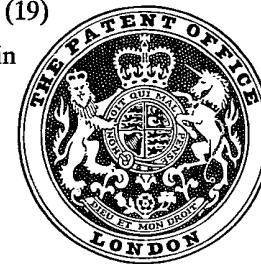


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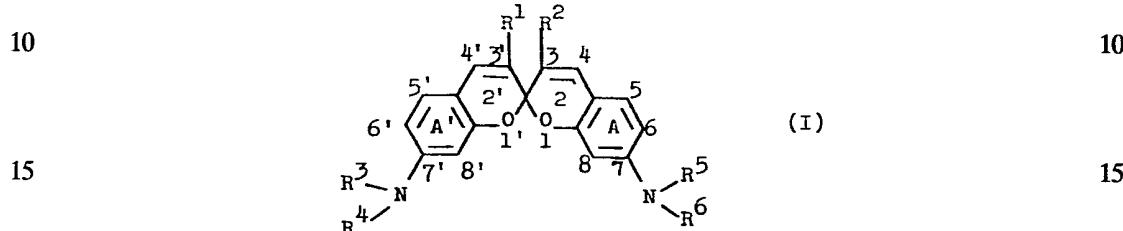


(54) SPIRODIPYRAN DYE INTERMEDIATES FOR COPYING PROCESSES

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

5 The present invention relates to novel components useful as dye intermediates for copying processes.

According to the invention there are provided spirodipyrans of the general formula I



where R¹ is hydrogen, alkyl of 1 to 12 carbon atoms, phenyl which is unsubstituted or substituted by alkyl of 1 to 4 carbon atoms, methoxy, ethoxy, chlorine or bromine, or phenylalkyl of 7 to 10 carbon atoms, and R² is hydrogen, or R¹ and R² together are dimethylene, trimethylene or tetramethylene, which are unsubstituted or substituted by alkyl of 1 to 12 carbon atoms; R³ and R⁴ each independently are hydrogen, alkyl of 1 to 12 carbon atoms, cyano-, chlorine-, methoxy- or ethoxy-substituted alkyl of 2 to 4 carbon atoms or trimethylene which is unsubstituted or substituted by 1 to 3 methyl groups and is bonded to the carbon atom in the 6-position or 6'-position, as the case may be, of the adjacent benzene ring and, R⁵ and R⁶ each independently are alkyl of 1 to 12 carbon atoms, cyano-, chlorine-, methoxy- or ethoxy-substituted alkyl of 2 to 4 carbon atoms, phenylalkyl of 7 to 10 carbon atoms, phenyl which is unsubstituted or substituted by alkyl of 1 to 4 carbon atoms, chlorine or bromine, or trimethylene bonded to the carbon atom in the 8-position or 8'-position, as the case may be, of the adjacent benzene ring, and one or both of the groups



may alternatively be a pyrrolidine, piperadine, morpholine, thiomorpholine, N'-alkylpiperazine (alkyl being of 1 to 4 carbon atoms) or isoindoline radical; and the rings A and A' are unsubstituted or substituted by alkyl of 1 to 3 carbon atoms. The substituents R³, R⁴, R⁵ and R⁶ may be identical or different.

Examples of substituents R¹ are, apart from hydrogen, methyl, ethyl, propyl, β-methylpropyl, n-butyl, hexyl, octyl, nonyl, decyl, dodecyl, phenyl, p-tolyl, p-ethylphenyl, p-propyl- phenyl, p-tert.-butylphenyl, p-methoxyphenyl, p-ethoxyphenyl, chlorophenyl, bromophenyl, benzyl, β-phenylethyl, β-phenylpropyl and δ-phenylbutyl.

Specific examples for R^1 and R^2 together are dimethylene, trimethylene, β -alkyltrimethylene (where alkyl is of 1 to 12 carbon atoms), eg. β -methyltrimethylene, β -tert.-butyltrimethylene, β -n-heptyltrimethylene, β -n-octyltrimethylene, β -n-nonyltrimethylene, β -n-dodecyltrimethylene, and tetramethylene.

5 For tinctorial and technological reasons, dye intermediates of the formula I where R^1 is phenyl or R^1 and R^2 are trimethylene which in the β -position carries an alkyl radical of 1 to 12 carbon atoms, preferably of 4 to 12 carbon atoms, eg. tert.-butyl, heptyl, octyl, nonyl or dodecyl, are preferred.

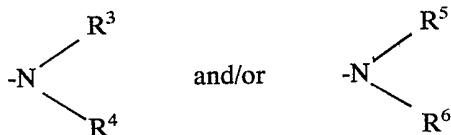
10 Specific examples of radicals R^3 , R^4 , R^5 and R^6 are methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, dodecyl, β -chloroethyl, β -cyanoethyl, β -methoxyethyl, γ -methoxypropyl, γ -ethoxypropyl, β -ethoxyethyl, benzyl, β -phenyl-ethyl, γ -phenylpropyl, β -phenylpropyl and δ -phenylbutyl. Of these, the preferred meanings of R^3 , R^4 , R^5 and R^6 are alkyl of 1 to 6 carbon atoms and benzyl; R^3 and R^5 may, in addition, be cycloalkyl of 5 to 7 carbon atoms, especially cyclohexyl.

