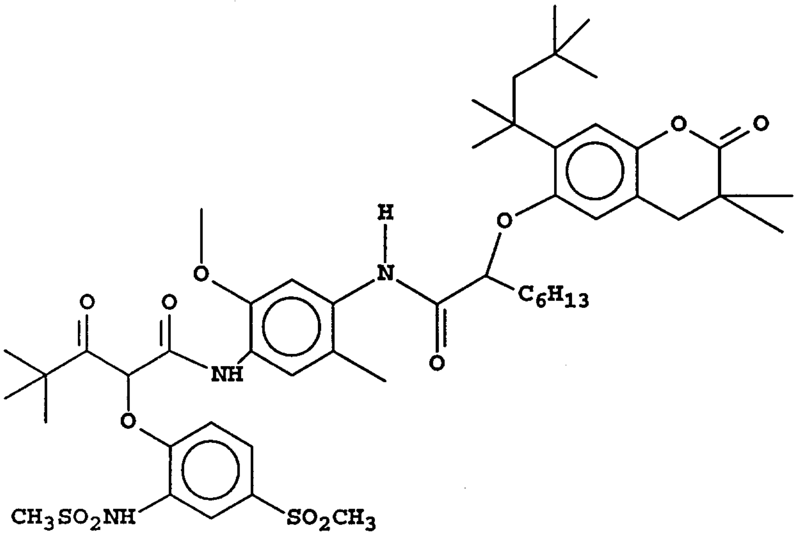
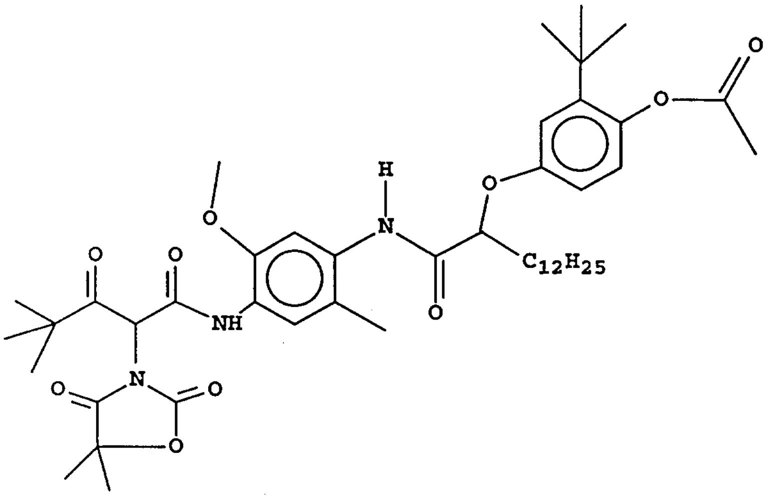
Y-7



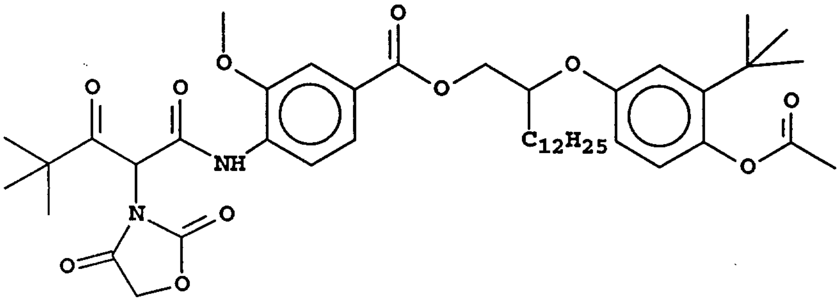
H
N
O
O
O
O
NH
O
O
C6H13
O
CH3SO2NH
SO2CH3

