# THE CHEMISTRY OF SPIROPYRANS

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CONTENTS



## I. INTRODUCTION

Whereas dibenzospiropyrans (XXI) (1, 2) were synthesized many years ago, substituted products of XXI (5, 16), benzo-α-naphthospiropyran (XXXI) (11), benzo-β-naphthospiropyran (XXII) (4, 9, 12), di-β-naphthospiropyran (XXIII) (3, 4, 5, 8, 11, 12), α,β-dinaphthospiropyran (XXIV) (11, 12), benzoxanthospiropyran (XXX) (15), xantho-β-naphthospiropyran (XXIX) (15), and benzo-β-naphthoisospiropyran (XXV) (10, 11, 13) have been only recently prepared. The present review summarizes the methods of preparation and chemical properties of these compounds. A discussion of the theories concerning their color phenomena is also given.

## II. METHODS OF PREPARATION

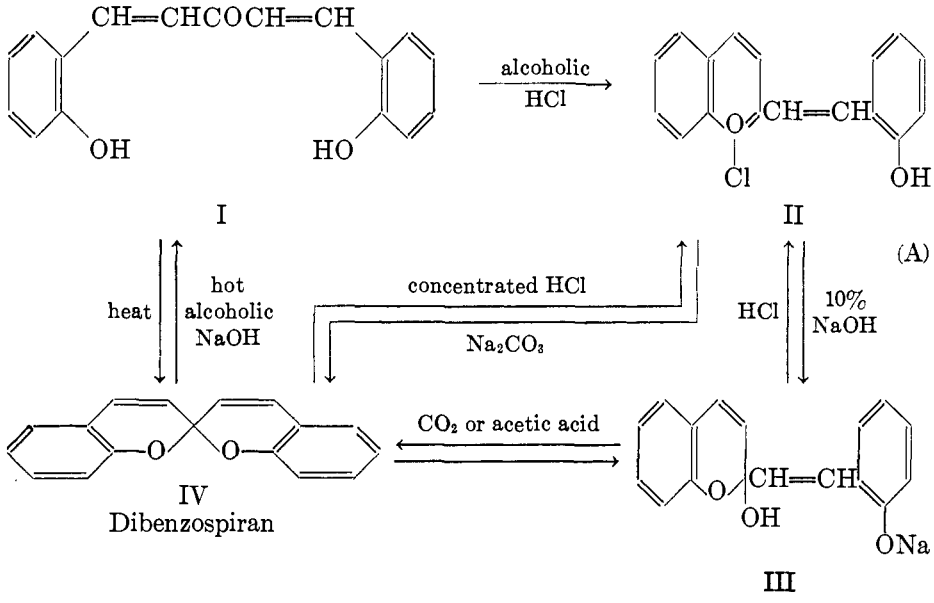
The general method for the preparation of spiropyrans consists in hydrolyzing the synthesized benzo- or naphtho-pyrylium salts. The condensation of salicylaldehyde, or of 2-naphthol-1-aldehyde and substances of analogous structure in an acid medium, with an aliphatic or aromatic ketone containing an acidic methylene group next to the carbonyl (1) leads to the formation of pyrylium salts which on treatment with ammonia give substituted spiropyrans.

### *A. Spiropyrans derived from aliphatic ketones*

#### (1) Acetone and aliphatic analogues

Decker and Felser (2) obtained the sodium salt of 2-*o*-hydroxystyrylbenzopyranol (III) by the action of 10 per cent aqueous sodium hydroxide solution on

2-*o*-hydroxystyrylbenzopyrylium chloride (II), which was prepared by the action of alcoholic hydrogen chloride on the condensation product (I) obtained from salicylaldehyde and acetone. When the sodium salt was treated with carbon dioxide or acetic acid, dibenzospiropyran (IV) was obtained (compare scheme A).

