This invention relates to the 1-phenyl-3,3-dimethylspiro (2'H-1'-benzopyran) - 2',2'-indoline compound of the formula:

\[
\begin{align*}
R & \quad \text{wherein } R \text{ is one or more independently selected radicals, to be specified hereinafter; at one or more of the 5', 6', 7', \text{ and 8'} positions.}
\end{align*}
\]

These compounds vary in their stability, due to thermal activity, the unsubstituted compound being reversibly colorable and stable in solution in the colored state only at low temperature—say about minus 60 degrees centigrade or below—in the absence of change-provoking light, whereas those derivatives having the substituents or radicals hereinafter disclosed in any of the 5', 6', 7' and 8' positions, which tend to weaken the spiro-carbon-to-oxygen 2'-1' bond, and are reversibly colorable, are characterized by having low thermal stability when in the colored form (short-half-life compounds) at higher temperatures, such as at room temperatures and above, but within the range of normal human activity temperatures.

It should be understood that the novel compounds of this invention will, in the absence of exposure to short-wave-length change-provoking light, remain in the colorless state indefinitely, when in solution, either at or about normal room temperatures, and that said compounds when in the colored state, in solution, not only will quickly revert to the colorless form by the action of longer-wave-length change-provoking light, but will also, even in the dark, rapidly revert to said colorless state, by thermal activity, at or about normal room temperatures. The rate of reversion is temperature-dependent, the rate increasing with increasing temperature. The rate at which these compounds revert from the colored form to the colorless form is normally expressed as the half-life of the colored form of the compound and is a quantitative measure of the thermal stability of such compounds at or about room temperature. It has been found that, when properly modified, various classes of compounds, particularly spiropyran compounds, may be made in which the room temperature thermal stability of the colored form varies from a half-life of a fraction of a second to a half-life of several months. The thermal stability of the novel compounds of this invention falls in the category of short-half-life compounds, said half-life varying from about a few minutes to less than a second.

A suitable method for determining the half-life of the colored form of the instant compound is to determine, at a selected wave-length, the rate of decrease in absorptance of a solution of the compound while kept in the dark, over a known time interval, and, by use of the well-known rate formulas and a graph plot of the variables, to calculate the interval of time required for the absorptance to decrease from a maximum value to half this value.

By the term "solution," as used herein, is meant the homogeneous mixture of one or more of the claimed compounds with a solid or liquid substance.

Among the many possible radicals or substituents which may be attached at any one of the 5', 6', 7', and 8' positions are the following: CH₃, CH₂CH₃; CH(CH₃)₂; C(C₆H₅); the phenyl group C₆H₅; CF₃; CN; COCH₃; CO₂CH₂; CO₂H; NH₂; NHCH₂; NH₂CH₂; NH₂COCH₃; N(CH₃)₂; NO₂; PO₃H₂; OCH₂; O₃C₆H₅; O(CH₂)₅CH₃; O(CH₃)₂; SO₂CH₂; SO₂NH₂; S(CH₃)₂; f; Cl; Br; i; IO₂; CH₂CH={CH₂}; and CO₂CH₃.

Any of the above radicals or substituents or group of sterically compatible substitutents or radicals may be selected for attachment to said positions, and such compounds may be prepared by condensing the selectively substituted salicylaldehyde (to give substrates in the 5', 6', 7', and 8' positions, as desired) with 1-phenyl-3,3-dimethyl-2-methylindoline.

As is evident from the foregoing, a large number of 1-phenyl compounds of the type disclosed are within the
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The scope of the invention; however, the preferred compounds are defined as compounds having the following structural formula:

\[
\begin{align*}
R_1 & = \text{a member selected from the group consisting of } -\text{NO}_2 \text{ and } -\text{OCH}_3 \text{ in the 6' and 8' positions, respectively; } & -\text{NO}_2 \text{ in the 6' position; and } & -\text{NO}_2 \text{ in the 6' and 8' positions.}
\end{align*}
\]

Even though the intermediate 1-phenyl-3,3-dimethyl-2-methylamino-2-methylenedione is not a novel compound, the method of preparing it will be described, inasmuch as no method for its preparation appears to have been published.