Y-8



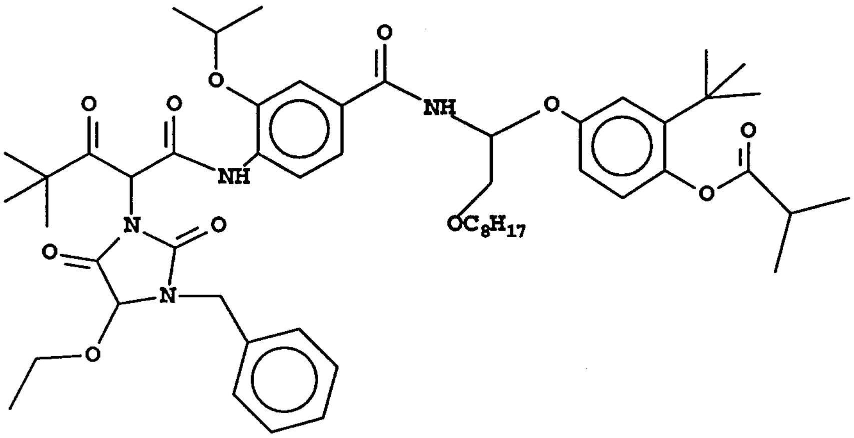
H
N
O
O
O
O
NH
O
C12H25
N
O
O
O

Y-9

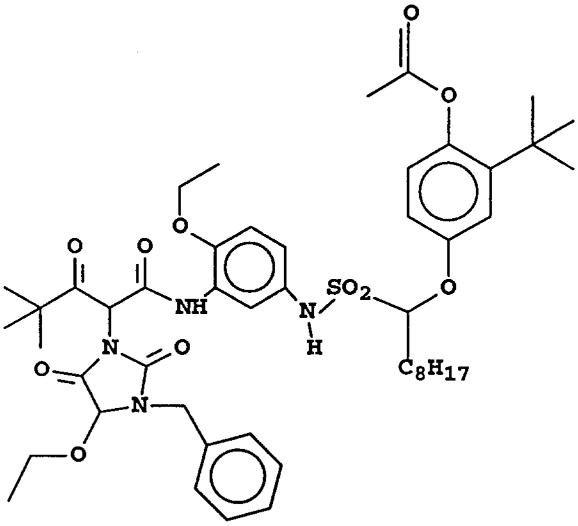


O
O
O
O
O
NH
O
C12H25
O
O
N
O
O
O

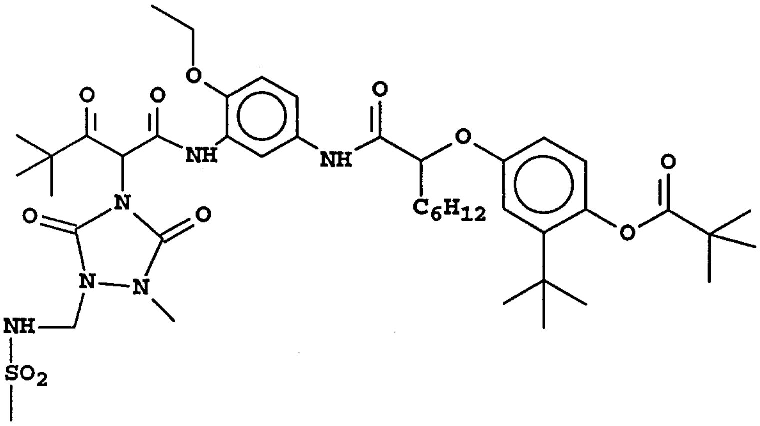
Y-10


O
O
O
O
NH
NH
O
O
O
N
O
O
N
O
OC8H17

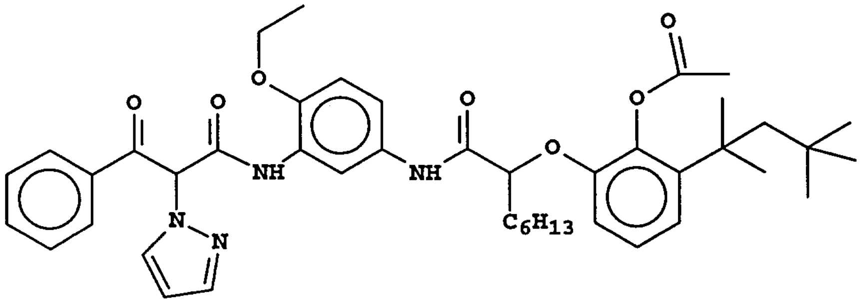
Y-11


O
O
O
O
O
NH
SO2
N
H
O
N
O
O
N
O
C8H17

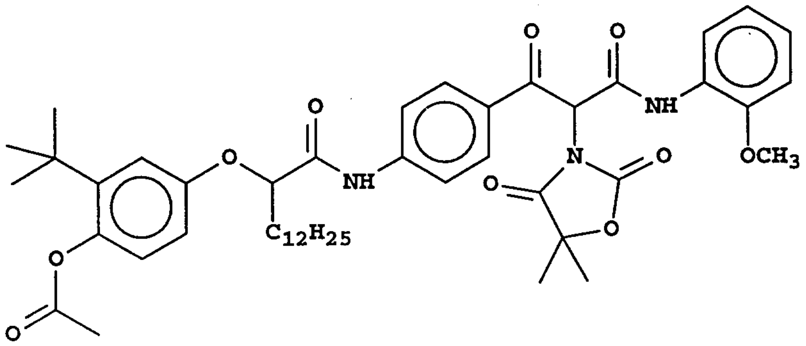
Y-12


O
O
O
NH
O
NH
O
N
O
O
N
N
NH
SO2
C6H12
O
O

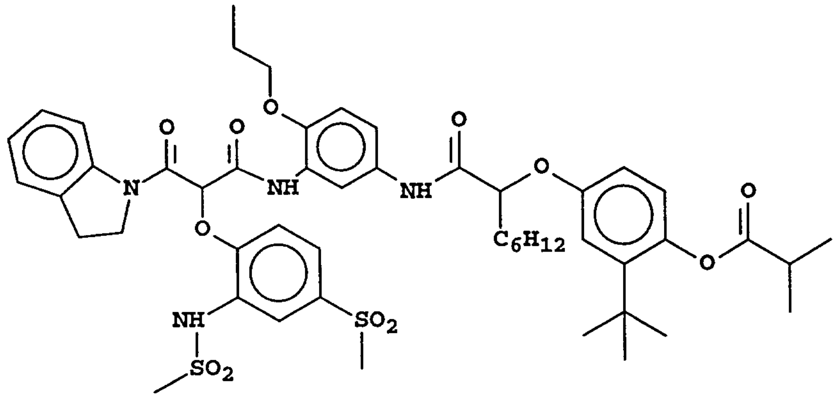
Y-13



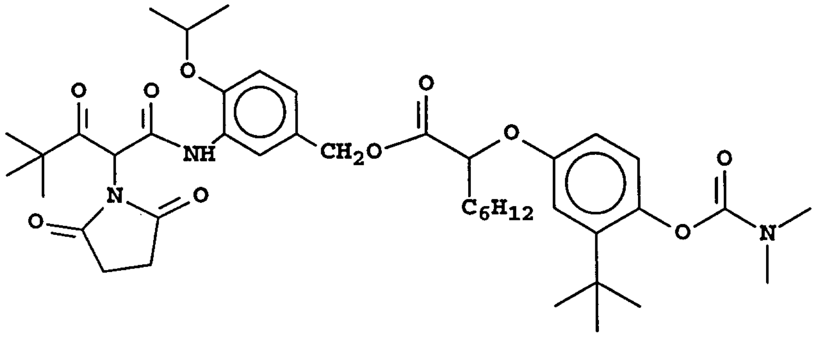
Y-14



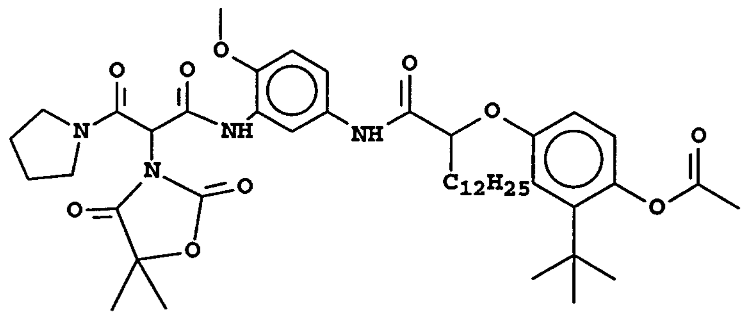
Y-15



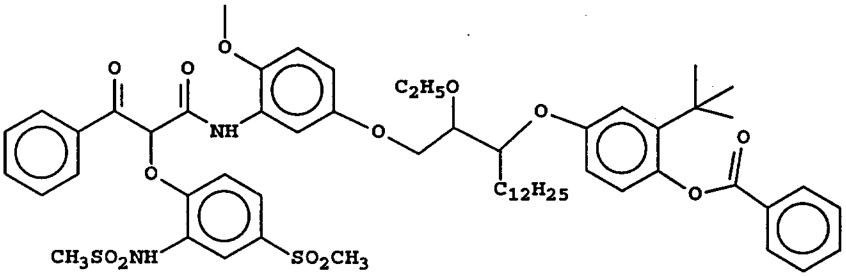
Y-16



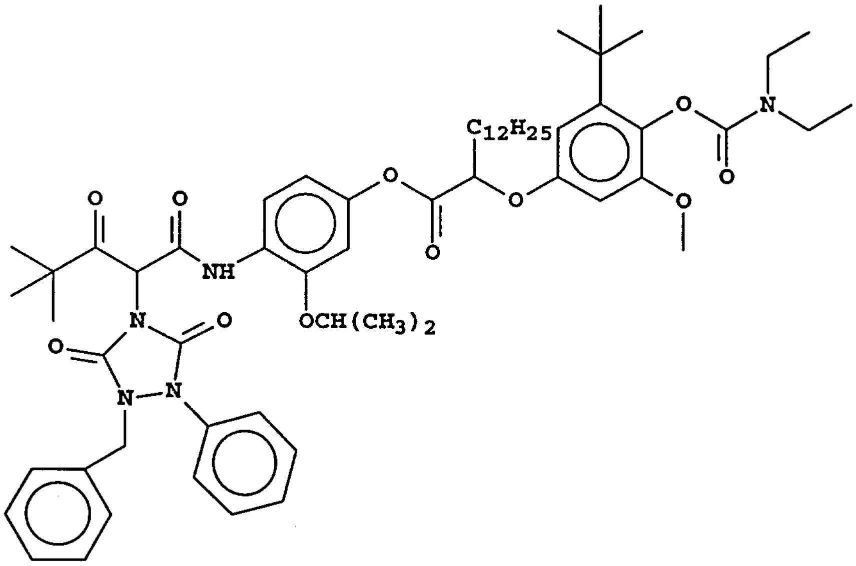
Y-17


C12H25
NH
NH
N
N
O

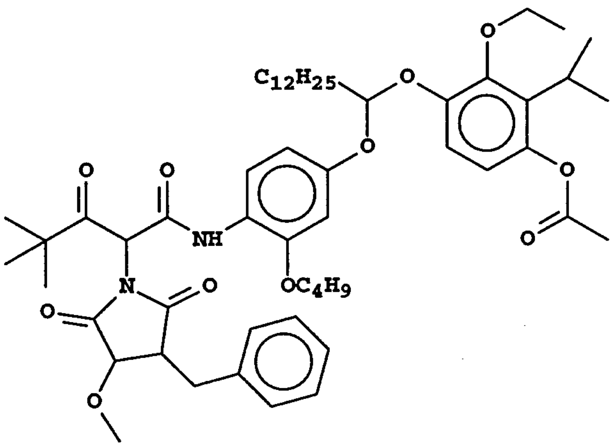
Y-18


C2H5O
C12H25
NH
CH3SO2NH
SO2CH3

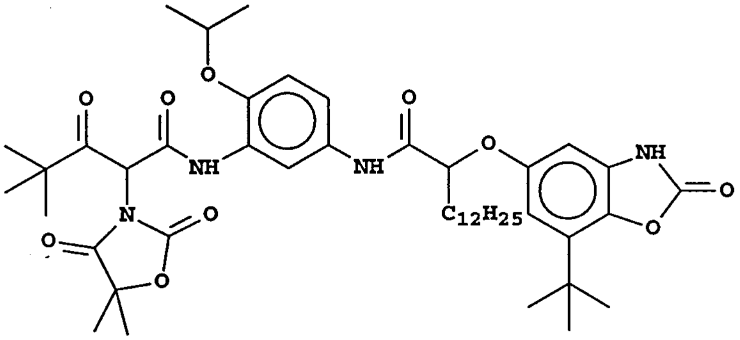
Y-19


C12H25
NH
OCH(CH3)2
N
N
N

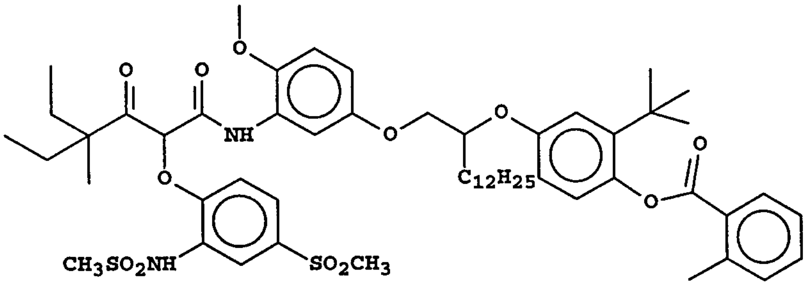
Y-20



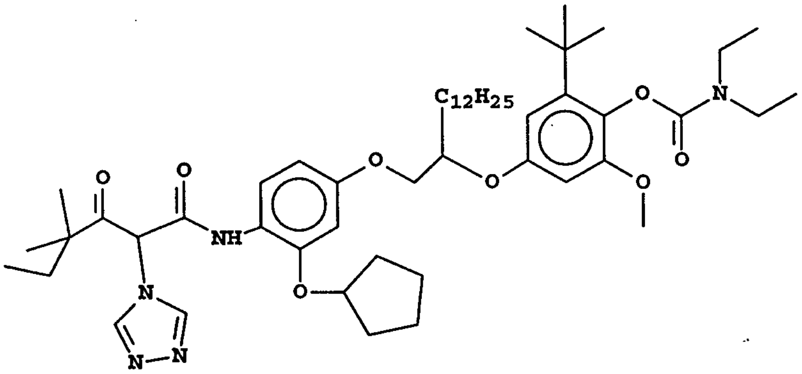
Y-21



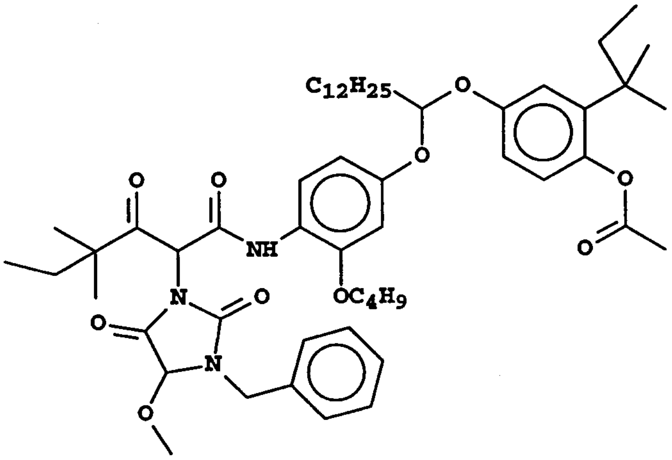
Y-22



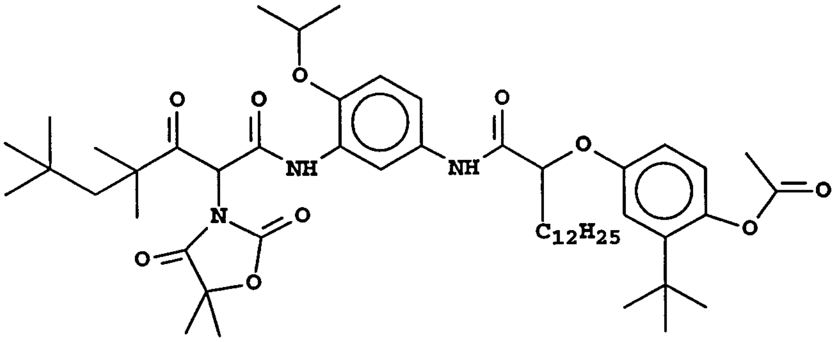
Y-23



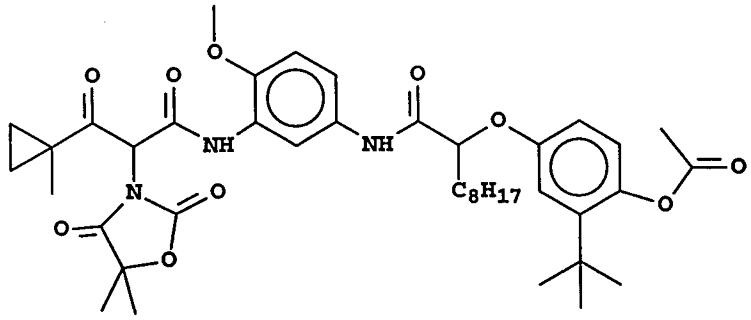
Y-24



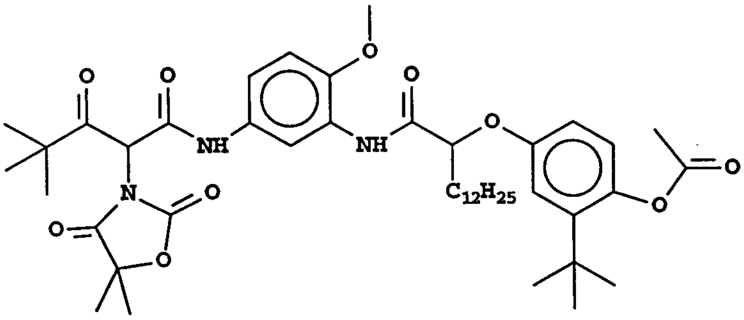
Y-25



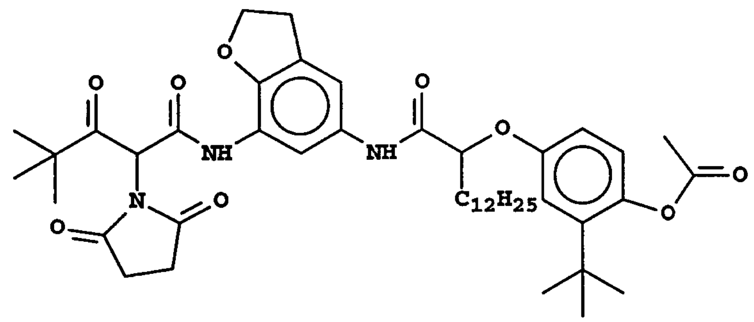
Y-26



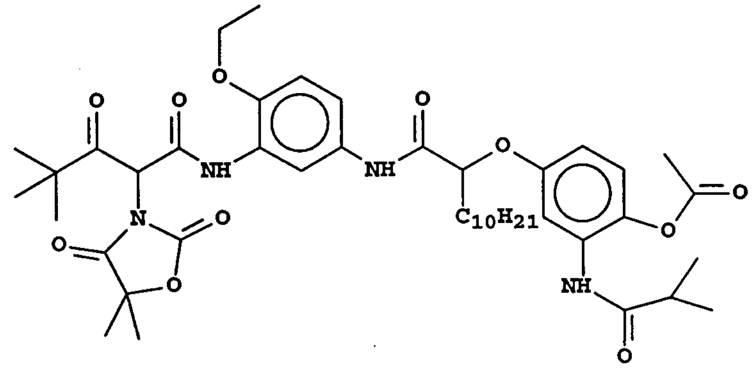
Y-27



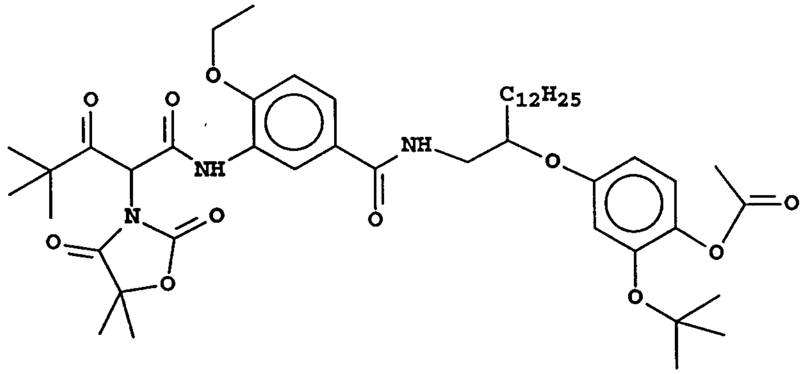
Y-28



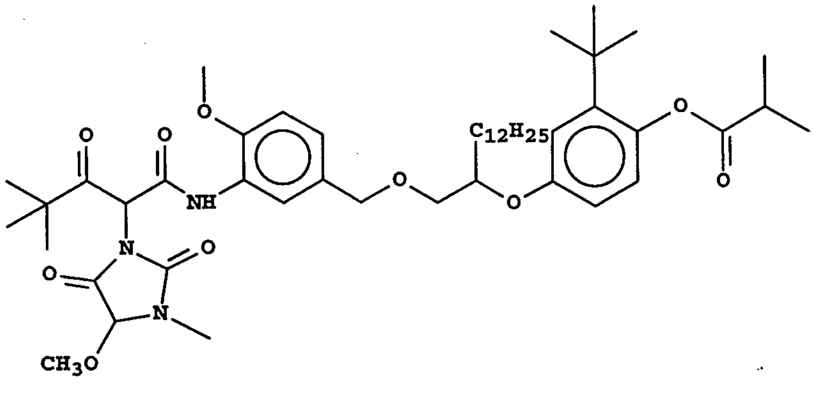
Y-29



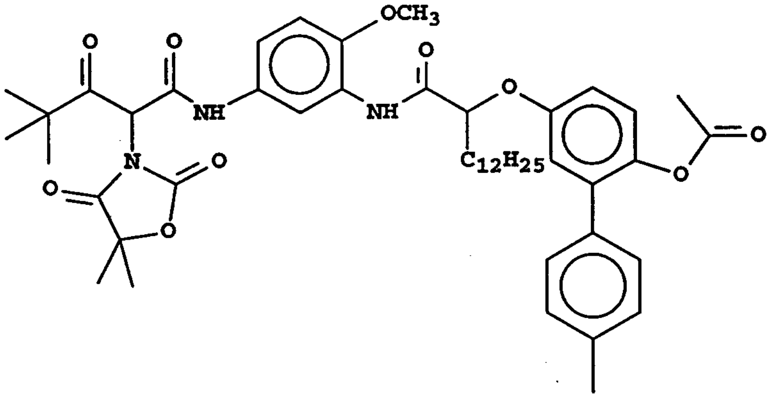
Y-30



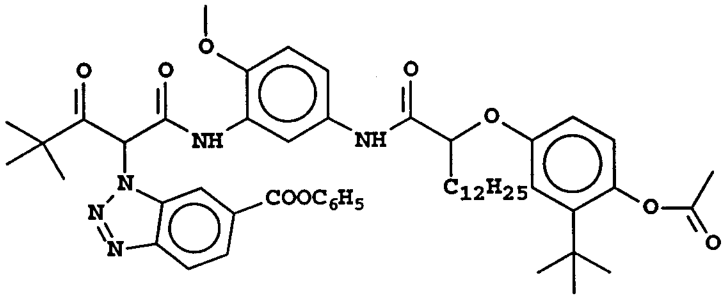
Y-31



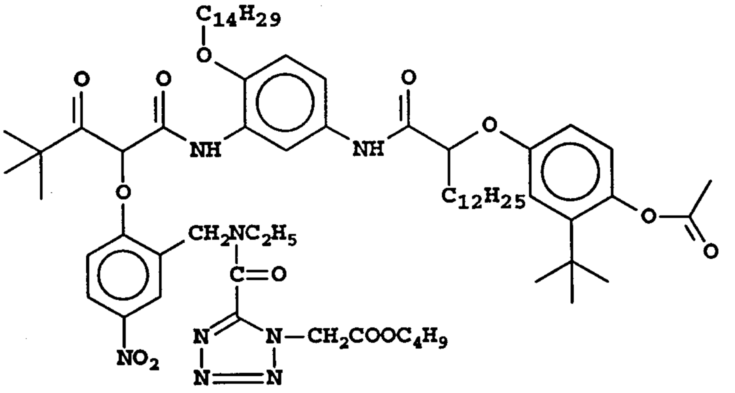
