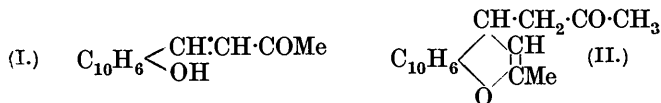


II.—*Styrylpyrylium Salts. Part VIII. 3-Styryl Derivatives of β -Naphthapyrylium Chloride.*

By ROBERT DICKINSON and ISIDOR MORRIS HEILBRON.

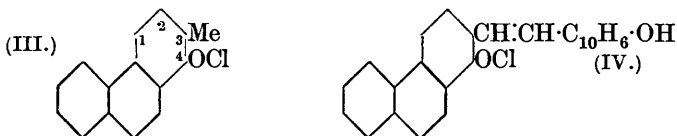
IN continuation of previous work, a study has been made of the styryl derivatives of β -naphthapyrylium chloride.

We were unable to prepare them by a method analogous to that used by Buck and Heilbron (J., 1922, 121, 1198), since the condensation of 2-naphthol-1-aldehyde with acetone in the presence of alkali failed to give the expected β -2-hydroxy-1-naphthylvinyl methyl ketone (I). The only pure product isolated was 1-acetonyl-3-methyl-1:4- β -naphthapyran (II), which was obtained in poor yield, the bulk of the reaction product being an amorphous, yellow solid which resisted all attempts at purification.



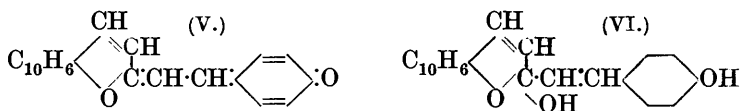
Attempts were next made to prepare 3-methyl- β -naphthapyrylium chloride (III) with a view to condensing it further with aromatic aldehydes to the styryl derivatives (compare Buck and Heilbron, J., 1923, 123, 2521), but this method failed because the condensation

of 2-naphthol-1-aldehyde with acetone in acid solution gave solely 3-(β -2'-hydroxy-1'-naphthylvinyl)- β -naphthapyrylium chloride (IV).



The salts were ultimately obtained in good yield by the condensation of 2-naphthol-1-aldehyde with styryl methyl ketones by means of dry hydrogen chloride—a somewhat unexpected result, since the corresponding condensation for styrylbenzopyrylium salts was unsatisfactory (Buck and Heilbron, J., 1922, 121, 1198).

The styryl- β -naphthapyrylium salts are highly coloured, crystalline compounds closely resembling the 2-styrylbenzopyrylium salts in properties. For example, 3-*p*-hydroxystyryl- β -naphthapyrylium chloride gives a red aqueous solution which, on high dilution, becomes purplish-blue, and then, with a trace of sodium bicarbonate, cornflower-blue, and finally almost colourless. As in other similar cases, we attribute the colour change from red to blue, which is displayed only by those salts having a free hydroxyl in the 4'-position, to the formation of the quinonoid anhydro-base (V), which then hydrates to the colourless carbinol base (VI).



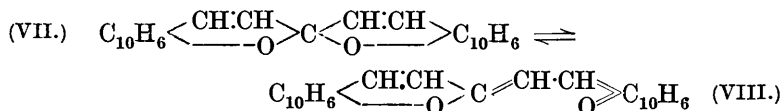
The view that the similar colour changes observed in the anthocyanidin series of salts are due to the same structural rearrangements (Buck and Heilbron, J., 1922, 121, 1203) has been criticised by Willstätter and Schmidt (*Ber.*, 1924, 57, 1945) as failing to account for the reactions of malvidin and cænidin chlorides, both of which, according to Willstätter, contain methoxyl groups in the 4'-position (*Annalen*, 1915, 408, 83, 122). Such formulations are, however, supported neither by Gatewood and Robinson in the case of malvidin (J., 1926, 1959) nor by Anderson and Nabenhauer for cænidin (*J. Amer. Chem. Soc.*, 1926, 48, 2997).