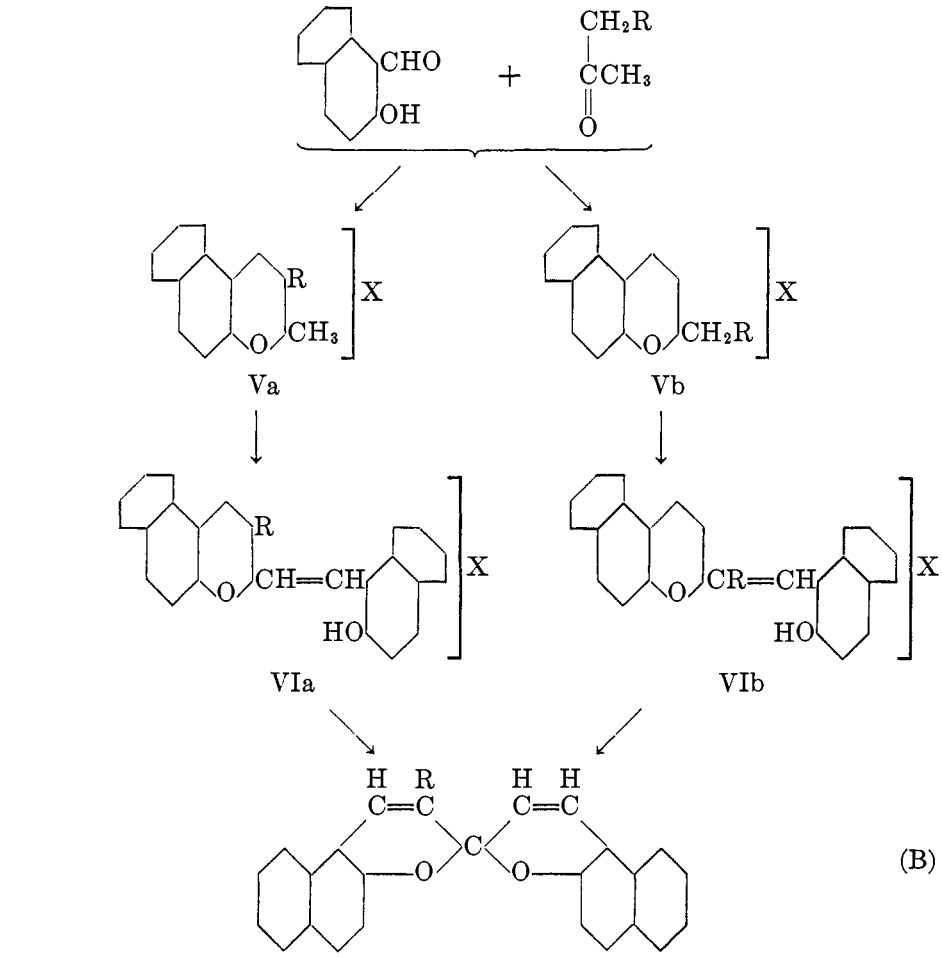


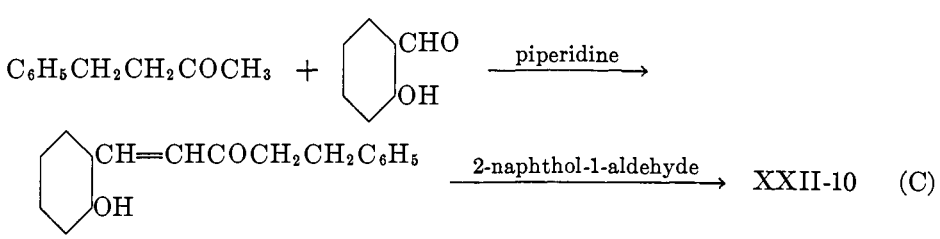

Dilthey and Wizinger (6) proved that the reaction between the *o*-hydroxyaldehyde and the acetone derivatives takes place (using a condensing agent of an acidic nature) in two stages. The intermediate product, e.g., $\alpha$-methylbenzopyrylium salt (Va or Vb), for which two constitutions (compare scheme B) are possible, may be isolated and used in preparing asymmetrically substituted spiropyrans by treatment with different aldehydes.

The salt of the type VI (*o*-hydroxystyrylbenzopyrylium salt) can be isolated even if the components are allowed to react in molecular proportions (1:1). Examples of ethyl methyl ketone with salicylaldehyde and 2-naphthol-1-aldehyde and their corresponding spiropyrans are quoted. The corresponding di-$\beta$-naphthospiropyrans (XXIII) have been successively prepared (3, 14).

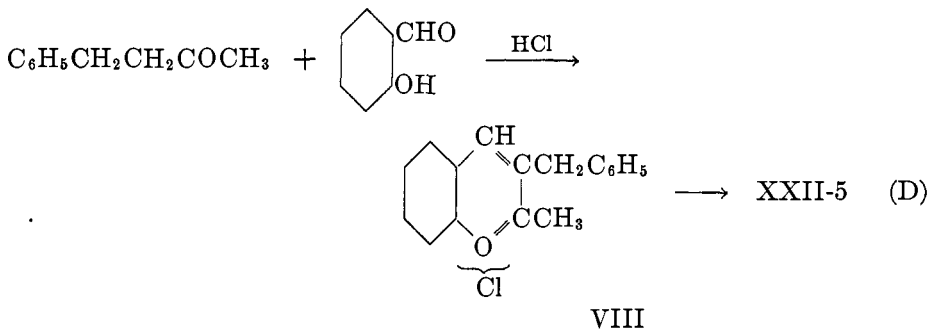
### (2) $\beta$-Phenethyl methyl ketone

Heilbron and coworkers (9) have stated that the methyl and not the methylene group is reactive in the case of $\beta$-phenethyl methyl ketone in the presence of piperidine. Thus, $\beta$-phenethyl methyl ketone condenses with salicylaldehyde in the presence of piperidine, yielding an unsaturated ketone (VII) which, when further condensed with 2-naphthol-1-aldehyde, leads to 3′-benzyl-$\beta$-naphthospiropyran (XXII-10) (compare scheme C).