Y-32



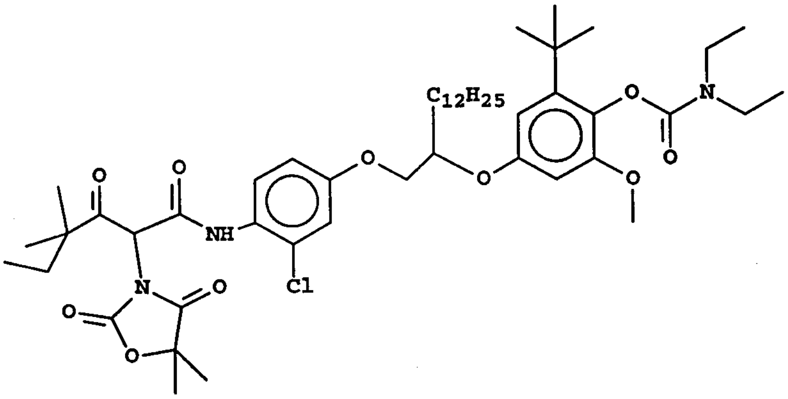
Y-33



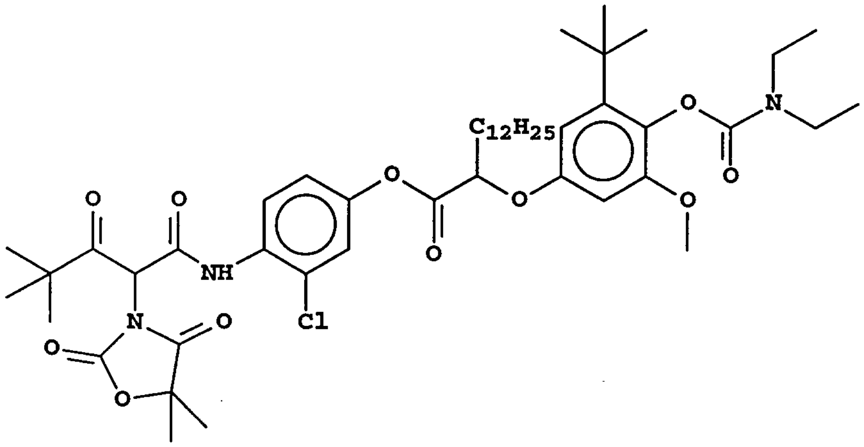
Y-34



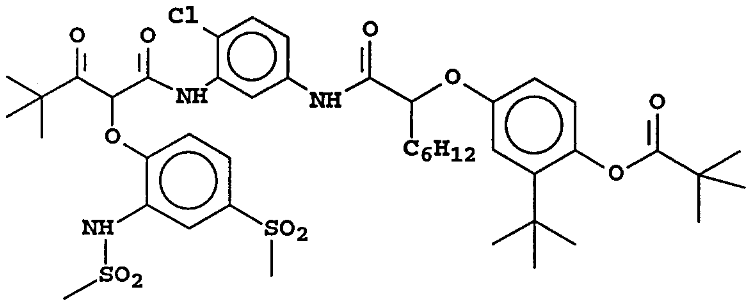
Y-35



Y-36



Y-37



Unless otherwise specifically stated, substituent groups which may be substituted on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any group or groups as herein mentioned. Suitably, the group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, or sulfur. The substituent may be, for example, halogen, such as chlorine, bromine or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-t-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-t-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyloxy, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentyl-phenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-t-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecylphenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N,N-dimethylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropylsulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; carbonyl, such as acetyl, (2,4-di-t-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl methoxycarbonyl, butoxycarbonyl, tetradecyloxycarbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxycarbonyl, and dodecyloxycarbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-toluylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-t-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbonyloxy; amine, such as phenylanilino, 2-chloroanilino, diethylamine, dodecylamine; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups, etc. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

