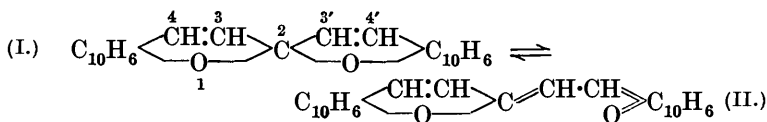


CCXVIII.—*Styrylpyrylium Salts. Part IX. Colour Phenomena associated with Benzonaphtha- and Dinaphtha-spiropyran.*

By ROBERT DICKINSON and ISIDOR MORRIS HEILBRON.

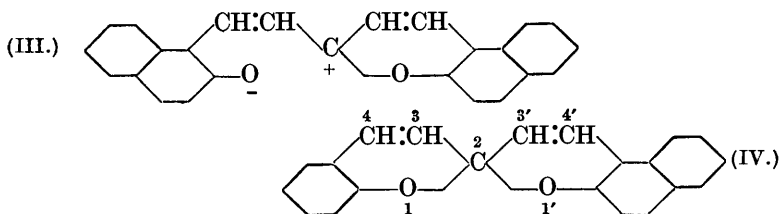
IN a previous communication (this vol., p. 14) a preliminary account was given of the remarkable property exhibited by di- β -naphthaspiropyran of forming in cold inert solvents colourless solutions which develop an intense violet-blue colour on heating; on cooling, the colour disappears and the substance may be recovered unchanged. This phenomenon, which may be repeated any number of times, we tentatively suggested might be accounted for by intramolecular change from the *spiro*-type (I) to the ortho-quinonoid system (II), a view which has been advanced by Löwenbein and



Katz also (*Ber.*, 1926, **59**, 1377), who almost simultaneously observed the same effects in the case of the 3-methyl, phenyl, and benzyl derivatives of the above compound.

On the other hand, Dilthey, Berres, Hölterhoff, and Wübken (*J. pr. Chem.*, 1926, **114**, 179), who have also examined this phenomenon, reject the quinonoid hypothesis on the grounds that (i) whereas true quinones mostly show a bathochromic effect in piperidine solution and never a hypsochromic action, di- β -naphthaspiropyran gives only a yellow solution which is unaffected by heat (compare Dilthey and Wizinger, *Ber.*, 1926, **59**, 1856), and (ii) neither dibenzospiropyran nor mixed benzo- β -naphthaspiropyran show any alteration in colour either on melting or in solvents, although quinone formation is equally possible in both cases. They conclude that the appearance of colour is due to ionic dissociation, the

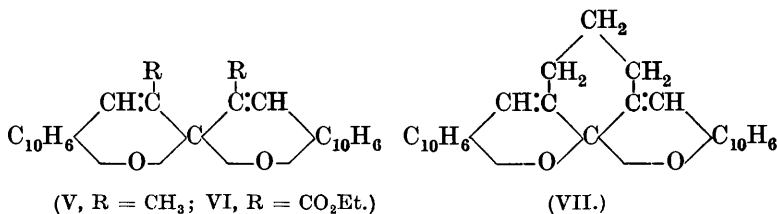
coloured form being represented as a heteropolar molecule of the type (III) :



The possibility of the phenomenon being due to free radical formation has been considered by Löwenbein and by Dilthey, both concluding that such a view is incorrect. Dilthey treated a hot solution of di- β -naphthaspiropyran in chlorobenzene with a stream of oxygen for an hour, and was unable to detect any change; a similar result was obtained with hydrogen. These two experiments show the absence of trivalent carbon and univalent oxygen, respectively. We have repeated the former, and also, on passing oxygen through a solution of the compound in toluene at 100°, could not detect any change, even after 15 hours' treatment. Further, we find that the colour is unchanged by the addition of quinol, a reagent which almost instantaneously reduces all the known types of radicals, with disappearance of the colour (compare Ingold, *Ann. Rep.*, 1924, **21**, 115—121). In addition, both Löwenbein and Dilthey have definitely shown that the molecular weights of these compounds are normal, whether the solution is coloured or not.