15 R^4 and R^6 may also be phenyl which may or may not be substituted, eg. phenyl, tolyl, chlorophenyl, bromophenyl, ethylphenyl or butylphenyl.

For tinctorial and technological reasons, methyl, ethyl, butyl, propyl, hexyl and/or benzyl are particularly preferred amongst the radicals mentioned for R^3 , R^4 , R^5 and R^6 .

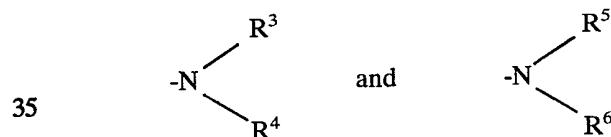
Very particularly preferred dye intermediates (I) are those where

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are dimethylamino, diethylamino, dipropylamino, dibutylamino, dihexylamino or dibenzylamino and where

30



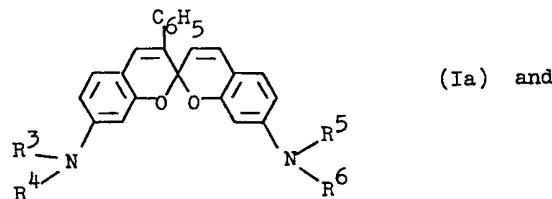
are identical or different.

40 The spirodipyrans of the formula I are pale-colored to colorless compounds. Their solutions in an inert, organic solvent give bluish-green to green colorations in contact with electron-attracting substances. Typical examples of electron acceptors are carboxylic acids and mineral acids, kaolin, bentonite, activated clay, aluminum silicate, attapulgite or any desired clay, acidic polymeric materials, eg. condensation products of phenols and/or phenol-sulfonic acids, and metal oxides or salts, e.g. zinc oxide, aluminum oxide, zinc chloride, iron stearate or cobalt naphthenate.

45 Because of these properties, the new compounds of the formula I can be used as chromogens (dye intermediates) in pressure-sensitive recording materials, copying materials or other pressure-sensitive duplicating systems.

50 Preferably, the compounds according to the invention, in organic solvents such as chlorinated paraffins, halogenated or partially hydrogenated biphenyl, alkylbenzenes, alkylnaphthalenes, alkylated dibenzylbenzene, paraffin oil, mineral oil or conventional solvents such as toluene or xylene, are enclosed, in the form of a solution or suspension, in micro-capsules and are used in this form for the manufacture of papers for pressure-sensitive copying processes. On contact with electron-attracting materials under appropriate pressure due to writing or typewriting, a bluish-green to green coloration is produced.

55 For this purpose, spirodipyrans of the formulae



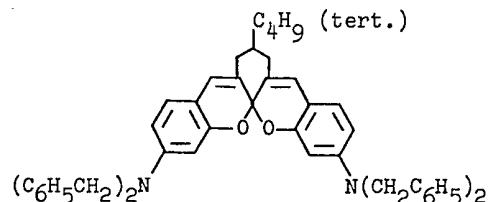
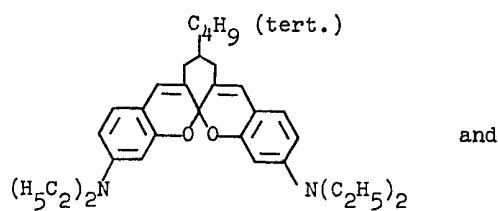
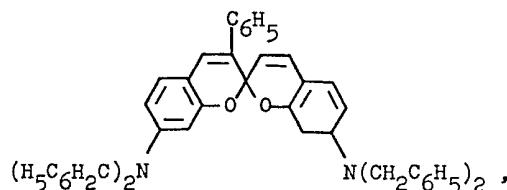
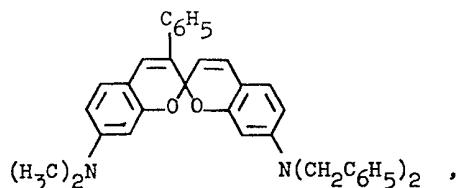
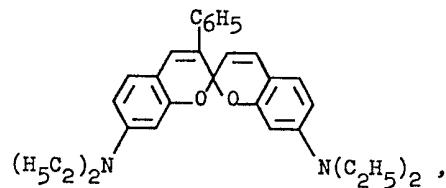
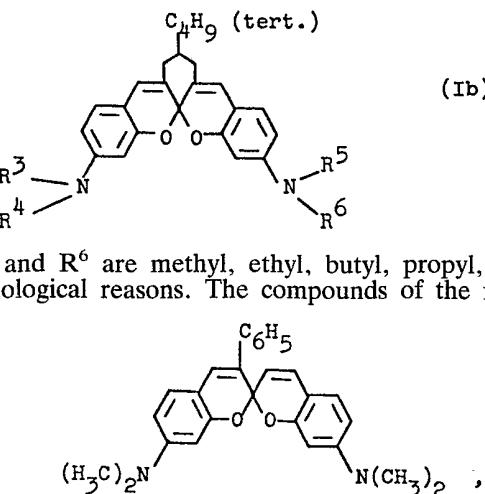
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(Ib) ,