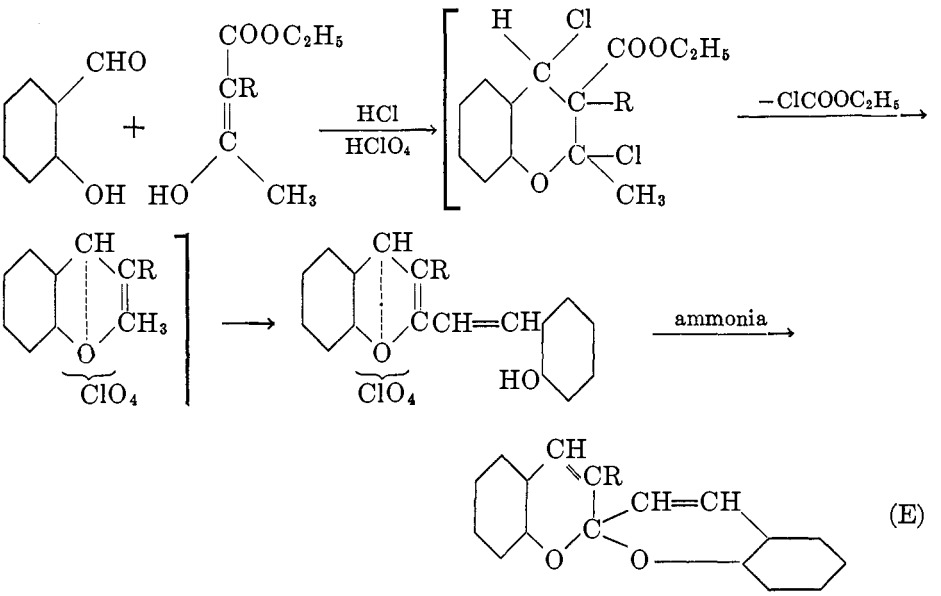




The same result is obtained when sodium hydroxide is employed in place of piperidine; when the condensation is carried out with hydrochloric acid, salicylaldehyde and β-phenethyl methyl ketone give a different product as a result of the methylene group entering into the reaction. Thus the pyrylium salt (VIII) formed reacts with 2-naphthol-1-aldehyde, yielding 3-benzylbenzo-β-naphthospiropyran (XXII-5) (compare scheme D).




(3) Acetoacetate derivatives and acetonedicarboxylic ethyl ester

Löwenbein and Katz (16) obtained 3-methyldibenzospiropyran (XXI-2) by the action of ethyl $\alpha$-methylacetoacetate on salicylaldehyde in ethereal solution in the presence of hydrochloric acid and perchloric acid, followed by treatment of the 2-*o*-hydroxystyryl-3-methylbenzopyrylium perchlorate formed with ammonia (compare scheme E).




Similarly, ethyl or methyl benzylacetoacetate and salicylaldehyde yield 3-benzyldibenzospiropyran (XXI-3), and with 2-naphthol-1-aldehyde, 3-benzyldinaphthospiropyran (XXIII-5) is obtained. Dickinson and Heilbron (4), using ethyl acetonedicarboxylate, obtained ethyl di-$\beta$-naphthospiropyran-3,3′-dicarboxylate (XXIII-10).

(4) Cyclic ketones

3,3′-Dimethylene- (XXVI) and 3,3′-tetramethylene-di-$\beta$-naphthospiropyran (XXVIII) were prepared, respectively, by condensing cyclopentanone and cyclo-

heptanone with 2-naphthol-1-aldehyde in the presence of hydrogen chloride, followed by hydrolysis of the resultant pyrylium salt (11). In the case of cyclohexanone, 3,3′-trimethylenedi-β-naphthospiropyran (XXVII) was obtained (8).

(5) Dibenzyl ketone

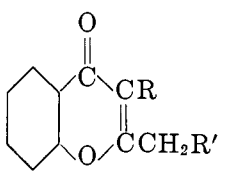
The condensation of 2-naphthol-1-aldehyde with dibenzyl ketone (8) has been studied by Heilbron and coworkers (5). 3,3′-Diphenyldibenzospiropyran (XXI-4) is obtained by condensing two molecules of salicylaldehyde with one molecule of dibenzyl ketone (5).

*B. Spiropyrans derived from 9-methyl- and 9-ethyl-xanthylinium salts*

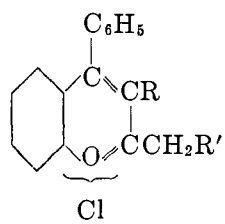
Xantho-β-naphthospiropyran (XXIX) is obtained by the condensation of methylxanthenol and 2-naphthol-1-aldehyde in the presence of hydrogen chloride gas. In the case of salicylaldehyde, benzoxanthospiropyran (XXX) is obtained (15).

*C. Spiropyrans derived from substituted chromones*

The general method for the preparation of spiropyrans consists in converting the appropriate *o*-hydroxyphenyl ketone into the chromone (IX) from which the pyrylium salt (X) is obtained when treated with phenylmagnesium bromide, followed by decomposition with concentrated hydrochloric acid. Condensation of X with 2-naphthol-1-aldehyde yields the naphthovinylpyrylium salt, from which the corresponding spiropyran results on hydrolysis, e.g.:



IX



X

4-Phenyl-3′-methylbenzo-β-naphthospiropyran (XXII-12) (12) is obtained from 2-ethylchromone (IX: R = H, R′ = $CH_3$) when treated with phenylmagnesium bromide, forming 4-phenyl-2-ethylbenzopyrylium chloride (X: R = H; R′ = $CH_3$) as mentioned above.