If desired, the photographic element can be used in conjunction with an applied magnetic layer as described in Research Disclosure, November 1992, Item 34390 published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND, and as described in Hatsumi Kyoukai Koukai Gihou No. 94-6023, published March 15, 1994, avaliable from the Japanese Patent Office, the contents of which are incorporated herein by reference. When it is desired to employ the inventive materials in a small format film, Research Disclosure, June 1994, Item 36230, provides suitable embodiments.

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, September 1994, Item 36544, available as described above, which will be identified hereafter by the term "Research Disclosure". The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

Except as provided, the silver halide emulsion containing elements employed in this invention can be either negative-working or positive-working as indicated by the type of processing instructions (i.e. color negative, reversal, or direct positive processing) provided with the element. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through V. Various additives such as UV dyes, brighteners, antifoggants, stabilizers, light absorbing and scattering materials, and physical property modifying addenda such as hardeners, coating aids, plasticizers, lubricants and matting agents are described, for example, in Sections II and VI through VIII. Color materials are described in Sections X through XIII. Scan facilitating is described in Section XIV. Supports, exposure, development systems, and processing methods and agents are described in Sections XV to XX. Desirable photographic elements and processing steps including other components suitable for use in photographic elements of the invention are also described in Research Disclosure, Item 37038, February 1995.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England, incorporated herein by reference.

With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known Kodak C-41 color process as described in The British Journal of Photography Annual of 1988, pages 191-198. Where applicable, the element may be processed in accordance with color print processes such as the RA-4 process of Eastman Kodak Company as described in the British Journal of Photography Annual of 1988, Pp 198-199. Such negative working emulsions are typically sold with instructions to process using a color negative method such as the mentioned C-41 or RA-4 process. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. Such reversal emulsions are typically sold with instructions to process using a color reversal process such as E-6. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Preferred color developing agents are p-phenylenediamines such as:

