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3,131,219

NITRO AND AMINO KETONES

Elkan R. Blout, Belmont, and Myron S. Simon, Newton Center, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed Jan. 8, 1962, Ser. No. 164,996
4 Claims. (Cl. 260—575)

This invention relates to chemistry and, more particularly, to novel chemical compounds.

A principal object of this invention is to provide novel chemical compounds which are useful as silver halide developing agents.

Another object of this invention is to provide novel chemical compounds which are useful intermediates.

Still another object is to provide syntheses for preparing the novel compounds of this invention.

It is a further object of the present invention to provide novel compounds, products, developer compositions, and processes employing such novel compounds, products and developer compositions for the development of silver halide emulsions.

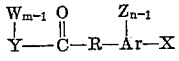
Other objects of this invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and relation and order of one or more of such steps with respect to each of the others, and the products and compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

The novel silver halide developing agents of this invention may be represented by the formula:

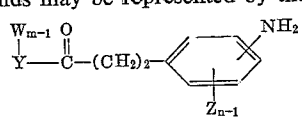
(V)



wherein Ar is an aryl nucleus, such as a benzene or naphthalene nucleus; each W is an alkoxy group, preferably a lower alkoxy group such as methoxy, ethoxy, etc., an alkyl group, preferably a lower alkyl group such as methyl, ethyl, isopropyl, etc., or a halogen such as chlorine; each Z is an alkoxy group, preferably a lower alkoxy group such as methoxy, ethoxy, etc., an alkyl group, preferably a lower alkyl group such as methyl, ethyl, isopropyl, etc., a hydroxyl group, or a halogen such as chlorine; *m* is a positive integer from 1 to 4, inclusive; *n* is a positive integer from 1 to 5, inclusive; R is an alkylene group having at least two carbon atoms, preferably a lower alkylene group such as ethylene; X is an amino group; and Y is an o-dihydroxyphenyl or a p-dihydroxyphenyl developer group. Preferably, Z is lower alkoxy, *n* is a positive integer from 1 to 3, inclusive, W is lower alkyl or chlorine, and *m* is a positive integer from 1 to 3, inclusive.

In a preferred embodiment, Ar is a benzene nucleus, R is an ethylene group, X is a primary amino group, and such compounds may be represented by the formula:

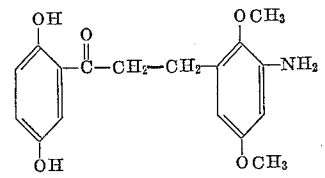
(B)



wherein Y, *m*, *n*, W and Z have the same meaning as above.

A preferred compound within the group represented by Formula B is:

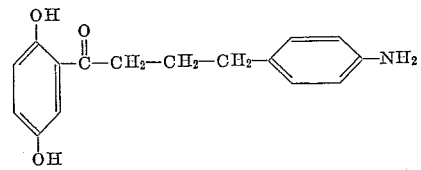
(1)



2[-β-(2′,5′-dimethoxy-3′-amino-phenyl)-propionyll] hydroquinone

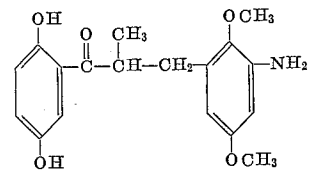
As examples of other useful silver halide developing agents within the scope of this invention, mention may be made of the following compounds:

(2)



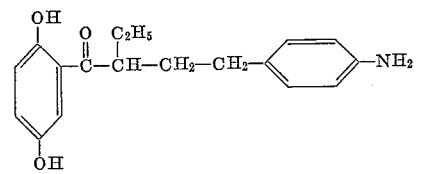
2-[δ-(4′-amino-phenyl)-butyryl]-hydroquinone

(3)



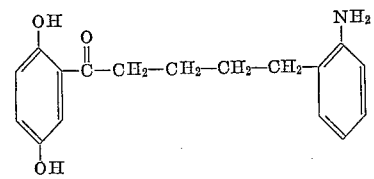
2-[β-(2′,5′-dimethoxy-3′-amino-phenyl)-α-methyl-propionyl]-hydroquinone

(4)



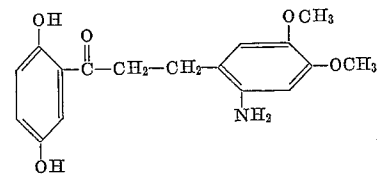
2[γ-(4′-amino-phenyl)-α-ethyl-butyryl]-hydroquinone