On the other hand, when 2-ethyl-α-naphtho-γ-pyrone and 3-methyl-2-ethyl-α-naphtho-γ-pyrone (the terms naphtho-α-pyrone and naphtho-γ-pyrone are used in place of naphthocoumarin and naphthochromone, respectively (12)), they give rise to the new series of α,β-dinaphthospiropyrans, e.g., 4-phenyl-3′-methyl-α,β-dinaphthospiropyran (XXIV-1) and 4-phenyl-3,3′-dimethyl-α,β-dinaphthospiropyran (XXIV-4) (11, 12).

Similarly, when 4-phenyl-2,3-dimethyl-α-naphthopyrylium perchlorate was condensed with salicylaldehyde, followed by hydrolysis, 4′-phenyl-3′-methylbenzo-α-naphthospiropyran (XXXI) was obtained (11).

### *D. Isospiropyrans*

The substitution of coumarin derivatives for chromone derivatives in the preparation of spiropyrans leads to the formation of the corresponding isospiropyrans (XXV). 7-Methoxy-2-phenyl-3,4-dimethylcoumarin, when treated with phenylmagnesium bromide as usual, yields 7-methoxy-2-phenyl-3-methylbenzo-β-naphthoisospiropyran (XXV-2) (10, 11, 13).

## III. CHEMICAL PROPERTIES

The spiropyrans listed in table 1 are well-crystallized substances, stable to heat, oxygen, and hydrogen. A hot solution of di-β-naphthospiropyran (XXIII-1) in chlorobenzene, when treated with a stream of oxygen for 1 hr. (6) or in toluene at 100°C. for 15 hr. (4), proved to be practically stable. Similar results were obtained with hydrogen (6).

### *A. Action with acids*

Spiropyrans seem, in general, to react with acids to give the corresponding colored salts, e.g., when dibenzospiropyran (IV, scheme A) is treated with concentrated hydrochloric acid, one ring of the spiropyran is readily opened, yielding the colored 2-*o*-hydroxystyrylbenzopyrylium salt (II).

Dilthey and Wübken (8) showed that if the 3- and 3′-hydrogen atoms are substituted, e.g., as in 3′-methylbenzo-β-naphthospiropyran (XXII-7), there is a marked decrease in the tendency to salt formation with acids; it may become so small that, in the usual condensation with hydrochloric acid, the salt cannot be obtained at all and the spiropyran formation may be easily overlooked. For example, Decker (1) found that 3,3′-diethylspirodibenzopyran yields no salt even when its solution is saturated with hydrogen chloride gas.

Spiropyrans gave coloration with concentrated sulfuric acid ranging from orange in the case of 3,3′-dimethyl-β-dinaphthospiropyran (XXIII-8) (8) to ruby-red in the case of benzo-β-naphthospiropyran (XXII-1) (4).

Similarly, trichloroacetic acid develops the color, while acetic acid fails in the case of xantho-β-naphthospiropyran (XXIX) and benzoxanthospiropyran (XXX) (15).

### *B. Action with alkalies*

The action of warm alcoholic potassium hydroxide on di-β-naphthospiropyran (XXIII-1) gradually gives a blood-red solution, probably owing to the formation of the potassium salt of the corresponding dinaphthylvinyl ketone (3); compare Decker (2) in the case of dibenzospiropyran (IV, scheme A). Ethyl di-β-naphthospiropyran-3,3′-dicarboxylate (XXIII-10) resists the action of boiling alcoholic potassium hydroxide (4).

### *C. Action with Grignard reagents*

Schönberg, Mustafa, and Asker (19) have investigated the action of Grignard solutions on the thermochromic spiropyrans. The reaction of spirodi-β-naphthopyran (XI) with various Grignard reagents, e.g., phenylmagnesium bromide

TABLE 1

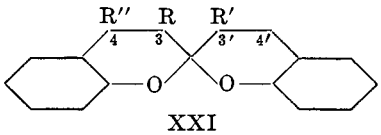
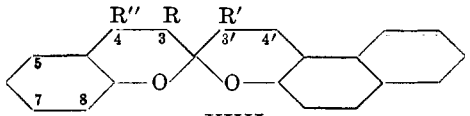
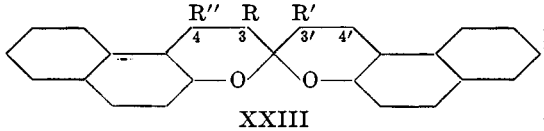
| SPIROPYRAN | COLOR OF THE MELT | COLOR IN BOILING INERT SOLVENTS |
|---|---|---|
|  XXI | | |
| XXI-1: R = R′ = R″ = H | No color | Colorless |
| XXI-2: R = $CH_3$; R′ = R″ = H | No color | Colorless |
| XXI-3: R = $C_6H_5CH_2$; R′ = R″ = H | No color | Colorless |
| XXI-4: R = R′ = $C_6H_5$; R″ = H | No color | Colorless |
|  XXII | | |
| XXII-1: R = R′ = R″ = H | Purple | Wine-red in xylene |
| XXII-2: R = $CH_3$; R′ = R″ = H | Purple | Wine-red in xylene |
| XXII-3: R = $CH(CH_3)_2$; R′ = R″ = H | Purple | Purple in xylene |
| XXII-4: R = $C_6H_5$; R′ = R″ = H | Purple | Faint color in xylene; strong reddish blue in nitrobenzene |
| XXII-5: R = $CH_2C_6H_5$; R′ = R″ = H | Purple | Reddish purple in xylene |
| XXII-6: R = β-$CH_2CH_2C_6H_5$; R′ = R″ = H | Deep purple | Intense purple in xylene |
| XXII-7: R = H; R′ = $CH_3$; R″ = H | No color | Colorless in xylene or veratrole |
| XXII-8: R = H; R′ = $CH(CH_3)_2$; R″ = H | No color | Colorless in xylene or veratrole |
| XXII-9: R = H; R′ = octyl; R″ = H | No color | Colorless in diphenyl ether |
| XXII-10: R = H; R′ = $CH_2C_6H_5$; R″ = H | No color | Colorless in xylene |
| XXII-11: R = H; R′ = β-$CH_2CH_2C_6H_5$; R″ = H | No color | Colorless in xylene or veratrole |
| XXII-12: R = H; R′ = $CH_3$; R″ = $C_6H_5$ | No color | Colorless in xylene, veratrole, or diphenyl ether |
| XXII-13: R = H; R′ = $CH_3$; R″ = $C_6H_5$, 7-$OCH_3$ | No color | Colorless in xylene, veratrole, or diphenyl ether |
|  XXIII | | |
| XXIII-1: R = R′ = R″ = H | Tarry at 260°C. | Purple in xylene or nitrobenzene at 100°C. |
| XXIII-2: R = $CH_3$; R′ = R″ = H | Not reported | Blue-violet in xylene |