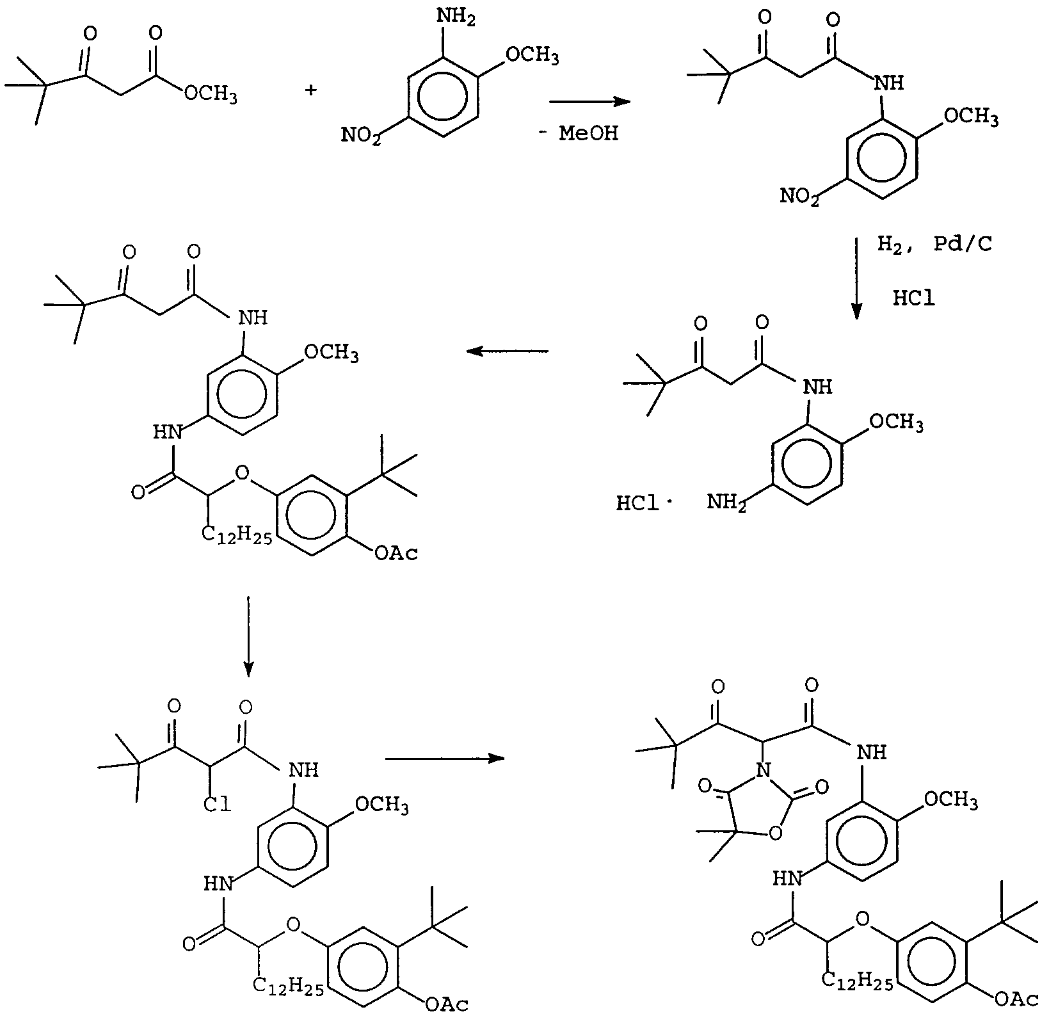
4-amino-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline sesquisulfate hydrate,
4-amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline sulfate,
4-amino-3-(2-methanesulfonamido-ethyl)-N,N-diethylaniline hydrochloride and
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

Development is usually followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

The entire contents of the various patent applications, patents and other publications referred to in this specification are incorporated herein by reference.

Synthetic Example

The synthesis of the couplers of the invention is accomplished using conventional reactions. The following is a typical method for preparing coupler Y-2 of the invention which may be employed in an analogous manner to prepare other couplers of the invention.



Synthesis of Example Yellow Coupler Y-2:

Preparation of 2-(4,4-dimethyl-3-oxovaleramido)-4-nitroanisole.

Methyl-4,4-dimethyl-3-oxovalerate (15.8 g, 0.1 mol) and 2-methoxy-5-nitroaniline (16.8 g, 0.01 mol) were taken up in toluene (150 mL) in a round bottomed flask fitted with a Dean-Stark trap. The mixture was heated to a vigorous reflux while the MeOH side-product was distilled off and removed. After 4 hours, the mixture was cooled and the toluene removed *in vacuo.* The residue was recrystallized from acetonitrile to yield 27 g of the desired condensation product.

Preparation of 2-(4,4-dimethyl-3-oxovaleramido)-4-aminoanisole hydrochloride.

A solution of 2-(4,4-dimethyl-3-oxo-valeramido)-4-nitroanisole (20 g) in EtOH (100 mL) with 1 g Pd/C was catalytically reduced under hydrogen to give the corresponding amine in quantitative yield. After filtering the mixture, HCl gas was bubbled through the solution. Upon cooling, white crystals of 2-(4,4-dimethyl-3-oxo-valeramido)-4-aminoanisole hydrochloride formed. The crystals were collected and dried *in vacuo* to yield 17 g of product.

Preparation of 2-(4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)acetamido]anisole.

A solution of 2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)-acetylchloride (19.4 g, 0.043 mol) in acetonitrile (100 mL) was added to a solution of 2-(4,4-dimethyl-3-oxovaleramido)-4-aminoanisole hydrochloride (13.1 g, 0 043 mol) in acetonitrile (50 mL). Diisopropylethylamine (11.2 g, 0.086 mol) was added dropwise. After 1 hour, EtOAc (100 mL) was added. The mixture was submitted to an aqueous, acidic workup. The organics were dried over MgSO4, filtered and the solvents removed *in vacuo.* The isolated product (27 g) was suitably pure for use in the next step.

Preparation of 2-(2-chloro-4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)acetamido]anisole.

To a solution of 2-(4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)acetamido]anisole (25.0 g, 0.0367 mol) in dichloromethane (150 mL) was added sulfuryl chloride (2.9 mL, 0.0367 mol). The mixture was stirred for 30 minutes at room temperature. The solvent was removed *in vacuo.* The product was formed quantitatively and was suitably pure for use in the next reaction.

Preparation of 2-[4,4-dimethyl-2-(4,4-dimethyloxazolidinedione)-3-oxovaleramido]-4-[2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)-acetamido]anisole.

A solution of 2-(2-chloro-4,4-dimethyl-3-oxovaleramido)-4-[2-dodecyl-2-(4-aceto-3-*tert*-butylaryloxy)-acetamido]anisole (15.0 g, 0.021 mol), 4,4-dimethyloxazolidinedione (3.4 g, 0.026 mol) and triethylamine (2.2g, 0.023 mol) in acetonitrile (200 mL) was stirred and heated to reflux. After 4 hours, the mixture was cooled to room temperature and submitted to aqueous, acidic workup. The organics were extracted into EtOAc, dried over MgSO4, filtered and the solvent stripped *in vacuo.* The residue was recrystallized from isopropyl ether to yield 15.2 g (90%) of the desired yellow coupler. The results of NMR analysis were consistent with the compound Y-2. 1H NMR (CDCl3/TMS): d = 0.9 (t, 3 H), 1.4 (m, 46 H), 2.3 (s, 3H), 3.9 (s, 3 H), 4.6 (t, 1 H), 5.6 (s, 1 H), 6.9 (m, 4H), 7.8 (d, 1 H), 8.1 (m,br, 2 H), 9.0 (s, 1H). MS (FDMS) m/e = 807

C45 H65 N3 O10			
calc	66.89	H 8.11	N 5.2
found	66.85	H 8.01	N 5.0

Photographic Examples

Preparation of Photographic Elements

Dispersions of the couplers were prepared in the following manner, exemplified with representative coupler Y2. In one vessel, 1.55 g of the coupler, Y2, 0.72g of dibutyl phthalate, 0.6g of 2-(2-butoxyethoxy)ethyl acetate and 4.6g of ethylacetate were combined and warmed to 60°C to dissolve. In a second vessel, 21.2g of 11.55% gelatin, 2.44g of Alkanol XC™ (surfactant and trademark of E. I. Dupont Co., USA) and 9.62g of water were combined and warmed to 40°C. The two mixtures were combined and passed three times through a Gaulin colloid mill.