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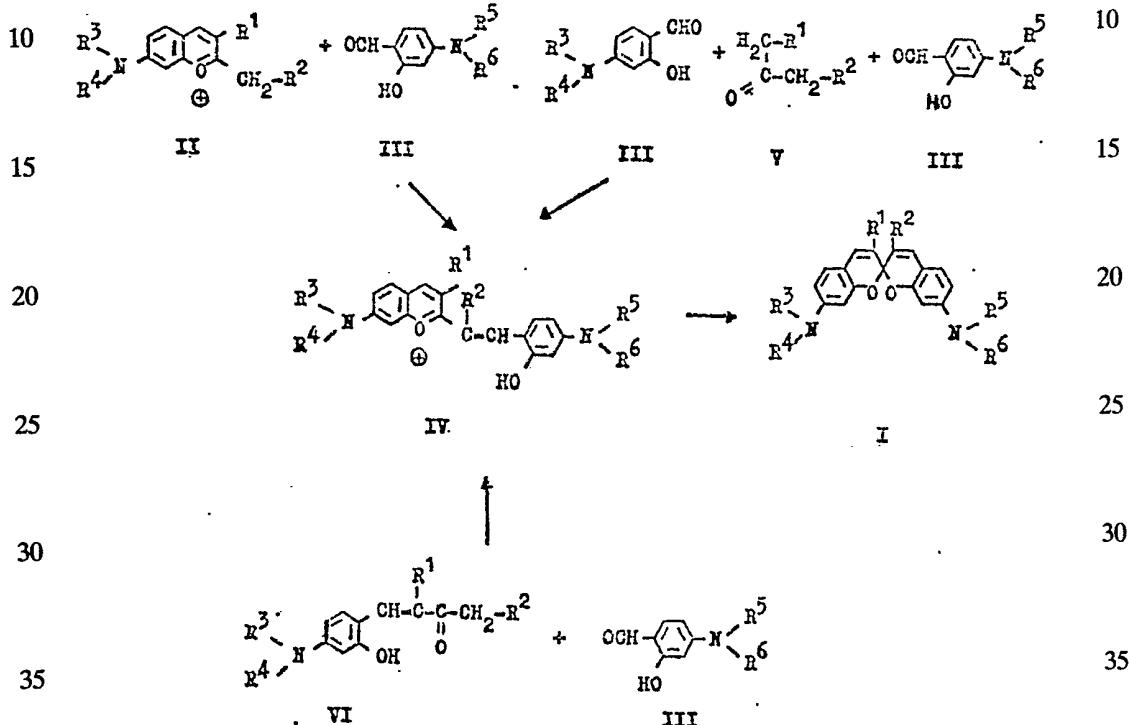
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where R^3 , R^4 , R^5 and R^6 are methyl, ethyl, butyl, propyl, hexyl and/or benzyl, are preferred for technological reasons. The compounds of the formulae



are very particularly preferred for tinctorial and technological reasons.

The dye intermediates I may be synthesized by cyclizing the o-hydroxyaryl-styryl compounds of the formula IV. The compounds of the formula IV can be obtained, for example, by condensing benzo-pyrylium salts of the formula II with N-substituted 5 p-aminosalicyl-aldehydes of the formula III. The compounds of the formula IV can also be manufactured by condensing the ketones of the formula V with the aldehydes of the formula III or by reacting the chalcones of the formula VI with the aldehydes of the formula III by conventional methods in accordance with the following equations:



The condensations are advantageously carried out in organic solvents which are liquid at the reaction temperature, e.g. alcohols, carboxylic acids, carboxylic acid anhydrides, 40 carboxylic acid amides, hydrocarbons or acetonitrile, in the presence or absence of acid or basic condensing agents, e.g. zinc chloride, phosphoric acid, hydrogen chloride, toluenesulfonic acid, boric acid, pyridine, piperidine, triethylamine or ammonium acetate in the conventional amounts for condensation reactions of the type in question. Generally speaking, the condensation is carried out at from 20 to 120°C.

45 The cyclization of compounds of the formula IV to give the pyran derivatives can be carried out together with the condensation or subsequently in the same or a separate process stage, by conventional methods, in the presence or absence of basic substances, e.g. sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium acetate, potassium acetate, ammonia, aliphatic amines or pyridine. The crystalline 50 spirodipyrans which separate out from this solution can be used, directly or after purification, e.g. by re-crystallization or reprecipitation, as dye intermediates for copying processes.

55 Examples of suitable starting compounds of the formulae II, III and V, for the manufacture of the compounds IV, are:

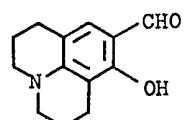
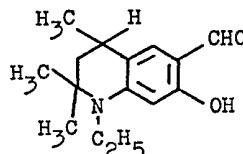
55 a) Benzopyrylium salts of the formula II in the form of their chlorides, perchlorates, tetrafluoroborates, tetrachloroferrates and trichlorozincates, in particular 2-methyl-3-phenyl-tetrafluoroborates, tetrachloroferrates and trichlorozincates, in particular 2-methyl-3-phenyl-7-dimethylamino-benzopyrylium, 2-methyl-3-phenyl-7-diethylamino-benzopyrylium, 2-methyl-3-phenyl-7-dibenzylamino-benzopyrylium, 2-methyl-3-p-tolyl-7-dimethylamino-benzopyrylium, 2-methyl-3-p-anisyl-7-diethylamino-benzopyrylium, 2-methyl-3-p-chlorophenyl-7-diethylamino-benzopyrylium, 2-methyl-7-diethylamino-benzopyrylium and 2-methyl-7-dimethylamino-benzopyrylium salts.