We have now made a very extensive examination of various *spiropyrans*, and whereas we are in agreement with Dilthey that the colour effect is ionic in character, it will be shown that other factors enter into the case. In the first place, we have prepared *benzo- β -naphthaspiropyran* (IV) by the acid condensation of 2-naphthol-1-aldehyde with *o*-hydroxystyryl methyl ketone, followed by hydrolysis of the resulting styrylpyrylium salt, and find that it exhibits, contrary to Dilthey's generalisation, the characteristic colour changes in solution, a wine-red colour being developed in hot solvents. We have also prepared the 3- and 3'-*methyl* derivatives of (IV). The former was obtained by condensing 2:3-dimethylbenzopyrylium chloride (Decker and Fellenberg, *Annalen*, 1909, **364**, 26) with 2-naphthol-1-aldehyde and resembles the parent *benzo- β -naphthaspiropyran* in all respects, giving a deep red solution in boiling xylene and melting to a reddish-purple liquid. On the other hand, the isomeric 3'-*methylbenzo- β -naphthaspiropyran*, the preparation of which from the condensation of 2-naphthol-1-

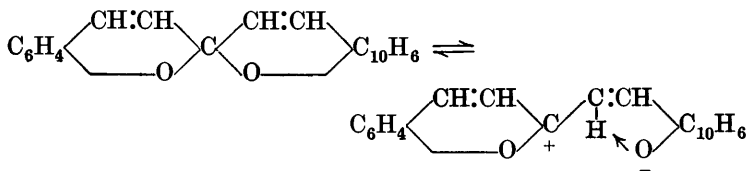
aldehyde with *o*-hydroxystyryl ethyl ketone definitely fixes its structure, gives no coloured solutions in boiling solvents, nor does it melt to a coloured liquid. This compound is undoubtedly identical with that obtained by Dilthey and his co-workers (*loc. cit.*), who, however, from their method of preparation were unable definitely to fix its constitution. We have also prepared 3 : 3'-*dimethyl*di- β -*naphthaspiropyran* (V), *ethyl di- β -naphthaspiropyran-3 : 3'-dicarboxylate* (VI), and 3 : 3'-*trimethylenedi- β -naphthaspiropyran* (VII), none of which gives rise to highly coloured solutions.



These experiments taken in conjunction with the work of Löwenbein and Katz (*loc. cit.*) lead to the conclusion that the conditions necessary for colour development are not wholly governed, as stated by Dilthey and his co-workers (*loc. cit.*), by the loading of the *spiropyran* with two naphthalene nuclei, but that the determining factors are (a) *at least one naphthalene nucleus must be present* and (b) *the 3'-carbon atom in the naphthapyran ring must be unsubstituted*.

The obvious deduction to be drawn from (a) is that the ionised molecule arises through scission of the naphthapyran ring. Furthermore, when it is considered that the system thus produced contains a strongly polar, conjugated group, $\bar{O}-C=C-\overset{4'}{C}H=\overset{3'}{C}H-\overset{+}{R}$ (in which R represents the positively charged pyran residue), it will be seen that conditions peculiarly conducive to co-ordinated ring formation exist. In this connexion, factor (b) becomes operative. In the first place, it definitely proves that the quinonoid formulation fails to account for the observed facts. Secondly, it follows that, so long as the 3'-carbon atom in the benzo- β -naphthaspiropyran is unsubstituted, "chelate" formation can readily occur, but that this process is absolutely precluded when any other group is substituted for the free hydrogen atom. The same condition holds for the di- β -naphthaspiropyran: here the positions 3 and 3' are identical, but at least one of them must be unsubstituted. The cumulative experimental evidence has consequently forced us to the conclusion that the colour development is the result of a series of changes in which equilibrium is established between the neutral

spiropyran and an ionised "chelate" compound, as represented by the following formulæ :



We are extending this investigation to include the influence of substitution in the 4- and 4'-positions of the *spiropyran* nucleus. It remains to be mentioned that we have so far failed to obtain a pyrylium salt or *spiropyran* by the condensation of 2-naphthol-1-aldehyde with dibenzyl ketone; two compounds have been isolated, the constitutions of which are under investigation.

EXPERIMENTAL.

Benzo-β-naphthaspiropyran (IV).—A solution of 2-naphthol-1-aldehyde (5 g.) and 2-hydroxystyryl methyl ketone (5 g.) in alcohol (40 c.c.) was treated with 60% perchloric acid solution (9 c.c.), saturated with dry hydrogen chloride, and kept for 3 days at 0°. The separated crystalline solid was then washed with ether, and shaken with concentrated ammonia in presence of excess of ether until it had dissolved. After being washed and dried, the dark ethereal solution was concentrated. The crystalline crust which separated was recrystallised first from ether, then twice from acetone with charcoal, and finally from aqueous acetone. The *spiropyran* was obtained in small, colourless, glistening plates; these darkened at about 160° and melted at 168—169° to a deep purple liquid which very slowly resolidified, on cooling, with gradual fading of the colour.

The *spiropyran* is soluble in concentrated sulphuric acid, giving a ruby-red solution, and develops with boiling alcoholic sodium hydroxide a purplish-red colour. Its colourless solutions in acetone, benzene, and xylene become wine-red on heating, the colour disappearing again on cooling. On warming with alcohol, a similar colour develops, but it is more purple, and is still more so when water is added to the solution (Found : C, 84.4; H, 4.4. $\text{C}_{21}\text{H}_{14}\text{O}_2$ requires C, 84.6; H, 4.7%).

3'-Methylbenzo-β-naphthaspiropyran.—Perchloric acid (8 c.c. of 60%) was added to a solution of 2-naphthol-1-aldehyde (5 g.) and 2-hydroxystyryl ethyl ketone (5 g.) in alcohol (40 c.c.), and the whole saturated with hydrogen chloride. The separated microcrystalline perchlorate was washed with ether, suspended in benzene,

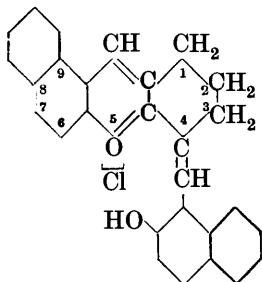
and treated with a few drops of concentrated ammonia. Water was then added and the benzene solution was separated, dried, and, after concentration, treated with light petroleum, whereupon crystals slowly separated (yield, about 2.5 g.). These were twice recrystallised from absolute alcohol (charcoal), finally being obtained in clusters of colourless, silky needles, m. p. 177—178° (Dilthey, *loc. cit.*, describes pale yellowish needles, m. p. 174°). This *spiropyran* shows no colour change when heated with inert solvents, such as xylene. In concentrated sulphuric acid, the solution is orange-red (Found: C, 84.2; H, 5.3. $C_{22}H_{16}O_2$ requires C, 84.6; H, 5.1%).

3-Methylbenzo- β -naphthaspiropyran.—A solution of salicylaldehyde (2 g.) and methyl ethyl ketone (1.2 g.) in glacial acetic acid (6 c.c.) was saturated with hydrogen chloride and kept for a few hours to enable the primary condensation to become complete; 2-naphthol-1-aldehyde (2.9 g.), dissolved in acetic acid (9 c.c.), was then added, the colour changing from red to purple. After 12 hours, ether was gradually added, the pyrylium chloride slowly crystallising. This was collected, washed with ether, and shaken in ethereal suspension with an aqueous solution of sodium acetate until the colour was discharged. The ethereal solution, after being washed, dried, and concentrated, deposited pale greenish-yellow prisms, which were recrystallised first from ether and then from acetone, giving faintly greenish-yellow prisms. These darkened at 145° and melted at 149° to a purple liquid; on cooling, the colour faded but did not disappear completely until the substance had solidified, after several days. Colourless solutions of the *spiropyran* in acetone, xylene, etc., become wine-red on heating, the colour disappearing again on cooling. Its ruby-red solution in concentrated sulphuric acid is faintly fluorescent (Found: C, 84.5; H, 5.3. $C_{22}H_{16}O_2$ requires C, 84.6; H, 5.1%).

3 : 3'-Dimethyl-di- β -naphthaspiropyran (V).—A hot solution of 2-naphthol-1-aldehyde (2.1 g.) and diethyl ketone (1 c.c.) in glacial acetic acid (10 c.c.) was saturated with hydrogen chloride. After the mixture had been kept at 0° for several days, a small amount of the pyrylium chloride separated in green needles. These were removed, and the mother-liquor was treated with excess of perchloric acid; chocolate-brown needles of the salt slowly separated. Both products were dissolved in acetone (the chloride giving a violet and the perchlorate a dark red solution) and, while hot, treated with dilute ammonia, drop by drop, until the colour was discharged. The *spiropyran* crystallised from the yellow acetone solutions, either on evaporation or on the addition of water. Recrystallised from benzene, the compound separated in pale lemon-

yellow rhombs, m. p. 238° to an olive-green liquid. It does not exhibit any colour changes when heated with solvents (Found: C, 85.9; H, 5.1. $C_{27}H_{20}O_2$ requires C, 86.2; H, 5.3%).

4-2'-Hydroxy-1'-naphthylidene-1:2:3:4-tetrahydro-8:9-benzanthrylium Chloride (annexed formula).—A solution of 2-naphthol-1-aldehyde (5 g.) and cyclohexanone (2 c.c.) in alcohol (50 c.c.) was saturated with hydrogen chloride and kept for 12 hours at 0°. The separated crystalline solid (yield, 95%) was washed with ether and recrystallised from absolute formic acid previously saturated with hydrogen chloride. The salt separated in dark brown, glistening needles, insoluble in water and sparingly soluble in alcohol to a reddish-purple solution. In concentrated sulphuric acid its colour is orange-red (Found: C, 74.1; H, 5.2; Cl, 7.4. $C_{28}H_{21}O_2Cl \cdot HCO_2H$ requires C, 74.0; H, 4.9; Cl, 7.5%).



3:3'-Trimethylenedi-β-naphthaspiropyran (VII).—The above-mentioned salt (2 g.), suspended in boiling alcohol (50 c.c.), was treated with sodium acetate, the heating being continued until the colour of the pyrylium salt was discharged, a curdy, greenish-yellow solid separating. After drying, this was twice crystallised from benzene, separating in minute, sulphur-yellow rhombs, m. p. 233—234° (decomp.). The yellow benzene solution exhibits a fine green fluorescence. The spiro β pyran is not appreciably soluble in alcohol, and does not fluoresce in concentrated sulphuric acid. A cherry-red colour slowly develops on prolonged boiling with alcoholic potash. This spiro β pyran does not exhibit any colour changes on heating in solvents (Found: C, 86.5; H, 5.4. $C_{28}H_{20}O_2$ requires C, 86.6; H, 5.2%).

Ethyl Di-β-naphthaspiropyran-3:3'-dicarboxylate (VI).—A solution of 2-naphthol-1-aldehyde (2 g.) and ethyl acetonedicarboxylate (1.2 g.) in hot alcohol (12 c.c.) was saturated with hydrogen chloride, and the passage of the gas was maintained until the solution was cold. After 2 days, the dark, crystalline deposit was washed with ether, suspended in hot acetone (which became bright red), and treated with dilute ammonia drop by drop until the colour was discharged. Alternatively, the pyrylium salt may be suspended in ether and hydrolysed by shaking it with aqueous sodium acetate, but the former method is preferred. The acetone solution, after being filtered, was treated with water until crystallisation ensued. Recrystallised from acetone, or benzene and light petroleum, the spiro β pyran formed pale sulphur-yellow rhombs, m. p. 205—207°. It is very stable to hydrolysing agents, resisting the action of

alcoholic potash, but with acids it readily reverts to the pyrylium salt (Found : C, 75.5; H, 4.9. $C_{31}H_{24}O_6$ requires C, 75.6; H, 4.9%).

We desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) which enabled this research to be carried out.

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[Received, May 27th, 1927.]