The photographic elements were prepared by coating the following layers in the order listed on a resin-coated paper support:

1st layer

Gelatin	3.23 g/m^2

2nd layer

Coupler dispersion	8.8×10^{-4} mole coupling moieties/m^2
AgCl emulsion	0.28g Ag/m^2 and blue-sensitized

3rd layer

Gelatin	1.4 g/m^2
Bis(vinylsulfonylmethyl)ether	0.14 g/m^2

Exposing and processing of Photographic Elements

The photographic elements were subjected to stepwise exposure to blue light and processed as follows at 35° C:

Color Developer	45 seconds
Bleach-Fix	45 seconds
Wash (running water)	90 seconds

The developer and bleach-fix were of the following compositions:

Developer	
Water	700 mL
Triethanolamine	12.41 g
Blankophor REU TM (Mobay Corp)	2.3 g
Lithium polystyrene sulfonate (30%)	0.3 g
N,N-diethylhydroxylamine (85%)	5.4 g
Lithium sulfate	2.7 g
N-{2-[(4-amino-3-methylphenyl)ethylamino]-ethyl}-methanesulfonamide, sesquisulfate	5.0 g
1-hydroxyethyl-1,1-diphosphonic acid (60%)	0.81 g
Potassium carbonate, anhydrous	21.16 g
Potassium chloride	1.6 g
Potassium bromide	7.0 g
Water to make	1.0 L
pH at 26.7°C adjusted to 10.2	

Bleach-Fix	
Water	700 mL
Solution of Ammonium thiosulfate(56.4% plus Ammonium sulfite (4%)	127.4 g
Sodium metabisulfite	10.0 g
Acetic Acid (glacial)	10.2 g
Solution of Ammonium ferric ethylenediaminetetraacetate (44%) + ethylenediaminetetraacetic acid (3.5%)	110.4 g
Water to make	1.0 L
pH at 26.7° C adjusted to 6.7	

Photographic Tests

Yellow dyes were formed upon processing of the photographic elements. The coatings were assessed sensitometrically for the following characteristics:

D-max (the maximum density to blue light),
Dmin (the minimum density to blue light),
Contrast (the ratio of (S-T)/0.6 where S is the density at a log exposure 0.3 units greater than the Speed value, and T is the density at a log exposure 0.3 units less than the Speed value),
Speed (the relative reciprocal of exposure required to yield a density to blue light of 1.0), and
Lambda-max (the wavelength of peak absorption at a density of 1.0).

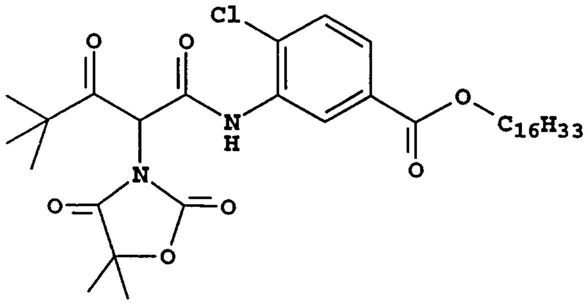
The data is reported in Table I. The data shows that the couplers of the invention are comparable or superior in sensitometry to the comparison couplers.

Table I

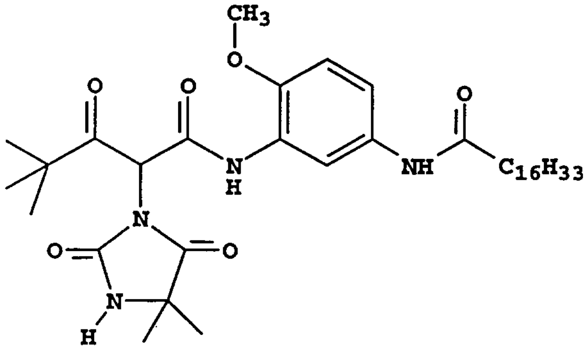
Sensitometric Data						
Coupler	Type	Dmax	Dmin	Contrast	Speed	λmax
Y-1	Inv	2.75	0.06	2.65	182.4	439
Y-2	Inv	2.75	0.09	2.65	188.4	439
Y-3	Inv	2.74	0.08	2.64	198.1	438
Y-4	Inv	2.76	0.09	2.80	199.5	437
Y-5	Inv	2.83	0.05	2.84	186.9	436
Y-6	Inv	2.81	0.08	2.59	197.0	440
C-1	Comp	2.70	0.05	2.55	191.7	446
C-2	Comp	2.62	0.05	2.60	188.2	438
C-3	Comp	2.42	0.06	2.40	177.6	441
C-4	Comp	2.71	0.04	2.51	178.4	442

The comparative couplers were as follows:

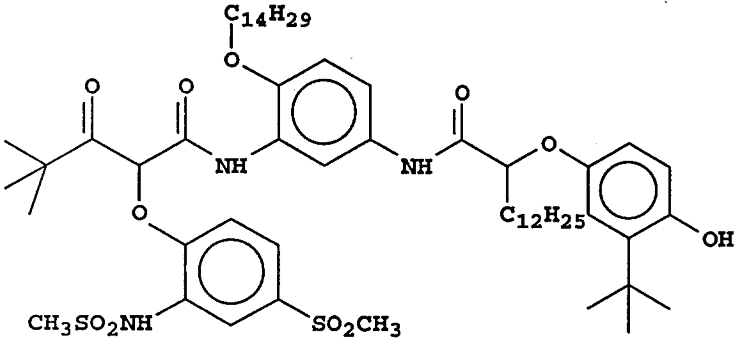
C-1



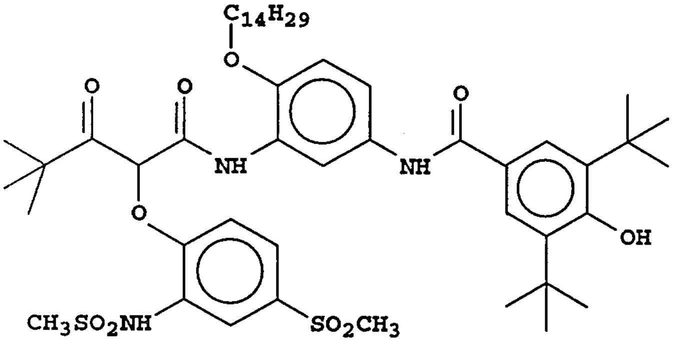
C-2



C-3



C-4



Couplers C-1 and C-2 represent couplers actually in use in commercial photographic film. Couplers C-3 and C-4 are provides as additional comparisons.

Light Stability Test

The coating strips were exposed to a high intensity Xenon light source at a luminous flux level of 50 Klux with a WRATTEN 2C filter interposed between the light source and sample. After 2 weeks and 4 weeks, the strips were removed and the decrease in density from initial densities of 1.7, 1.0 and 0.5 were measured. The data is recorded in Table 2 as a measure of the per cent dye retained for each sample dye. These results compare the light fastness of dyes from couplers of the present invention with those of the comparisons.

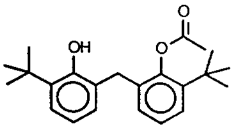
Table II

Coupler	Type	Dye Retained from Initial Density 1.0	
		14-Day	28-Day
Y-1	Inv	96%	85%
Y-2	Inv	96%	86%
Y-3	Inv	91%	79%
Y-4	Inv	91%	82%
Y-5	Inv	94%	79%
Y-6	Inv	95%	85%
C-1	Comp	51%	17%
C-2	Comp	72%	40%
C-3	Comp	78%	40%
C-4	Comp	91%	77%

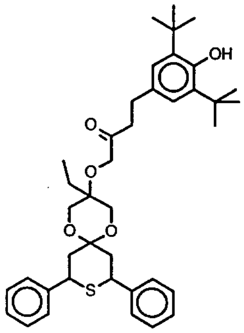
As can be seen from Table II, the couplers of the invention have superior light fastness as compared to couplers C-1 and C-2 typically used in the art and are advantageous over comparisons C-3 and C-4. The amount of dye remaining after exposure averages 82.6% for the inventive couplers compared to an average of 43.5% for the comparative couplers. At 14 days the corresponding values are 93.8 and 73.0, respectively. The inventive couplers are stable enough that they can be used without light stabilizing addenda when a neutral fade position with typical magenta and cyan dyes is desired.