60 b) Suitable aldehydes of the formula III are above all the compounds of the formula XI a (with Z=H) mentioned in German Laid-Open Application DOS 2,413,281. Specific examples are:

65 4-dimethylaminosalicylaldehyde, 4-diethylaminosalicylaldehyde, 4-dimethylamino-5-

5 methyl-salicylaldehyde 4- β -cyanoethyl-methyl-amino-salicylaldehyde, 4-di- β -cyanoethylaminosalicylaldehyde, 4-di-n-propylamino-salicylaldehyde, 4-di-n-butylaminosalicylaldehyde, 4-di-n-hexylaminosalicylaldehyde, 4-di-n-dodecylaminosalicylaldehyde, 4-cyclohexylamino-salicylaldehyde, 4- β -methoxyethylmethylamino-salicylaldehyde, 4-di- β -chloroethylamino-salicylaldehyde, 4-dibenzyl-amino-salicylaldehyde, 4-N-pyrrolidyl-salicylaldehyde, 4-N-piperi-dinyl-salicylaldehyde, 4-(N'-methyl-N-piperazinyl)-salicylaldehyde, 4-N-morpholinyl-salicylaldehyde and 4-N-isoindolinyl-salicylaldehyde, as well as the o-hydroxy-benzaldehydes of the formulae

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10

15

c) Specific examples of suitable ketones of the formula V are acetone, methyl ethyl ketone, methyl isobutyl ketone, 5-methyl-hexan-2-one, tridecan-2-one, phenylacetone, p-tolylacetone, p-anisylacetone, p-chlorophenylacetone, p-ethoxyphenylacetone, p-bromophenylacetone, benzylacetone, 1-phenyl-pentan-4-one, 1-phenyl-hexan-5-one, cyclohexanone, 4-tert.-butyl-cyclohexanone, 4-n-octyl-cyclohexanone, 4-n-heptylcyclohexanone, 4-n-nonyl-cyclohexanone, 4-n-dodecyl-cyclohexanone, cyclopentanone and cycloheptanone.

d) Examples of compounds of the formula VI are:

1-(o-hydroxy-p-dimethylamino-phenyl)-2-phenyl-but-1-en-3-one, 1-(o-hydroxy-p-diethylamino-phenyl)-2-phenyl-but-1-en-3-one, 1-(o-hydroxy-p-dimethylamino-phenyl)-2-(p-tolyl)-but-1-en-3-one, 1-(o-hydroxy-p-dibenzylamino-phenyl)-2-phenyl-but-1-en-3-one, 1-(o-hydroxy-p-pyrrolidino-phenyl)-2-phenyl-but-1-en-3-one and 1-(o-hydroxy-p-diethylamino-phenyl)-2-(p-anisyl)-but-1-en-3-one.

20

The preparation and isolation of the new compounds of the formula I is explained in more detail in the Examples which follow. In these, parts are by weight.

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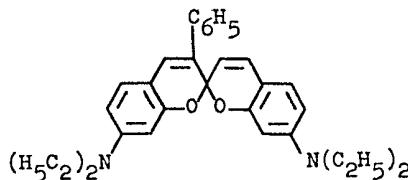
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Example 1

24.5 parts of 2-methyl-3-phenyl-7-diethylaminobenzopyrylium tetrachloroferrate and 9.6 parts of p-diethylaminosalicylaldehyde in 100 parts of alcohol are heated under reflux for one hour. Hydrogen chloride gas is then passed into the reaction solution at from 40 to 50°C until saturation is reached, after which the mixture is stirred for 3 hours at 20°C. The crystalline dye is isolated and stirred in 30 parts of 25 percent strength ammonia solution and 100 parts of toluene until completely decolorized. The toluene phase is separated off and concentrated to one-fifth. 11.5 parts of 3'-phenyl-7,7'-bis-diethylamino-2,2'-spirodi(2H-1-benzopyran) of the formula

45



45

50

are precipitated from this solution by adding 50 parts of alcohol.

50

Melting point 170 - 172°C.

If a solution of this compound is enclosed in microcapsules and coated onto paper and the coated side is laid on an acid receptive coating, a green coloration is produced on the latter when writing on the paper so as to destroy the capsules and bring their contents into contact with the receptive coating.