(5)



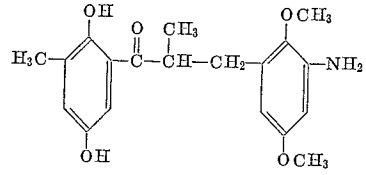
2-[δ-(2′-amino-phenyl)-valeryl]-hydroquinone

(6)



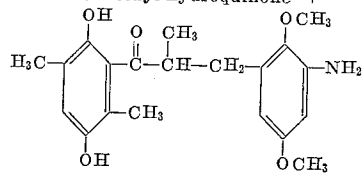
2-[β-(3′,4′-dimethoxy-6′-amino-phenyl) propionyl]-hydroquinone

(7)



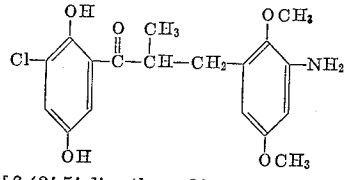
2-[β-(2',5'-dimethoxy-3'-amino-phenyl)-α-methyl-propionyl]-6-methyl-hydroquinone

(8)



3,6-dimethyl-2-[β-(2',5'-dimethoxy-3'-amino-phenyl)-α-methyl-propionyl]-hydroquinone

(9)

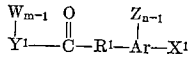


6-chloro-2-[β-(2',5'-dimethoxy-3'-amino-phenyl)-α-methyl-propionyl]-hydroquinone

Where desired, the amino compounds of this invention may be present in the form of acid addition salts, e.g., the hydrochloride.

One method of preparing developing agents within the scope of this invention comprises reacting an appropriate derivative of a dihydroxyphenyl ketone, i.e., a derivative which suitably protects the hydroxyl groups of said compound during reaction, e.g., a dialkoxy, a diaryloxy or a diarylalkoxy phenone derivative of said compound, with a nitro-aryl-aldehyde in the presence of an alkaline condensing agent, e.g., sodium, in a methanol medium, to form a compound of the formula:

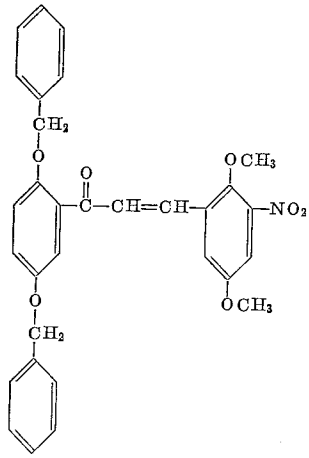
(C)



wherein W, Z, Ar, *m* and *n* have the meanings heretofore given; Y^1 is a protected dihydroxyphenyl group, e.g., a p-bis-alkoxyphenyl, an o-bis-aryloxyphenyl, or a p-bis-aryloxyphenyl group, etc; R^1 is an unsaturated alkylene radical, e.g., vinylene (—CH=CH—) and its homologues; and X^1 is a nitro group; and catalytically hydrogenating said compound thus saturating the double bond, reducing the nitro group and liberating the hydroxy groups, e.g., hydrogenolyzing the dibenzyloxy protective groups of said compound.

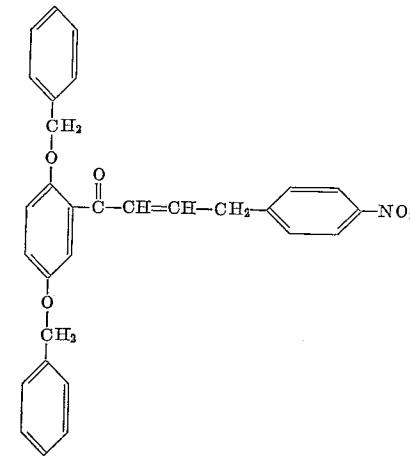
As examples of useful intermediates within the scope of Formula C, mention may be made of the following compounds:

(1a)



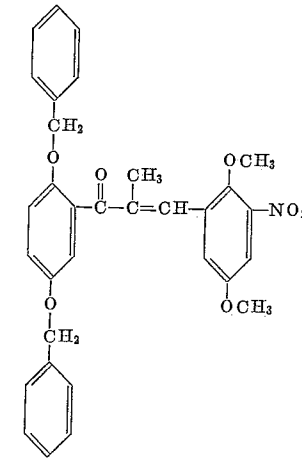
2,5-dibenzyloxy-phenyl (2,5-dimethoxy-3-nitro)-styryl ketone