In preparing 1-phenyl-3,3-dimethyl-2-methylamino-2-methylenedione, the first step consists of forming the hydrochloride salt of N,N-diphenylhydrazine as follows:

A 198-gram (1.0 mole) sample of N-nitroso diphenylamine was added to 1250 ml. of 95% ethanol in a 3-liter flask, and to this mixture was added 233 grams (3.5 moles) of zinc dust. The reaction mixture was cooled to below 10 degrees centigrade and maintained below that temperature during the addition of 240 ml. of glacial acetic acid. Addition of the acid took about 11/2 hours. After the addition of the acid, the reaction mixture was filtered, and the filtrate obtained was reduced to one fourth of its volume by evaporation on a steam bath and then diluted with its own volume of water. The resulting solution was treated with about 400 ml. of concentrated hydrochloric acid, and the salt formed was collected on a filter. The salt of the N,N-diphenyl hydrazine present was separated from the by-products by partially dissolving the collected precipitate in warm very dilute hydrochloric acid and removing the undissolved by-products by filtration. The filtrate was treated with concentrated hydrochloric acid, and the salt of the hydrazine (101 grams, which is 0.45 mole), which precipitated, was removed by filtration, giving the hydrochloride salt of N,N-diphenylhydrazine, which has the structure

\[
\begin{align*}
\text{N} & \text{H} - \text{N} - \text{H}_3 \text{Cl}.
\end{align*}
\]

The thus-made hydrochloride salt of N,N-diphenylhydrazine is condensed with methyl isopropyl ketone to form the N,N-diphenylhydrazine of methyl isopropyl ketone, which in turn is made to undergo ring closure to 1-phenyl-3,3-dimethyl-2-methylamino-2-methylenedione as follows:

A dried 26.5-gram (0.12 mole) amount of N,N-diphenylhydrazine hydrochloride is mixed with 11 grams (0.12 mole) of methyl isopropyl ketone in 100 ml. of absolute ethanol, and the mixture is refluxed for 11/2 hours with a drying tube attached to the condenser to exclude entry of water vapor. The solution then is cooled and filtered to remove any precipitated salts. To a flask containing the filtrate, which contains the just-prepared N,N-diphenylhydrazine of methyl isopropyl ketone, is added 110 grams of zinc chloride. The reaction mixture is protected from water vapor by a drying tube fixed to the neck of the flask and is stirred for 11/2 hours. The reaction mixture is made strongly basic with a concentrated aqueous solution of potassium hydroxide and then extracted with ethyl ether. The ether extract is dried and vacuum-distilled under a nitrogen atmosphere. The fraction which distills at 100–102°/0.01 mm. is collected as the desired 1-phenyl-3,3-dimethyl-2-methylamino-2-methylenedione, which has the structure:

In general, the novel compounds of the invention having selected radicals or substituents at the 5', 6', 7', and 8' positions are synthesized by condensing the intermediate 1-phenyl-3,3-dimethyl-2-methylamino-2-methylenedione with a substituted salicylaldehyde in which the substituents or radicals are so selected and located as to provide a condensation product having the desired radicals at one or more of the said 5', 6', 7', and 8' positions.

**Example I**

In this example will be described the preparation of the 6'-nitro-8'-methoxy derivative, having the structure:

\[
\begin{align*}
\text{H}_2 \text{C} - \text{C} & \text{H}_3 \\
\text{N} & \text{O} \\
\text{C} & \text{H}_3
\end{align*}
\]

A 2.0-frank (0.0085 mole) amount of 1-phenyl-3,3-dimethyl-2-methylamino-2-methylenedione and 1.67 grams (0.0085 mole) of 3-methoxy-5-nitrosalicylaldehyde are dissolved in 20 ml. of 95% ethanol, and the resulting solution is refluxed for two hours. The reaction contents is cooled and filtered to give 2.4 grams of the desired product, which on recrystallization from alcohol melts at 179.5 to 181 degrees centigrade.

**Example II**

In this example will be described the preparation of the 6'-nitro derivative, having the structure:

\[
\begin{align*}
\text{H}_2 \text{C} - \text{C} & \text{H}_3 \\
\text{N} & \text{O}_2 \\
\text{C} & \text{H}_3
\end{align*}
\]
This is prepared by the same method as the compound of Example I, except that 5-nitrosalicylaldehyde is used instead of 3-methoxy-5-nitrosalicylaldehyde, in equimolar amounts.

Example III

In this example, the preparation of the 6',8'-dinitro derivative will be described. This is prepared by the same method as the compound of Example II, except that 3,5-dinitrosalicylaldehyde is used instead of 3-methoxy-5-nitrosalicylaldehyde, in equimolar amounts. This compound has the structure

Other substituted salicylaldehydes, having substituents or radicals selected from the previously given list of substituents, may be used to make numerous other 1-phenyl compounds of the type within the scope of this invention by following the methods of preparation disclosed hereinabove.

What is claimed is:

The compound of the formula:

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