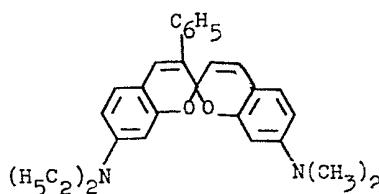
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Example 2

Condensing 2-methyl-3-phenyl-7-diethylamino-benzopyrylium tetrachloroferrate with p-dimethylaminosalicylaldehyde by the method described in Example 1 gives 3'-phenyl-7-dimethyl amino-7'-diethylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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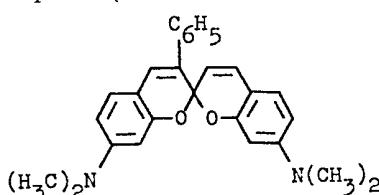
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10 having a melting point of 212 - 214°C.
In contact with acidic substances, this compound gives a green coloration.

10

Example 3
Reacting 2-methyl-3-phenyl-7-dimethylaminobenzopyrylium tetra-chloroferate with
15 p-dimethylaminosalicylaldehyde by the method described in Example 1 gives 3'-phenyl- 15
7,7'-bis-dimethylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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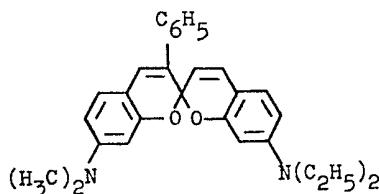
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25 having a melting point of 217 - 218°C.
In contact with acidic substances, the compound develops a green coloration.

25

Example 4
30 Condensing 2-methyl-3-phenyl-7-dimethylaminobenzopyrylium tetrachloroferate by the 30
method described in Example 1 with p-diethylaminosalicylaldehyde gives 3'-phenyl-7-
diethylamino-7'-dimethylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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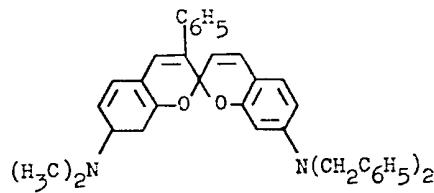
The compound melts at 143 - 144°C and gives a green coloration in contact with acidic substances.

40

45 Example 5

45 Reacting 2-methyl-3-phenyl-7-dimethylamino-benzopyrylium tetrachloroferate with p-
dibenzylaminosalicylaldehyde by the method described in Example 1 gives the compound
3'-phenyl-7-dibenzylamino-7'-dimethylamino-2,2'-spirodi-(2H-1-benzopyran) of the for-
mula

45



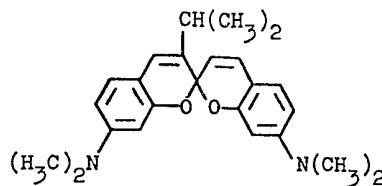
having a melting point of 189 - 191°C.

With electron acceptors, the compound gives a green coloration.

Example 6

5 Hydrogen chloride gas is passed into a solution of 10 parts of methyl isobutyl ketone, 33 parts of p-dimethylaminosalicylaldehyde and 14 parts of zinc chloride in 80 parts of methanol at from 40 to 50°C until saturation is reached. The mixture is then stirred for 12 hours at 20°C, the dye is isolated and the cyclizing (decolorizing) is carried out as described in Example 1. The compound 3-i-propyl-7,7'-bis-dimethylamino-spirodi-(2H-1-10 benzopyran) of the formula

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20 having a melting point of 110 - 112°C, is obtained.

20

In contact with acidic substances, the compound develops a bluish-green coloration.

The compounds shown below are prepared by the methods described in the preceding examples. The hues developed on contact with acidic substances are shown in the right-hand column.

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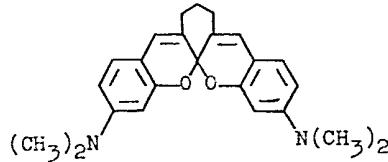
	Example	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	Hue	
30	7	p-H ₃ CC ₆ H ₄ -	H	CH ₃	23	CH ₃	CH ₃	green	30
	8	p-H ₃ COOC ₆ H ₄ -	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	green	
	9	p-CIC ₆ H ₄ -	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	green	
35	10	-C ₆ H ₅	H	C ₂ H ₅	C ₂ H ₅	CH ₃	p-CIC ₆ H ₄	green	35
	11	-C ₆ H ₅	H	C ₂ H ₅	C ₂ H ₅	CH ₃	p-H ₃ CC ₆ H ₄	green	
40	12	-H	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	bluish green	40
	13	-C ₆ H ₅	H	C ₂ H ₅	C ₂ H ₅	-CH ₂ -		green	
	14	-C ₆ H ₅	H	C ₂ H ₅	C ₂ H ₅	-CH ₂ -		green	
45	15	-C ₆ H ₅	H	C ₂ H ₅	C ₂ H ₅	-CH ₂ -O-CH ₂ -	green		45
	16	-C ₆ H ₅	H	CH ₃	CH ₃	C ₆ H ₁₃ (n)	C ₆ H ₁₃ (n)	green	
50	17	-C ₆ H ₅	H	CH ₃	CH ₃	C ₃ H ₇ (n)	C ₃ H ₇ (n)	green	50
	18	C ₆ H ₅	H	CH ₃	CH ₃	C ₄ H ₉ (n)	C ₄ H ₉ (n)	green	
	19	C ₆ H ₅	H	CH ₃	CH ₃	C ₁₂ H ₂₅ (n)	C ₁₂ H ₂₅ (n)	green	
55	20	CH ₂ C ₆ H ₅	H	CH ₃	CH ₃	CH ₃	CH ₃	bluish green	55
	21	C ₂ H ₄ C ₆ H ₅	H	CH ₃	CH ₃	CH ₃	CH ₃	bluish green	
60	22	CH ₃	H	CH ₃	CH ₃	CH ₃	CH ₃	bluish green	60
	23	CH ₂ CH(CH ₃) ₂	H	CH ₃	CH ₃	CH ₃	CH ₃	bluish green	
	24	C ₁₀ H ₂₁ (n)	H	CH ₃	CH ₃	CH ₃	CH ₃	bluish green	
65	25	C ₃ H ₆ C ₆ H ₅	H	CH ₃	CH ₃	CH ₃	CH ₃	bluish green	65