TABLE 1—*Continued*

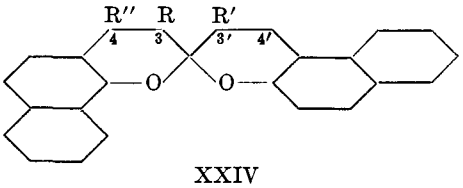
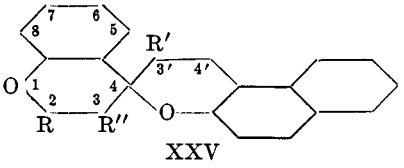
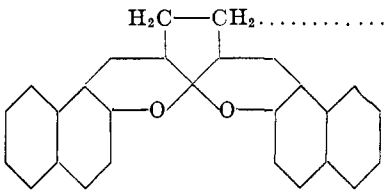
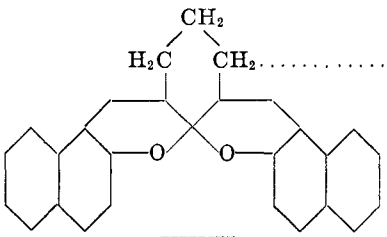
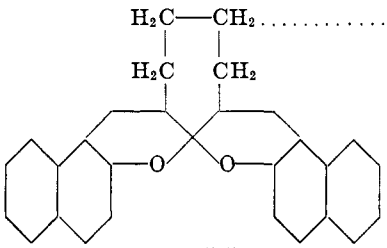
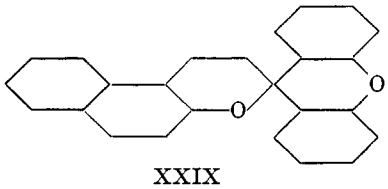
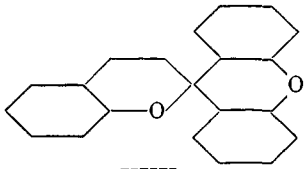
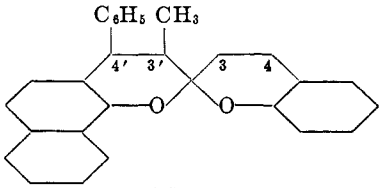
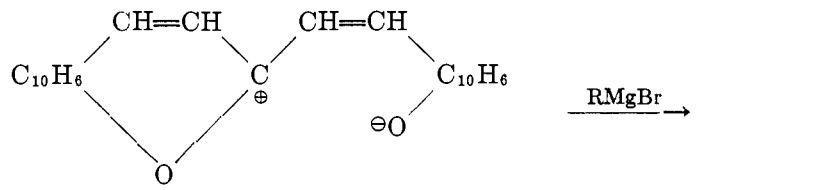
| SPIROPYRAN | COLOR OF THE MELT | COLOR IN BOILING INERT SOLVENTS |
|---|---|---|
| XXIII-3: R = amyl; R′ = R″ = H..... | Not reported | Violet in pyridine |
| XXIII-4: R = octyl; R′ = R″ = H..... | Not reported | Purple in xylene |
| XXIII-5: R = $CH_2C_6H_5$; R′ = R″ = H..... | Deep blue | Blue-violet in benzene; darker in xylene |
| XXIII-6: R = β-$CH_2CH_2C_6H_5$; R′ = R″ = H..... | Not reported | Blue-purple in xylene |
| XXIII-7: R = $C_6H_5$; R′ = R″ = H..... | Blue | Dark violet in naphthalene |
| XXIII-8: R = R′ = $CH_3$; R″ = H..... | Olive-green | Colorless in xylene |
| XXIII-9: R = R′ = $C_6H_5$; R″ = H..... | Not reported | Colorless in inert solvents |
| XXIII-10: R = R′ = $COOC_2H_5$; R″ = H..... | Not reported | Colorless in inert solvents |
|  XXIV | | |
| XXIV-1: R = H; R′ = $CH_3$; R″ = $C_6H_5$..... | Not reported | Colorless in xylene; pale violet in diphenyl ether |
| XXIV-2: R = $CH_3$; R′ = H; R″ = $C_6H_5$..... | Blue | The color developed is not specified |
| XXIV-3: R = R′ = H; R″ = $C_6H_5$..... | Deep purple | |
| XXIV-4: R = $CH_3$; R′ = $CH_3$; R″ = $C_6H_5$..... | Blue | Colorless in xylene; pale violet in diphenyl ether |
|  XXV | | |
| XXV-1: R = $C_6H_5$; R′ = H; R″ = $CH_3$..... | Purple | Intense purple in xylene or veratrole |
| XXV-2: R = $C_6H_5$; R′ = H; R″ = $CH_3$, 7-$OCH_3$. | Purple | Magenta in xylene |
| XXV-3: R = $C_6H_5$; R′ = H; R″ = $C_6H_5$, 7-$OCH_3$. | Purple | Deep blue in ether containing one drop of acetic acid; pale magenta in benzene below 0°C. |