Neutral fade could also be achieved even if extremely stable magenta and cyan dyes were utilized by incorporating light stabilizing addenda along with the yellow couplers of this invention in an analogous photographic format to that described above with the following weight ratios: Yellow coupler : coupler solvent such as dibutylphthalate : auxiliary solvent such as 2-(2-butoxyethoxy)ethylacetate : stabilizer addenda 54:15:18:13. The stabilizer addenda typically used are those exemplified by compounds 1-3 but are not limited to these. Also suitable are polymeric stabilizing addenda. The polymers can be homopolymers or copolymers which are miscible with the coupler and coupler solvent which are present, for example, as a latex or as an organic solution. Especially useful are polymers containing monomers derived from styrene and/or acrylics such as acrylamide (particularly t-butyl acrylamide such as P1 below where x=99 and y=1), acrylates, methacrylamides, and methacrylates.

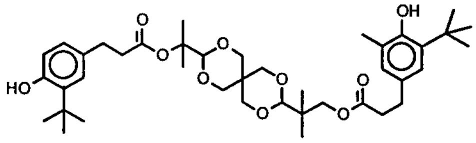
Table III describes 2-week and 4-week light fade data for dyes formed from representative couplers using compound 1 as stabilizing addenda.



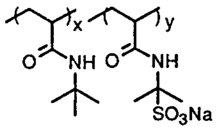
Compound 1



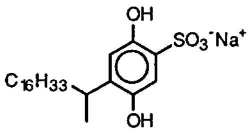
Compound 2



Compound 3



P1



ADD-1

Table III

Coupler + Compound 1			
Coupler	Type	Dye Retained from Initial Density 1.0	
		14 day	28 day
Y-1	Inv	97%	90%
Y-2	Inv	100%	93%
Y-3	Inv	96%	86%
Y-4	Inv	93%	84%
Y-5	Inv	93%	90%
Y-6	Inv	95%	85%
C-1	Comp	88%	69%
C-3	Comp	91%	71%

As shown in Table III, the couplers of this invention yield dyes which show highly superior resistance to light fade when coated with stabilizing addenda.

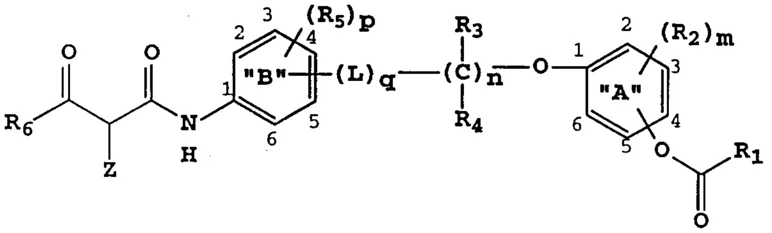
This can be particularly useful if one desires to use certain emulsion additives to achieve unique photographic features, as is sometimes done in the art. Although the presence of these emulsion additives give desirable photographic features, they can sometimes be detrimental to dye stability. Coupler Y-2 was coated in a format similar to that described above with the weight ratio of coupler : dibutylphthalate : stabilizing addenda of 3:2:1. Emulsion addenda ADD-1 was present in the emulsion in the amount of 0.88 mg/ft^2. The data in Table IV thus show that coupler Y-2 is still quite stable even without stabilizing addenda and can be made even more stable in the presence of stabilizing addenda.

Table IV

Dye Retained from Initial Density 1.0 Coupler + Addenda Emulsion with ADD-1			
Coupler	Type	Addenda	21 days
C-2	Comp	None	53%
Y-2	Inv	None	77%
C-2	Comp	Cmpd. 1	75%
Y-2	Inv	Cmpd. 1	84%
C-2	Comp	Cmpd. 2	74%
Y-2	Inv	Cmpd. 2	87%
C-2	Comp	Cmpd. 3	74%
Y-2	Inv	Cmpd. 3	87%
C-2	Comp	P1	74%
Y-2	Inv	P1	80%

Claims

1. A photographic element comprising a light sensitive silver halide emulsion layer having associated therewith an open chain α-carbonyl acetanilide yellow dye-forming coupler having the formula:



wherein

R_1 is selected from the group consisting of alkyl, aryl, heterocyclic, and amino groups, provided that R_1 may form a ring bonded to another carbon atom which is a member of Ring "A";
each R_2 is independently selected from the group consisting of those substituents having a Hammett's sigma value of 0 or less, and m is from 0 to 4;
each R_3 and R_4 for each of the n carbon atoms is independently selected from the group consisting of hydrogen, alkoxy, aryl, heterocyclic, aryloxy, and alkyl groups, and n is 0 to 16;
each R_5 is independently selected from the group consisting of halogen, amino, alkyl groups, and groups linked to the "B" ring by oxygen or sulfur, and p is 1 to 3, provided that two R_5 groups may join to form a ring;
each L is independently a divalent linking group and q is 0 to 3; and
Ring "A" is bonded indirectly to the 3-, 4-, or 5-position of Ring "B", R_6 is selected from the group consisting of

alkyl, aryl, and amino groups; and

(1) when an R_5 is halogen, Z is hydrogen or a coupling-off group selected from the group consisting of:
(a) an aryloxy or arylthio group;
(b) a heterocyclic group containing, in a five or six membered ring, one or two nitrogen atoms, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring; and
(c) a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group; and
(2) when no R_5 is halogen, Z is hydrogen, or a group capable of coupling-off when the coupler reacts with an oxidized color developing agent.

2. The element of claim 1 wherein said coupling-off group is a heterocyclic group containing, a nitrogen atom in a five or six membered ring, wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the ring.

3. The element of claim 1 wherein said coupling-off group is a benzotriazole group wherein the group Z is bonded to the remainder of the coupler through a nitrogen atom in the triazole group.

4. The element of claim 1 wherein said coupling-off group is an aryloxy or arylthio group.

5. The element of claim 1 wherein m is at least 1.

6. The element of claim 5 wherein there is at least one R_2 substituent on ring "A" ortho to the acyloxy group to which R_1 is attached.

7. The element of claim 6 wherein said at least one R_2 substituent on ring "A" ortho to the acyloxy group to which R_1 is attached contains branching.

8. The element of claim 7 wherein said at least one R_2 substituent on ring "A" ortho to the acyloxy group to which R_1 is attached is a branched alkyl group.

9. The element of claim 8 wherein said at least one R_2 substituent on ring "A" ortho to the acyloxy group to which R_1 is attached is selected from the group consisting of i-propyl, t-butyl, t-amyl, and t-octyl groups.

10. The element of claim 1 wherein R_1 contains at least 4 carbon atoms.

11. The element of claim 1 wherein at least one R_5 is bonded at the 2-,4-, or 6-position of ring "B".