(2a)



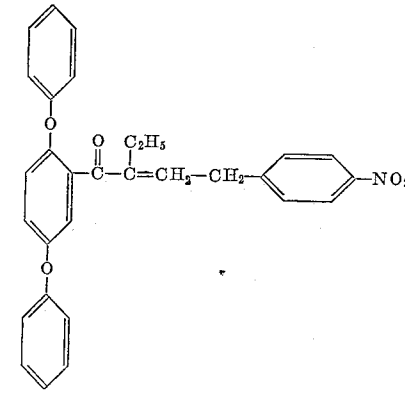
2,5-dibenzyloxy-phenyl 3-(4'-nitro-phenyl)-1-propenyl ketone

(3a)



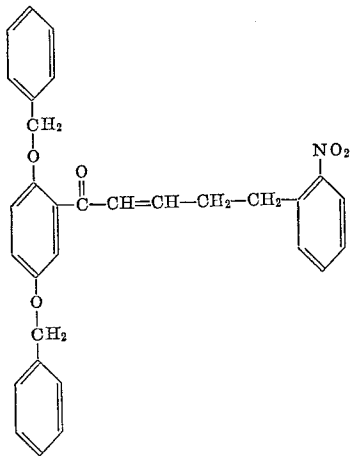
2,5-dibenzyloxy-phenyl (2,5-dimethoxy-3-nitro-α-methyl)-styryl ketone

(4a)



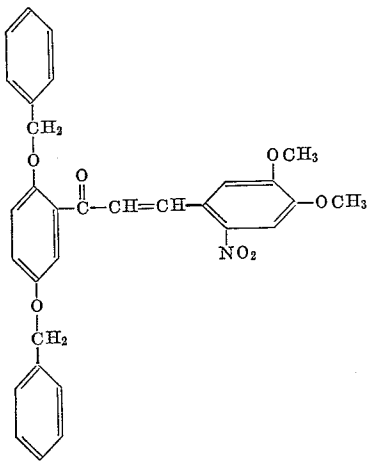
2,5-diphenoxy-phenyl 3-(4'-nitro-phenyl)-1-ethyl-1-propenyl ketone

(5a)



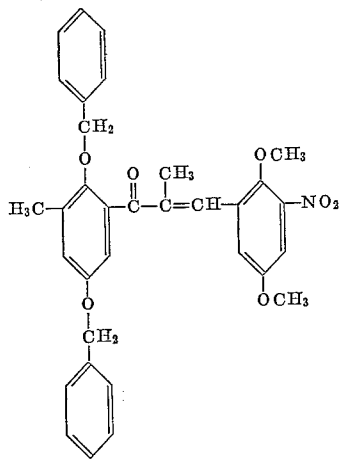
2,5-dibenzyloxy-phenyl 4-(2'-nitro-phenyl)-1-butenyl ketone

(6a)



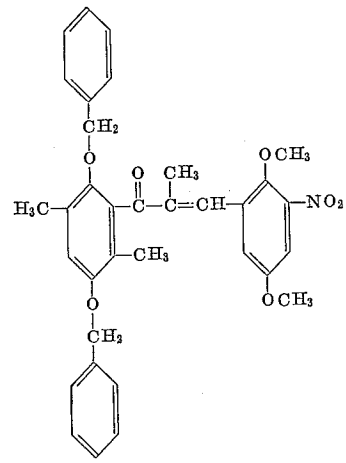
2,5-dibenzyloxy-phenyl β-(3,4-dimethoxy-6-nitro-phenyl)-vinyl ketone

(7a)



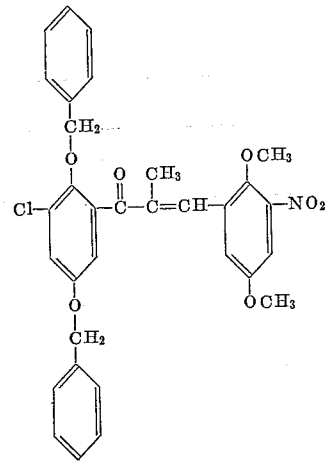
2,5-dibenzyloxy-6-methyl-phenyl (2,5-dimethoxy-3-nitro-α-methyl)-styryl ketone