Example 26

19.6 parts of cyclohexanone, 66 parts of p-dimethylamino-salicylaldehyde and 27 parts of zinc chloride are dissolved in 250 parts of methanol. Hydrogen chloride gas is passed in at 40°C until saturation is reached and the mixture is then stirred for 12 hours at 20°C. The dye 5 is isolated and is reacted further by the method described in Example 1. 42 parts of 3,3'-trimethylene-7,7'-bis-dimethylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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10



10

10 having a melting point of 228 - 230°C are obtained.

15 In contact with acidic substances, a bluish green coloration is obtained.

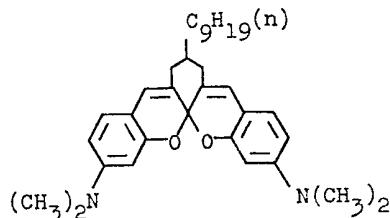
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Example 27

Condensing 4-nonylcyclohexanone with p-dimethylaminosalicylaldehyde by the method described in Example 26 gives 3,3'-(β -nonyl-trimethylene)-7,7'-bis-dimethylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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25

30 having a melting point of 148 - 150°C.

In contact with acidic substances, the compounds develops a bluish green coloration.

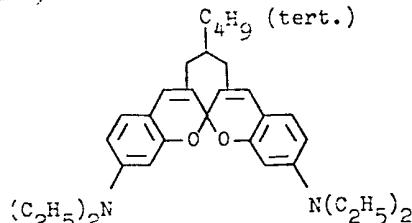
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Example 28

93 parts of 4-tert.-butylcyclohexanone and 232 parts of p-diethylaminosalicylaldehyde are dissolved in 750 parts of methanol. Hydrogen chloride gas is passed into the solution at 40°C until saturation is reached and the mixture is then stirred for 12 hours at 20°C. The dye solution is introduced into a mixture of 1,000 parts of toluene and 1,000 parts of 25 percent strength ammonia solution and stirred until completely decolorized. The toluene phase is separated off and concentrated to one-fifth and the oily residue is caused to crystallize by 40 boiling in alcohol. 150 parts of 3,3'-(β -tert.-butyltrimethylene)-7,7'-bis-diethylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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50 having a melting point of 183 - 184°C are obtained.

In contact with acidic substances, a bluish green coloration is obtained.

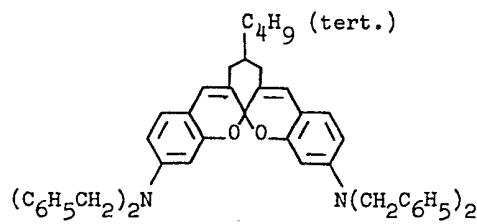
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Example 29

Reacting 4-tert.-butyl-cyclohexanone with p-dibenzylamino-salicylaldehyde by the method described in Example 28 gives 3,3'-(β -tert.-butyltrimethylene)-7,7'-bis-dibenzylamino-2,2'-spirodi-(2H-1-benzopyran) of the formula

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The melting point of the compound is 113 - 116°C.

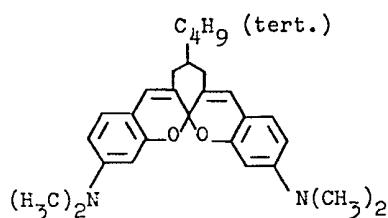
With acidic substances, the compound develops a bluish green coloration.

15

Example 30
Reacting 4-tert.-butylcyclohexanone with p-dimethylamino-salicylaldehyde by the method described in Example 28 gives the dye intermediate 3,3'-(β-tert.-butyltrimethylene)-7,7'-bis(dimethylamino)-2,2'-spirodi-(2H-1-benzopyran) of the formula

20

25



30

which has a melting point of 247 - 249°C and gives a bluish green color reaction on papers carrying an acidic coating.

The compounds listed in the table which follows were prepared by the methods described in Examples 26 to 30; the hues developed on contact with acidic substances are shown in the right-hand column.