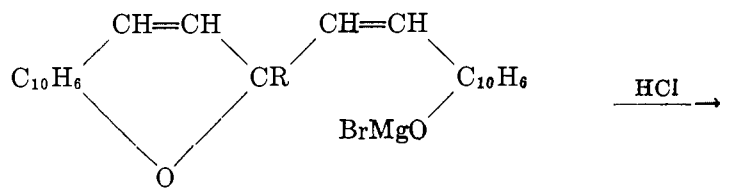
TABLE 1—*Continued*

| SPIROPYRAN | COLOR OF THE MELT | COLOR IN BOILING INERT SOLVENTS |
|---|---|---|
|  XXVI | Purple | Blue color in xylene |
|  XXVII | Blue | Faint color in diphenyl ether |
|  XXVIII | Not reported | Colorless in inert solvents, even in diphenyl ether |
|  XXIX | Deep red | Faint strawberry-pink in veratrole; deep in diphenyl ether |
|  XXX | Not reported | Colorless in diphenyl ether and dodecahydrosqualene |
|  XXXI | Not reported | Colorless in inert solvents |

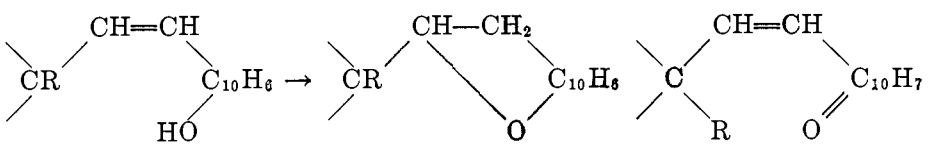
followed by hydrolysis, leads to the formation of 2,3-dihydrofuran derivatives (XIV) and not of phenolic compounds (XIII). XIV (R = $C_6H_5$) is insoluble in aqueous alkali solution; it is not attacked by ethereal diazomethane solution or by benzoyl chloride in the presence of pyridine, and is stable towards methyl sulfate in the presence of alkali. These properties make it improbable that the reaction product has the character of an enol or of a potential enol (XIII or XV). The diene reaction of XIV with maleic anhydride is negative. The reaction proceeds according to the following scheme:




XI



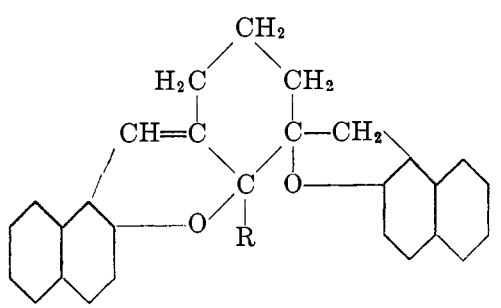

XII




XIII XIV XV

Similarly, the action of Grignard reagents on 3,3′-trimethylenespirodi-β-naphthopyran (XXVII) leads to products which show properties analogous to those of XIV (R = $C_6H_5$). These compounds are therefore formulated as XVI.

XXVII + RMgBr ⟶

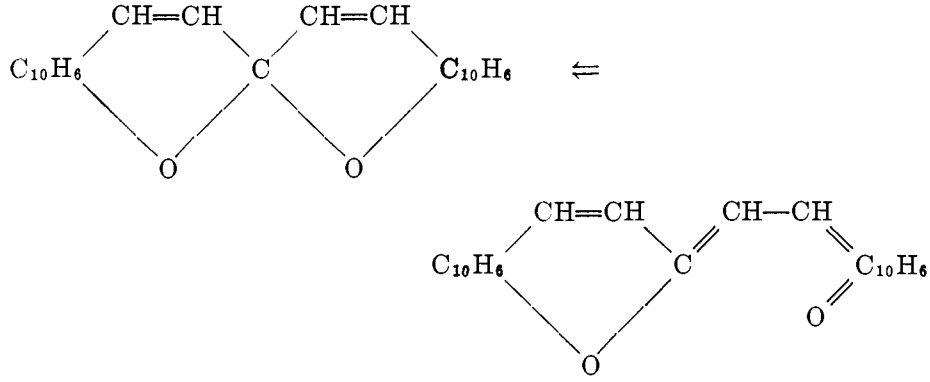



XVI

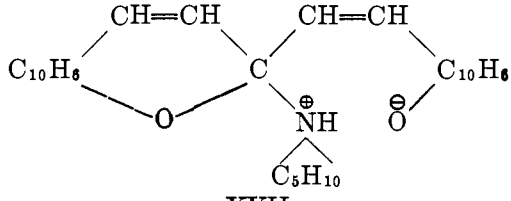
## IV. COLOR PHENOMENA ASSOCIATED WITH SPIROPYRANS

The substances mentioned in table 1 are, in general, colorless crystalline compounds; some of them exhibit the property of forming, in cold inert solvents, colorless solutions which develop an intense violet-blue color on heating; on cooling, the color disappears and the substance is recovered almost unchanged. This phenomenon has been studied chiefly by Heilbron, Löwenbein, Dilthey, and their respective schools.

One view which has been advanced by Löwenbein and Katz (16) accounts for this phenomenon by intramolecular change from the spiro type to the *o*-quinoid system, as illustrated below:

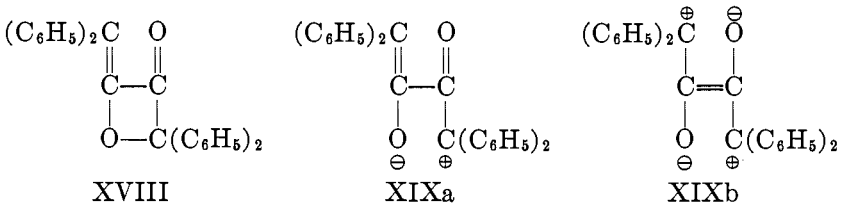


Dilthey and coworkers (6, 7) reject the quinoid hypothesis on the grounds that, whereas true quinones mostly show a bathochromic effect in piperidine solution and never a hypsochromic action, di-$\beta$-naphthospiropyran (XXIII-1) gives a yellow solution which is unaffected by heat (7). The disappearance of color in the salts formed by the interaction of the spiropyran and piperidine shows that the chromophore, the positively charged carbon atom, is absent (XVII).

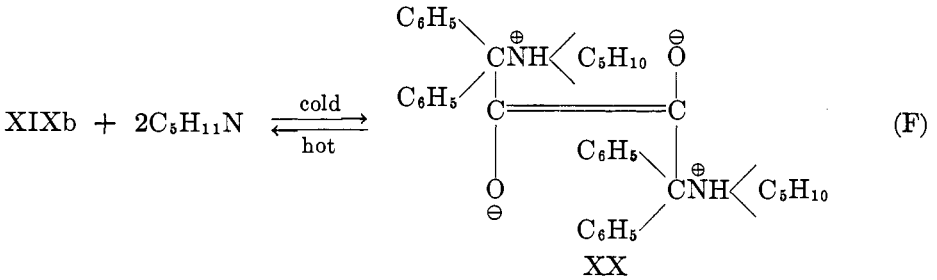


XVII

Salts of this type have so far not been isolated, but the correctness of Dilthey's conception is greatly strengthened by the observation of Schönberg and Sina (20) that the dimeric permanganate-colored diphenylketene (XVIII), which has the constitution of a betaine (XIXa or XIXb), dissolves in cold piperidine yielding an almost colorless solution, from which the colorless piperidinium salt (XX) may be obtained. When the salt is heated, piperidine is split off and the dimeric diphenylketene is regenerated (compare scheme F).

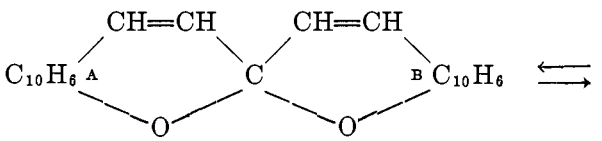


XVIII XIXa XIXb

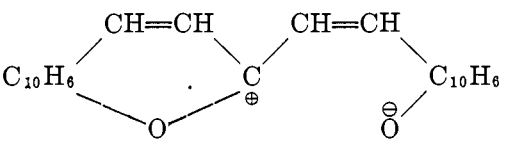


XIXb + $2C_5H_{11}N$ $\underset{\text{hot}}{\overset{\text{cold}}{\rightleftharpoons}}$ XX (F)

Dilthey and coworkers (6, 7) conclude that the appearance of color is due to ionic dissociation, the colored form being represented as a heteropolar molecule, as illustrated below.



(colorless in the cold)

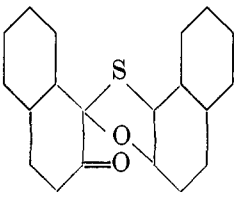


(violet-blue on heating) (G)

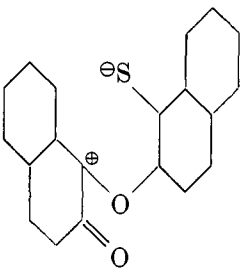
The possibility of the phenomenon being due to free-radical formation has been excluded by Dilthey (6, 7) and Löwenbein (16); both showed that the molecular weights of these compounds are normal, whether the solution is colored or not. Dickinson and Heilbron (4) found that the color is unchanged by the addition of quinol, a reagent which almost instantaneously reduces all the known types of radicals, with disappearance of the color.