(8a)



3,6-dimethyl-2,5-dibenzyloxy-phenyl (2,5-dimethoxy-3-nitro-α-methyl)-styryl ketone

(9a)



6-chloro-2,5-dibenzyloxy-phenyl (2,5-dimethoxy-3-nitro-α-methyl)-styryl ketone

It is to be noted, however, that where Ar of Formula C contains one or more alkoxy substituents, e.g., methoxy, Y^1 must be a radical such as a dibenzyloxyphenyl radical which is cleaved by hydrogenolysis in order to form the corresponding dihydroxyphenyl developer analogue, since if Y^1 is any of the other protected dihydroxyphenyl groups, dealkylation by hydrolysis to form the dihydroxyphenyl developing function Y will also cause removal of the alkyl moiety of the alkoxy substituent on Ar of Formula C e.g., demethylation.

Where the secondary or tertiary amine derivatives are desired, the amino group may be suitably alkylated, preferably before removing the hydroxy protective groups.

The following example illustrates the preparation of compounds within the scope of this invention and is given for purposes of illustration only.

Example 1

To prepare 2 - [β-(2',5'-dimethoxy-3'-amino-phenyl)-propionyl]-hydraquinone hydrochloride, 13.75 g. of 2,5-dibenzyloxyaceto-phenone, 8.7 g. of 2,5-dimethoxy-3-nitro-benzaldehyde and 0.164 g. of sodium dissolved in 15 cc. of dry methanol are mixed in approximately 600 cc. of methanol and allowed to stand approximately 12 hours at 20 to 25° C. The mixture is then concentrated to approximately 400 cc., cooled and filtered to yield 11 g. of 2,5-dibenzyloxy-phenyl (2,5-dimethoxy-3-nitro)-styryl ketone [Formula 1a] which melts at 120 to 122° C. The resulting filtrate is then concentrated to approximately

200 cc., cooled and filtered to yield 6 g. more of said product. The resulting filtrate is then concentrated to approximately 100 cc., cooled and filtered to yield 3 g. more of said product.

Analysis of the product shows:

	C	H	N
Calculated (percent)	70.85	5.1	2.7
Found (percent)	70.5	5.3	2.9

10 g. of said product are dissolved in 200 cc. of glacial acetic acid by heating and hydrogenated at 34.4 p.s.i. initial pressure in the presence of 10 g. of palladium-barium sulfate. A 9.9 p.s.i. uptake occurs in one hour. The resultant yellow filtrate is evaporated to an oil in a vacuum, dissolved in 10% hydrochloric acid, filtered, and partly evaporated. On standing 4.6 g. of khaki crystalline material, 2-[β-(2',5'-dimethoxy - 3' - amino-phenyl)-propionyl]hydroquinone hydrochloride, is precipitated, which melts at 164 to 166° C. and, when recrystallized from 10% hydrochloric acid, melts at 170 to 171° C. with decomposition.

Analysis of the product shows:

	C	H	N
Calculated (percent)	57.7	5.7	4.0
Found (percent)	58.0	5.8	4.0

This product can be used directly in subsequent diazotization reactions.

As was indicated previously, the novel dihydroxyphenyl compounds of Formula A or B are useful as photographic developing agents. When used alone, they are relatively weak. If, however, a small quantity of an accelerating developer, e.g., metol (p-methyl-aminophenol) or a 3-pyrazolidone, and particularly 1-phenyl-3-pyrazolidone, is added thereto, the combination is a very useful developing composition. As an example of a suitable photographic developer composition containing a compound of this invention and useful in conventional black-and-white tray or tank development the following is given for purposes of illustration only.

Example 2

	Percent
2-[γ-(2',5'-dimethoxy-3'-amino-phenyl) - propionyl]-hydroquinone	2
Sodium sulfite	2
Potassium bromide	0.5
1-phenyl-3-pyrazolidone	0.2
Sodium hydroxide	1
Water to make 100 cc.	

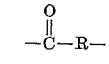
The novel class of silver halide developing agents of this invention are also useful in diffusion-transfer reversal photographic processes such as disclosed in U.S. Patent No. 2,543,181, issued to Edwin H. Land on February 27, 1951, wherein development is effected in the presence of a silver halide solvent, e.g., sodium thiosulfate, and a suitable image-receiving layer.