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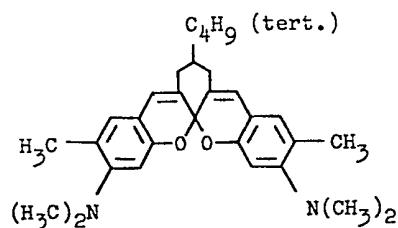
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Example	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	Hue
31	$\begin{array}{c} \text{C}_8\text{H}_{17}(\text{n}) \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ \text{C}_{12}\text{H}_{25} \end{array}$			CH_3	CH_3	CH_3	bluish green
32	$\begin{array}{c} -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ -(\text{CH}_2)_3\text{-} \end{array}$			CH_3	CH_3	CH_3	bluish green
33	$\begin{array}{c} \text{C}_4\text{H}_9 \text{ (tert.)} \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ -(\text{CH}_2)_2\text{-} \\ \\ -(\text{CH}_2)_4\text{-} \end{array}$			C_2H_5	C_2H_5	C_2H_5	bluish green
34	$\begin{array}{c} \text{C}_4\text{H}_9 \text{ (tert.)} \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ -(\text{CH}_2)_2\text{-} \\ \\ -(\text{CH}_2)_4\text{-} \end{array}$			CH_3	$\text{p-ClC}_6\text{H}_4\text{CH}_3$	$\text{p-ClC}_6\text{H}_4$	bluish green
35	$\begin{array}{c} \text{C}_4\text{H}_9 \text{ (tert.)} \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ -(\text{CH}_2)_2\text{-} \\ \\ -(\text{CH}_2)_4\text{-} \end{array}$			C_2H_5	C_2H_5	C_2H_5	bluish green
36	$\begin{array}{c} \text{C}_4\text{H}_9 \text{ (tert.)} \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ -(\text{CH}_2)_2\text{-} \\ \\ -(\text{CH}_2)_4\text{-} \end{array}$			CH_3	CH_3	CH_3	bluish green
37	$\begin{array}{c} \text{C}_4\text{H}_9 \text{ (tert.)} \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \\ \\ -(\text{CH}_2)_2\text{-} \\ \\ -(\text{CH}_2)_4\text{-} \end{array}$			$-(\text{CH}_2)_5$	$-(\text{CH}_2)_5$	$-(\text{CH}_2)_5$	bluish green
38	$\begin{array}{c} \text{C}_2\text{H}_4\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{C}_6\text{H}_5 \\ \\ -\text{CH}_2\text{-CH-CH}_2\text{-} \end{array}$						bluish green

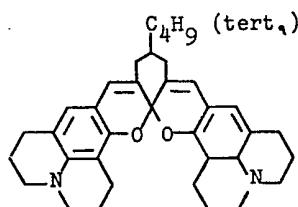
39	$-(CH_2)_3-$	C_2H_4CN	C_2H_4CN	C_2H_4CN	C_2H_4CH	bluish green
40	$-(CH_2)_3-$	C_2H_4Cl	C_2H_4Cl	C_2H_4Cl	C_2H_4Cl	bluish green
41	$-(CH_2)_3-$	CH_3	C_2H_4CN	CH_3	C_2H_4CN	bluish green
	C_4H_9 (tert.)					
42	$-CH_2-CH-CH_2-$	H	$\text{--} \text{H} \text{--}$	H	$\text{--} \text{H} \text{--}$	bluish green
	C_4H_9 (tert.)					
43	$-CH_2-CH-CH_2-$	CH_3	$C_2H_4OCH_3CH_3$	$C_2H_4OCH_3$	$C_2H_4OCH_3$	bluish green
	$C_7H_{15}(n)$					
44	$-CH_2-CH-CH_2-$	CH_3	CH_3	CH_3	CH_3	bluish green

The following compounds, which were prepared by the methods described in Examples 26 to 30, also give bluish green colorations in contact with acidic substances:

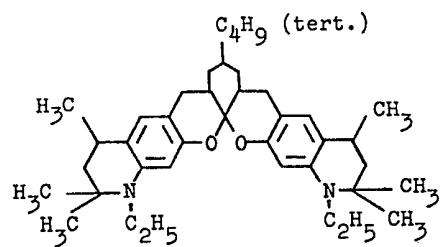
EXAMPLE 45



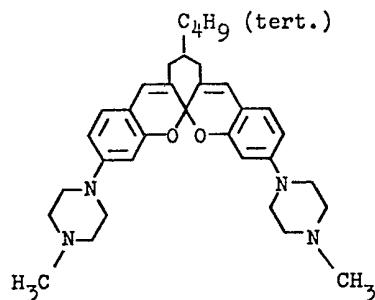
EXAMPLE 46



EXAMPLE 47

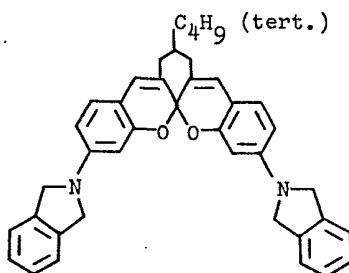


EXAMPLE 48



Example 49

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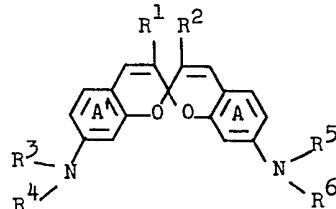
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WHAT WE CLAIM IS:

1. A spirodipyran of the general formula:-

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30 in which R^1 is hydrogen, alkyl of 1 to 12 carbon atoms, phenyl which is unsubstituted or substituted by alkyl of 1 to 4 carbon atoms, methoxy, ethoxy, chlorine or bromine, or phenylalkyl of 7 to 10 carbon atoms, and R^2 is hydrogen, or R^1 and R^2 together are dimethylene, trimethylene or tetramethylene, which are unsubstituted or substituted by alkyl of 1 to 12 carbon atoms; R^3 and R^5 each independently are hydrogen, alkyl of 1 to 12 carbon atoms, cyano-, chlorine-, methoxy- or ethoxy-substituted alkyl of 2 to 4 carbon atoms, cyclo-alkyl of 5 to 7 carbon atoms, phenylalkyl of 7 to 10 carbon atoms, or trimethylene which is unsubstituted or substituted by 1 to 3 methyl groups and is bonded to the carbon atom in the 6-position or 6'-position, as the case may be, of the adjacent benzene ring, and R^4 and R^6 each independently are alkyl of 1 to 12 carbon atoms, cyano-, chlorine-, methoxy- or ethoxy-substituted alkyl of 2 to 4 carbon atoms, phenylalkyl of 7 to 10 carbon atoms, phenyl which is unsubstituted or substituted by alkyl of 1 to 4 carbon atoms, chlorine or bromine, or trimethylene bonded to the carbon atom in the 8-position or 8'-position, as the case may be, of the adjacent benzene ring, and one or both of the groups $-NR^3R^4$ and $-NR^5R^6$ may alternatively be a pyrrolidino, piperidino, morpholino, thiomorpholino, N' -alkylpiperazino (alkyl being of 1 to 4 carbon atoms) or isoindolino radical; and the rings A and A' are unsubstituted or substituted by alkyl of 1 to 3 carbon atoms.

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50 2. A spirodipyran as claimed in claim 1 wherein R^1 is phenyl and R^2 is hydrogen or R^1 and R^2 together are β -alkyl-trimethylene (where alkyl is of 1 to 12 carbon atoms) R^3 , R^4 , R^5 and R^6 are each as defined in claim 1. 50

3. A spirodipyran as claimed in claim 1 wherein R^1 is phenyl and R^2 is hydrogen or R^1 and R^2 together are β -alkyl-trimethylene (where alkyl is of 4 to 12 carbon atoms) and R^3 , R^4 , R^5 and R^6 are, each independently, alkyl of 1 to 6 carbon atoms or benzyl.

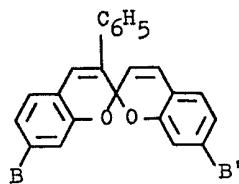
55 4. A spirodipyran as claimed in any one of claims 1 to 3 wherein R^3 , R^4 , R^5 and R^6 are, each independently, methyl, ethyl, butyl, propyl, hexyl or benzyl. 55

55 5. A spirodipyran as claimed in claim 4, wherein R¹ is phenyl and R² is hydrogen or R¹ and R² together are β -tert.-butyl-trimethylene.

6. A spirodipyran as claimed in claim 1 having the formula:-

1 19 3

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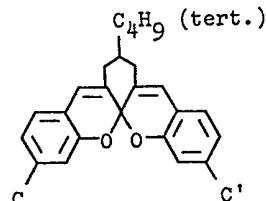
wherein B and B' are $-\text{N}(\text{CH}_3)_2$, $-(\text{C}_2\text{H}_5)_2$ or $-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$
 or B is $-\text{N}(\text{CH}_3)_2$ and B' is $-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$.

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7. A spirodipyrane as claimed in claim 1 and having the formula:

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where C and C' are $-\text{N}(\text{C}_2\text{H}_5)_2$ or $-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$.

25

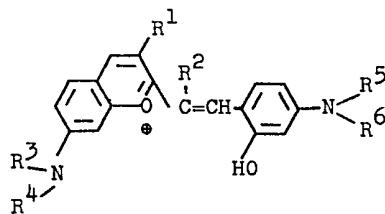
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8. A spirodipyrane as claimed in claim 1 and identified in any one of the foregoing specific Examples.

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9. A process for the manufacture of a spirodipyrane as claimed in claim 1 which process comprises cyclizing an o-hydroxy-arylstyryl compound of the general formula:-

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in which R¹, R², R³, R⁴, R⁵ and R⁶ are each as defined in claim 1.

10. A process as claimed in claim 9 wherein the cyclization is carried out in the presence of one or more basic substances.

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11. A process as claimed in claim 10 wherein sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, ammonia, an aliphatic amine or pyridine is used as basic substance.

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12. A process as claimed in claim 9 carried out substantially as described in any one of the foregoing specific Examples.

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13. A spirodipyrane as claimed in claim 1 whenever obtained by a process as claimed in any one of claims 9 to 12.

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14. A pressure-sensitive recording material, copying material or other duplicating system which contains one or more spirodipyrans as claimed in any one of claims 1 to 8 or 13 as dye intermediate.

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15. Microcapsules containing as encapsulated material a solution or suspension of a spirodipyrane as claimed in any one of claims 1 to 8 or 13.

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