Recently, Schönberg, Mustafa, and Asker (19) have shown that a possible approach to this color phenomenon may be to apply the theories used to explain the stability of the free radicals of the triphenylmethyl type. It has been pointed out (compare Gilman, *Organic Chemistry*, 2nd edition, page 1979) that the free radicals formed by the dissociation of hexaphenylethane are stabilized by resonance, and it seems possible that this theory may also explain the stability of the zwitter ions such as XI. On the other hand, the lowered stability of the spirans may be due to their non-polar configuration (see rings A and B in scheme G) interfering with the development of resonance.

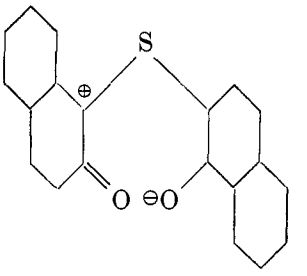
All the spiropyrans so far investigated show the betaine structure (compare scheme G) (18, 19, 20) only in solution and the question arises whether colored spiropyrans may be found which owe their color, even in the solid state, to the presence of a positively charged carbon atom. This seems to be the case. It has been found (17) that dehydro-β-naphthol sulfide (21) probably belongs to this group of substances. Structure XXXII does not explain the deep red color of the substance and it is believed that it must be regarded as an enol or thio-enol betaine (XXXIIIa or XXXIIIb).




XXXII

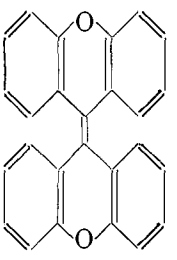



XXXIIIa

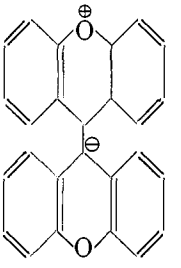



XXXIIIb

The thermochromic behavior of the spiropyrans may be related to that of certain ethylenes, e.g., XXXIVa and XXXIVb (18). This phenomenon has also been explained by the formation of betaines, as illustrated below:




XXXIVa
(colorless in the cold)




XXXIVb
(bluish-green on heating)

Dickinson and Heilbron (4) showed that the determining factors for the color development in spiropyrans are: (*a*) that at least one naphthalene ring be present and (*b*) that the 3′-carbon atom in the naphthopyran ring be unsubstituted. The color phenomenon is the result of a series of changes in which equilibrium is established between the neutral spiropyran and an ionized compound (compare scheme G).

Later, Dilthey and Wübken (8) drew a parallel between the ease with which spiropyrans undergo salt formation in the presence of acids (forming styrylpyryl-ium salts) and the ease with which they change color on heating in inert solvents: they regarded the two changes as analogous. Their arguments are based on the behavior of 3,3′-trimethylene-β-naphthospiropyran (XXVII), which develops a distinct color in boiling diphenyl ether and dissolves in acetic acid without color, i.e., no salt formation, but in trichloroacetic acid gives a violet color. Further investigations by Dickinson and Heilbron and coworkers (5) showed that while 3′-methylbenzo-β-naphthospiropyran (XXII-7) undergoes no color change in diphenyl ether, 3-methylbenzo-β-naphthospiropyran (XXII-2) develops the usual wine-red color; both dissolve in acetic acid yielding colored solutions due to salt formation. On the basis of Dilthey and Wübken's view (8), both substances would be expected to develop color in diphenyl ether. Their failure to do so shows that the ease of formation of the ionic anhydro base is not strictly comparable to salt formation.

According to the experimental facts, Heilbron and coworkers (4, 5, 9, 14) came to the following conclusions: (*a*) Dibenzospiropyrans (XXI-1) do not develop any color change on heating in inert solvents. (*b*) Benzo-β-naphthospiropyrans (XXII-1) containing a substituent in the 3′-position fail to give a color change. (*c*) Di-β-naphthospiropyrans (XXIII-1) containing a substituent in both the 3- and 3′-positions fail to give colored solutions. (*d*) Spiropyrans having a phenyl group at position 4 (in the benzo-β-naphthospiropyran molecule) (XXII) behave normally in developing the color change, except for 4-phenyl-3′-methylbenzo-β-naphthospiropyran (XXII-12) and its 7-methoxy derivative (XXII-13) which give a coloration on heating in xylene solution, although substituted in the 3′-position (11). (*e*) α,β-Dinaphthospiropyrans appeared to differ from those encountered in the di-β-naphthospiropyran series, since a coloration is developed even with substituents in both the 3- and 3′-positions, e.g., 4-phenyl-3,3′-dimethyl-α,β-dinaphthospiropyran (XXIV-4) (11, 12). (*f*) Benzo-α-naphthospiropyrans, e.g., 4′-phenyl-3′-methylbenzo-α-naphthospiropyran (XXXI), behaved normally in failing to give a colored solution in inert solvents of high boiling points. (*g*) Substituted benzo-β-naphthoisospiropyrans (XXV), e.g., 2-phenyl-3-methylbenzo-β-naphthoisospiropyran (XXV-1), where the 3′-position is unsubstituted, develop colored solutions as normal spiropyrans do (10, 12, 13).

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