It will be apparent that the relative proportions of the novel agents of the developer composition set forth above may be varied to suit the requirements of the operator. Thus it is within the scope of this invention to modify said developing composition by the substitution of preservatives, alkalies, silver halide solvents, etc., other than those specifically mentioned. It is also contemplated that where desirable the said developer composition may be modified by the inclusion of other common components of developer compositions such as restrainers, accelerators, etc. Similarly, the concentration of the developing agent may be varied over a wide range and, where desirable, either or both developing agents may be disposed in the photosensitive emulsion prior to the exposure of said emulsion.

The novel compounds of this invention are also highly useful chemical intermediates. They are especially useful in reactions wherein it is desired that reaction be restricted to the amino group.

In particular, the novel compounds of this invention, wherein X is a primary amino group, are useful as intermediates in the preparation of azo compounds. In the past it has been generally accepted that it is substantially impossible to diazotize a primary amino compound in the presence of a free hydroquinone group. However, it has been discovered that the novel compounds of this invention may be readily diazotized without the necessity of protecting the dihydroxyphenyl group's constituent hydroxyl radicals. Thus, the compounds of this invention are particularly useful in the preparation of azo compounds, for example, as disclosed in the copending application of Elkan R. Blout, Milton Green, Howard G. Rogers and Myron S. Simon, Serial No. 685,081, filed September 20, 1957.

The presence of the acyl group, i.e., the



group as a constituent component of the novel compounds of this invention, renders them highly stable in a photosensitive element during storage, as a result of their weak developing ability in the absence of the accelerating developer.

Suitable auxiliary or accelerating developers include hydroquinone, metol, amidol, benzylaminophenol, or a 3-pyrazolidone, such as 1-phenyl-3-pyrazolidone, etc. It will be apparent that the desired auxiliary developing agent may be disposed in the photosensitive element prior to the exposure of said element.

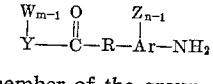
When employed as photographic developing agents, the novel dihydroxyphenyl compounds of this invention having an amino group may be introduced in the form of the free base or as salts thereof, such as the hydrochloride. Thus, the salt may be employed where the developing agent is to be incorporated in, on or behind the silver halide emulsion or where one desires to prepare a dry developer composition, the solvent being added to the dry composition prior to use.

This application is a continuation-in-part of copending application Serial No. 685,066, filed September 20, 1957, now abandoned.

Since certain changes may be made in the above processes, products and compositions without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

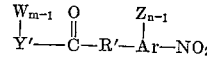
1. A compound of the formula:



wherein Y is a member of the group consisting of ortho- and para-dihydroxyphenyl; W is a member of the group consisting of chlorine and lower alkyl; *m* is a positive integer from 1 to 3, inclusive, R is lower alkylene having at least two carbon atoms; Ar is a member of the group consisting of phenylene and naphthylene; Z is lower alkoxy; and *n* is a positive integer from 1 to 3.

2. 2 - [β - (2'5' - dimethoxy - 3' - amino-phenyl) - propionyl]-hydroquinone.

3. A compound of the formula:



wherein Y' is a protected dihydroxyphenyl radical selected

from the group consisting of ortho- and para-bis-alkoxyphenyl, bis-aryloxyphenyl and bis-aralkoxyphenyl, W is a member of the group consisting of chlorine and lower alkyl; *m* is a positive integer from 1 to 3 inclusive; R' is divalent alkene; Ar is a member of the group consisting of phenylene and naphthylene; Z is lower alkoxy; and *n* is a positive integer from 1 to 3.

4. 2,5-dibenzyloxy-phenyl (2,5 - dimethoxy-3-nitro)-styryl ketone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,769,817 Martin et al. ---------- Nov. 6, 1956
3,062,884 Green ---------- Nov. 6, 1962

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,131,219 April 28, 1964

Elkan R. Blout et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 38, for "(∀)" read -- (A) --; column 2, line 13, for "-propionyll" read --propionyl --; line 27, for "δ-" read -- ϒ --; same column 2, line 65, for "-phenyl)propionyl" read -- -phenyl)-propionyl --; column 7, line 21, for "pionyl]hydroquinone" read -- pionyl]-hydroquinone --.

Signed and sealed this 3rd day of November 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents