Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.8; H, 7.1. Found: C, 75.8; H, 7.0.

The **perchlorate** was prepared with ethanolic perchloric acid and crystallized from ethanol, m.p. 261–262° (dec.); $[\alpha]^{25}_{D}$ −23.5 (*c* 0.44, water).

Anal. Calcd. fror $C_{17}H_{20}ClNO_6$: C, 55.2; H, 5.4. Found: C, 55.3; H, 5.4.

Treatment with diazomethane converted Δ^8-desoxymorphine to Δ^8-desoxycodeine.

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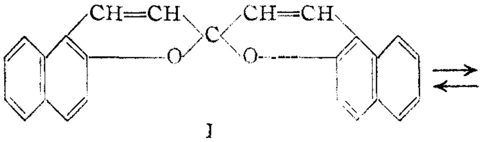
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, FOUAD I UNIVERSITY]

Some Adsorption Colors and their Significance for Thermochromic and Tautomeric Effects. II.[1] Experiments with Spiropyrans and with 1,3-Diketohydrindene

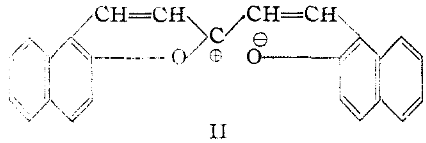
BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND WAFIA ASKER

Some thermochromic spiropyrans are adsorbed from their colorless, cold, benzene solutions with the production of color by dried silica gel or by alumina; decolorization is effected by treating the colored surface active material with methyl alcohol (elution). The color of the adsorbates on a silica gel and alumina is similar to the color shown by the thermochromic spiropyrans in hot, inert solvents, *e.g.*, cold (hot) benzene solutions of (I) are colorless (violet); whereas the color of the adsorbate (from cold benzene solutions) on a silica gel and on alumina is blue. The results are presented in Table I. When alumina is placed into the colorless benzene solution of 1,3-diketohydrindene (XIV), a violet adsorbate is formed, believed to be due to the enol form (XVa). When filter paper is moistened with the colorless, benzene solution of (XIV) and allowed to dry in a vacuum, it remains colorless, but when the dried filter paper is exposed to water vapor, it turns violet (formation of XVa). A theory is advanced to explain the adsorption colors described in the above paragraphs. Free radicals (*e.g.*, XIIa and XIIIa) do not form colored adsorbates on a silica gel or alumina. The red dehydro-2-naphthol-1-sulfide previously regarded as the spiro compound (X) is now believed to be a resonance hybrid (compare XIa and XIb).

(a) A number of bis-spiro-2-pyrans which are colorless in the cold state, are known to show reversible color changes (thermochromic changes); their solutions in cold, inert solvents are colorless, but become colored, *e.g.*, violet blue, on heating. This phenomenon has been studied chiefly by Heilbron, Löwenbein and Dilthey[2] and their respective schools and they all agree that the color change is due to ionic dissociation with the formation of a heteropolar molecule (comp. I ⇆ II).[3] The observation of Schönberg, Mustafa and Asker,[4a] relative to the action of the Grignard reagent on such spiropyrans, are in good agreement with the supposed betaine structure (comp. II), as the observations of Dilthey and co-workers[4b] are.

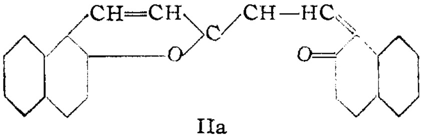

I

colorless solutions in the cold


II

violet-blue solutions on heating

It should, however be pointed out that the colored form has to be regarded as a resonance hybrid of many structures, *e.g.*, IIa.


IIa

Previously, it was thought that the colored forms might be regarded as free radicals, but this conception was rightly abandoned in view of the stability of the colored form toward oxygen[4]; also the thermostability of the colored forms is not in agreement with the free radical theory.

(b) We placed dried silica gel or alumina in cold, colorless, benzene solutions of some of the thermochromic bis-spiro-2-pyrans. From Table I, it is evident that the material acquired the same color, or a similar color, as shown by the thermochromic bis-spiro-2-pyrans in hot, inert solvents; coloration was effected instantaneously or within a few seconds, depending *inter alia*, on whether concentrated or diluted solutions were used; decolorization was effected by washing the colored, inorganic material with methyl alcohol.

These experiments are reminiscent of similar ones by E. Weitz and his school. According to Weitz and co-workers,[5] certain colorless compounds adsorbed on solid adsorbents are polarized by the strong, electric field present at the surface of the adsorbent to yield a colored compound, the color disappearing on elution. Thus the di- and triaminotriphenylmethanols (the colorless pseudobases of the corresponding Ph_3CH dyes) are adsorbed by silica gel and alumina, the color of the adsorbates corresponding to that of the dye salts (malachite green and crystal violet). The colorless compounds become colored as the result of polarization[6] on adsorption.

It is, however, possible that the adsorption color in the case of spiropyrans may be explained in a different way, namely, that there is an equilibrium between the colorless spiro form and the colored form not only in hot, but also in cold solutions. The colored form (its concentration in cold solutions is so small that the color cannot be detected) is adsorbed in preference. Thus, when the equilibrium in the solution is disturbed, the colored form

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[1] Schönberg and Asker, *Science*, **113**, 56 (1951), is to be regarded as Part I.

[2] See Mustafa, *Chem. Revs.*, **43**, 509 (1948).

[3] Dickinson and Heilbron, *J. Chem. Soc.*, 1699 (1927).

[4] (a) Schönberg, Mustafa and Asker, *ibid.*, 847 (1947); (b) Dilthey and Wizinger, *Ber.*, **59**, 1856 (1926).

[5] Weitz, *et al.*, *Z. Elektrochem.*, **46**, 222 (1940); **47**, 65 (1941); *Ber.*, **72**, 1740 (1939).

[6] Weitz and Schmidt, *ibid.*, **72**, 2099 (1939).

TABLE I

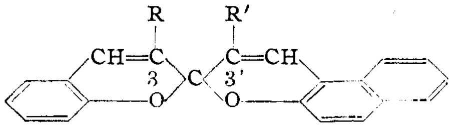
THE THERMOCHROMIC CHANGES ARE REVERSIBLE

Substance, -spiropyran	Color of the crystals	Color of benzene soln. Cold	Hot	Color of anisole soln. Cold	Hot	Color of SiO_2 when allowed to react on cold benzene soln.	Color of Al_2O_3 when allowed to react on cold benzene soln.
						Color developed on inorganic material disappeared by washing with methyl alcohol	
Benzo-β-naphtho (IIIa)	Yellow	Yellow	Violet	Yellow	Violet	Violet	Violet
3-Methylbenzo-β-naphtho (IIIb)	Colorless	Weak violet, almost colorless	Violet	Weak violet	Deep violet	Blue	Blue
3'-Methylbenzo-β-naphtho (IIIc)[a]	Colorless	Colorless	Colorless	Colorless	Colorless	Violet	Blue
Di-β-naphtho (IVa)[b]	Colorless	Colorless	Violet	Colorless	Deep violet-blue	Blue	Blue
3-Methyl-di-β-naphtho (IVb)[c]	Colorless	Colorless	Violet	Colorless	Violet	Blue	Blue
3-Amyl-di-β-naphtho (IVc)[d]	Colorless	Colorless	Pale violet	Colorless	Deep violet	Blue	Bluish-green
3-Phenyl-di-β-naphtho (IVd)[c]	Colorless	Colorless	Colorless	Colorless	Violet	Blue	Bluish-green
3,3'-Dimethylene-di-β-naphtho (V)[e]	Colorless	Colorless	Colorless	Colorless	Violet-blue	Blue	Bluish-black
3,3'-Trimethylene-di-β-naphtho (VI)[d]	Yellow	Yellow	Yellow	Yellow	Yellow	Violet	Blue (developed slowly)
Xantho-β-naphtho (VII)[f]	Colorless	Colorless	Pale pink	Colorless	Pink	Blue	Blue

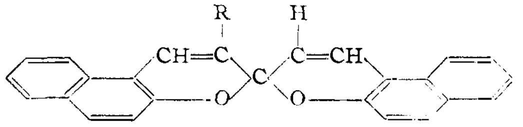
[a] Dickinson and Heilbron, *J. Chem. Soc.*, 1699 (1927). [b] Dickinson and Heilbron, *ibid.*, 14 (1927). [c] Dilthey, Berres, Hölterhoff and Wübken, *J. prakt. Chem.*, **114**, 179 (1926). [d] Dilthey and Wübken, *Ber.*, **61**, 963 (1928). [e] Heilbron, Heslop and Irving, *J. Chem. Soc.*, 430 (1933). [f] Irving, *ibid.*, 1093 (1929).

is re-formed and the process is repeated until the saturation point is reached with regard to adsorption.

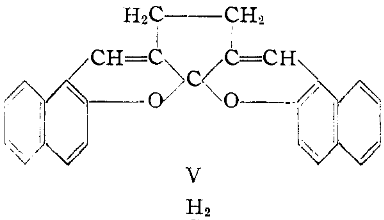
Attention should be drawn to the case of 3'-methylbenzo-β-naphthospiropyran (IIIc) which dissolves in hot, inert solvents (*e. g.*, xylene or anisole) without developing color. Nevertheless, this substance (IIIc) gives, as related compounds do, a colored adsorbate on silica gel and alumina.



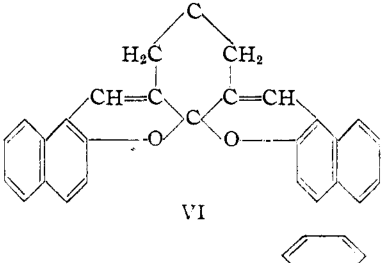
IIIa, R = R' = H
IIIb, R = CH_3, R' = H
IIIc, R = H, R' = CH_3



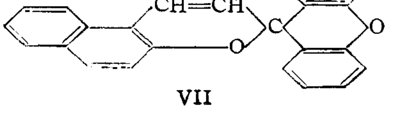
IVa, R = H; IVb, R = CH_3
IVc, R = amyl; IVd, R = C_6H_5



V

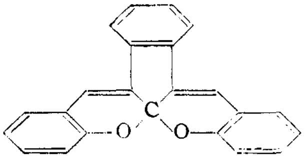


VI

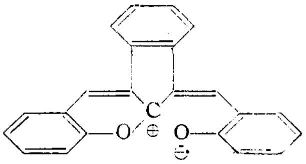


VII

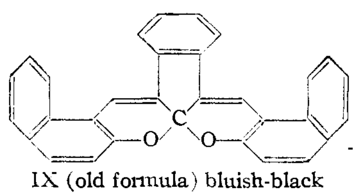
Spiropyrans which are Colored in the Solid State.—The spiropyrans described by Heilbron, Löwenbein and Dilthey are colorless or yellowish in the solid state. When looking for analogous compounds which are deeply colored, even in the solid state, our attention was drawn to phenylene-di-benzospiropyran and phenylene-di-β-naphthospiropyran for which Ruhemann and Levy[7] have advanced the formulas (VIII) and (IX), respectively. However, these formulas are not in accordance with their intense color and the betaine formulas (VIIIa) and a similar one for (IX) are now advanced, in addition to resonance structures, similar to IIa.



VIII (old formula) deep red



VIIIa (new formula)



IX (old formula) bluish-black

In this connection, we wish to draw attention to dehydro-2-naphthol-1-sulfide for which formula (X) is generally accepted.[8] In spite of the fact that (X) explains the formation of the dehydro-2-naphthol-1-sulfide (from bis-2-naphthol-1-sulfide by dehydrogenation) and some of its properties, (X) cannot be accepted since dehydro-2-naphthol-1-sulfide forms deep red crystals. We propose the

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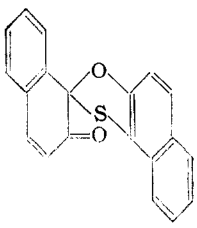
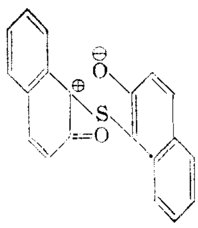
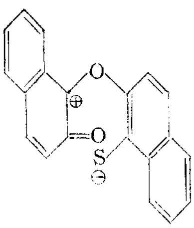
(7) Ruhemann and Levy, *J. Chem. Soc.*, **103**, 554 (1913).

(8) Comp. *inter alia*, Warren and Smiles, *ibid.*, 958 (1930).

formulas (XIa or XIb), since not only the color, but also the chemical properties of dehydro-2-naphthol-1-sulfide are in good agreement with this conception.


X


XIa

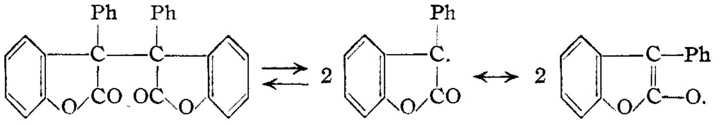

XIb

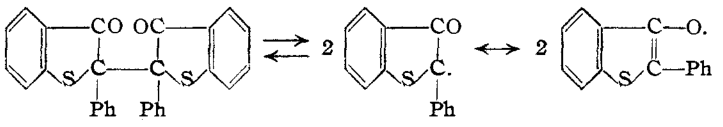
Huckins and Le Fèvre's Investigations.—The theory that the reversible color changes of some spiropyrans may be expressed or exemplified by (I ⇄ II), has recently been criticized by Huckins and Le Fèvre,[9] who accept the possibility that the thermally generated chromogenes of the di-β-naphthospiropyran (I) and of related substances are of the *o*-quininoid type (comp. IIa). This criticism is based on the fact that a benzene solution of 3-methylbenzo-β-naphthospiropyran (IIIb) which begins to show a distinct color at 40°, is deep violet at 60°; nevertheless, no change of polarization accompanied the alteration of color.

The colored form of the naphthospiropyrans, which is allied to the triphenylmethane dyes, has great coloring power. Taking into consideration (a) the intense color even of very dilute solutions of such spiropyrans which are colored in the solid state, and (b) the marked gradual increase in color when tetralin solutions of (IIIb) are heated from 60–200°, it seems not impossible that the benzene solution of (IIIb) at 60° contains only a very small proportion of the colored form, which explains the fact that no change of polarization accompanied the alteration in color.

Surface Active Substances and Ethane Derivatives which have the Power of Dissociation into Free Radicals.—Previously, it was stated that a free radical theory had been discussed to explain the thermochromic properties of (I) and of related compounds. Therefore, it seemed advisable to investigate whether the ethanes described in the title were capable of forming adsorption colors.

We worked with 2,2'-diketo-3,3'-diphenyl-3,3'-dicoumaranyl (XII)[10] and 2,2'-diphenylthioindigo-white (XIII); these substances form colorless solutions in the cold, but the hot solutions are colored in consequence of the formation of free radicals (XIIa and XIIIa, respectively), *e.g.*, the hot solution of XII in xylene is blue and of XIII. yellowish-green to Guignet's green.

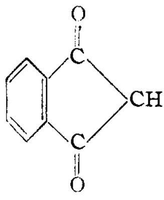

XII XIIa

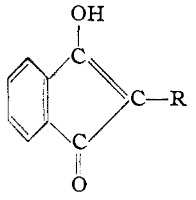

XIII XIIIa

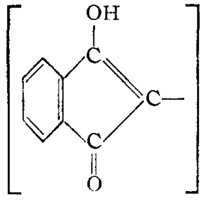
These thermochromic changes are reversible and show great similarity to the thermochromic changes observed in the case of (I) and of allied substances. However, in the case of (XII) and (XIII) no adsorption colors could be produced by a dried silica gel or alumina, as was the case with (I) and allied substances. This furnishes additional evidence that the free radical theory cannot be used to explain the thermochromic properties of (I) and of related compounds.

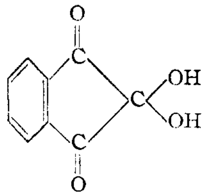
Adsorption Color of 1,3-Diketohydrindene (XIV).—The colorless substance gives a colorless solution in benzene; when activated alumina is added to the cold solution, the inorganic material acquires a violet color at once. It seems that the violet color is due to the enolic form (XVa) (comp. XVb dark red[11] and XVI violet[12]). When activated alumina is replaced by an air-dry silica gel or a silica gel freshly dried by heating, no color is developed.

We offer the following explanation: in the colorless benzene solution there exists an equilibrium XIV⇄XVa which strongly favors the left hand side; the solution is therefore colorless. But the activated alumina preferentially adsorbs XVa which accounts for the adsorption color. When in he above experiment XIV (in benzene) was replaced by ninhydrone (XVII), no adsorption colors were observed in either case (silica gel and alumina).


XIV


XVa, R = H
XVb, R = C_6H_5


XVI


XVII

When a filter paper (air-dry) was moistened with a colorless, benzene solution of 1,3-diketohydrindene (XIV), it remained colorless for some time after evaporation of the benzene, but after drying gradually became violet (about ten minutes). This experiment was carried out in the open air; when the experiment was carried out in a vacuum, no violet color was developed.

With the aim of investigating the factors playing a role in the development of this color, the effects

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(9) Huckins and Le Fèvre, *J. Chem. Soc.*, 2088 (1949).

(10) This experiment was done together with A. M. Gad.

(11) Hantzsch, *Ann.*, **392**, 287 (1912).

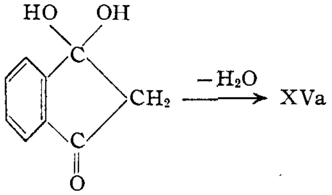
(12) Schönberg and Moubasher, *J. Chem. Soc.*, 366 (1944).

of moisture, oxygen, carbon dioxide and light were investigated independently.

Filter paper moistened with a benzene solution of (XIV) was allowed to dry in the absence of light (a) in a stream of dry carbon dioxide, (b) in a stream of dry oxygen and in both cases no violet color was developed.

When, however, the colorless filter paper was then exposed to water vapor, a deep violet color was developed after about 15 minutes in both cases (a) and (b).

The following working hypothesis is advanced: the absorbed molecules of (XIV) are in an activated state and are capable of adding water vapor quickly with the formation of (XVIII), followed by the splitting off of water giving XVa.



XVIII

The importance of water with regard to the formation of the enol form in the absence of adsorbents can be seen from the fact that 1,3-diketohydrindene (XIV) dissolves in cold acetone without color, but that a violet color is developed on addition of water. Schwarzenbach and Felder[13] state that at 20° the concentration of the enol form in water is 1.6%.

Experimental

The silica gel was Protek-Sorb, grade A or B; the activated alumina was obtained from Peter Spence and Sons, Ltd., London. Both substances were heated (one-half to one minute) with a free flame before use.

Experiments with 1,3-Diketohydrindene (XIV) (a) In Oxygen.—The apparatus used (*cf.* Fig. 1) was covered during the experiment with a cloth (to avoid the exposure to dispersed light). The filter paper, which was placed on the glass wool, was moistened with the benzene solution of 1,3-diketohydrindene (XVI) from (A) and care was taken that no benzene solution remained in the stem of the dropping funnel. The dry oxygen which entered the apparatus *via* (B) was prepared by sucking a stream of air which passed through (a) aqueous concentrated sodium hydroxide solution, (b) a tower filled with solid sticks of sodium hydroxide, (c) an empty tower, (d) concentrated sulfuric acid, (e) a tower filled with phosphorus pentoxide and (f) an empty bubbler, before entering the apparatus. It was found that, after the duration of the experiment (about 30 minutes), no color was developed on the dry filter paper (Genuine Whatman, W. & R. Balston, Ltd.). Then the empty bubbler (f) was filled with conductivity water and the stream of oxygen, purified as above, allowed to enter the apparatus *via* the bubbler (f). After 15 minutes, the filter paper acquired a deep violet color.

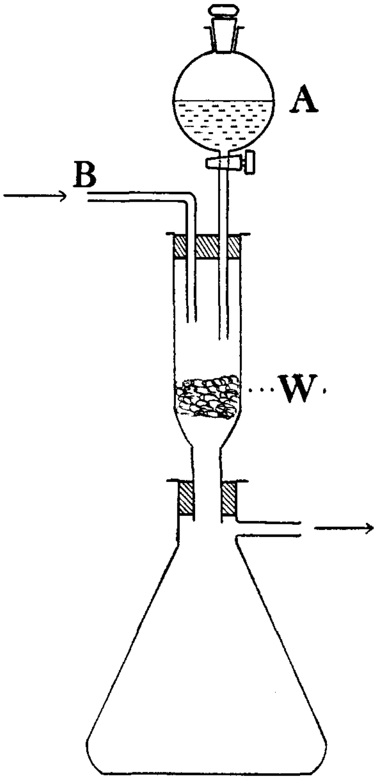


Fig. 1.—Apparatus: W, glass wool.

(b) **In Carbon Dioxide.**—This was carried out in a similar manner with the same result. Carbon dioxide was developed from a Kipp apparatus and purified by allowing the gas to pass through dilute silver nitrate solution (to absorb hydrogen chloride gas), then through concentrated sulfuric acid, phosphorus pentoxide and an empty bubbler before entering the apparatus.

(c) **In a Vacuum.**—In this experiment, tube (B) was closed and the apparatus connected with an oil pump. No color was developed after one hour. When the dry filter paper was then exposed to water vapor, the violet color developed quickly.

Color of 1,3-Diketohydrindene in Acetone and in Acetone–Water Mixture.[14]—(a) This substance dissolved in acetone without color; when, however, water (tap-water or water twice distilled over potassium permanganate) was added, then a violet solution was obtained.

(b) 0.1 g. of 1,3-diketohydrindene (XVI) was placed in a long test-tube (quartz) and 10 cc. of water (purified as above) was added; no color was observed. Then 10 cc. of acetone (ANalaR, Hopkin's & Williams) was added and the tube was shaken; a violet color was developed which darkened when the tube was allowed to stand with frequent shaking in the dark for five minutes.

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[13] Schwarzenbach and Felder, *Helv. Chim. Acta*, **27**, 1701 (1944).

[14] This experiment was done together with R. Moubasher.