All the styryl- β -naphthapyrylium salts, on treatment with aqueous sodium hydroxide, give colourless solutions which slowly become intensely red. This colour change, which may possibly be due to fission of the pyrylium ring, is being investigated.

The parent substance, 3-styryl- β -naphthapyrylium chloride, is interesting in that Buck and Heilbron (*loc. cit.*) were unable to prepare the corresponding benzopyrylium salt, and further because

it differs from its derivatives : its colour in water is bright orange, and solutions in water, alcohol, and concentrated sulphuric acid all show a remarkably intense greenish-yellow fluorescence; this property is only exhibited by its derivatives in the last solvent.

3-(β -2'-Hydroxy-1'-naphthylvinyl)- β -naphthapyrylium chloride (IV) is readily changed by water, added to an alcoholic solution, or by sodium acetate into the colourless *di*- β -naphthaspiropyran (VII).



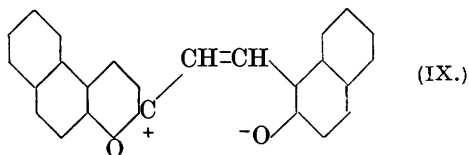
A remarkable property of this compound is its behaviour in high-boiling solvents. Its colourless solution in nitrobenzene or xylene develops, at about 100°, a purple colour which becomes progressively deeper and more intense as the temperature rises; on cooling, the reverse phenomena are observed. These changes may be repeated any number of times without the least sign of permanent decomposition. Although this behaviour resembles that accompanying the decomposition of hexa-aryl ethanes and of certain phenolic peroxides into free radicals (compare Gomberg, *Chemical Reviews*, 1925, 1, 91), a similar decomposition does not take place here, molecular-weight determinations at high temperatures giving normal values. It is tentatively suggested that the purple colour may be due to a change in the valency distribution (VII \rightleftharpoons VIII). The possibility of both pyran rings opening in a similar manner has not been overlooked, but is regarded as unlikely.

On boiling with alcoholic potash, *di*- β -naphthaspiropyran gradually gives a blood-red solution, probably owing to formation of the potassium salt of the corresponding dinaphthylvinyl ketone. An examination of this question and a study of other similarly constituted *spiropyrans* are now in progress.

Since the completion of this work a communication has appeared by Löwenbein and Katz (*Ber.*, 1926, 59, 1377) dealing with the preparation of certain 2-aryl derivatives of (IV) obtained by the condensation of 2-naphthol-1-aldehyde with α -arylacetoacetic esters. These compounds also yield *di*- β -naphthaspiropyrans analogous to (VII), all of which exhibit similar colour changes in high-boiling solvents. The conclusions arrived at by these authors to account for the phenomenon are wholly in harmony with the views expressed above.

Dilthey and Wizinger (*Ber.*, 1926, 59, 1856) announce in a preliminary notice that they also have prepared *di*- β -naphthaspiropyran, but no details of their method are available. These authors,

who have approached the problem from another direction, regard the coloured form as a dipolar anhydride (IX) of the normal *spiropyran*.



EXPERIMENTAL.

1-Acetyl-3-methyl-1:4-β-naphthapyran (II).—2-Naphthol-1-aldehyde (5 g.) (Fosse, *Bull. Soc. chim.*, 1901, 25, 371) was dissolved in a mixture of alcohol and acetone (20 c.c. of each) and treated with 50% potassium hydroxide (8 c.c.). The mixture was gently heated under reflux for 3 hours, and after cooling, the blood-red liquid was extracted with ether. The ethereal solution was washed, dried, and concentrated, whereupon a small quantity of a crystalline solid separated. The remainder of the extract consisted of an unworkable brown resin. After three recrystallisations from alcohol, the solid was obtained in faintly yellow, fern-like aggregates, m. p. 152—153°. The compound, which is insoluble in water and aqueous sodium hydroxide, gives no coloration with alcoholic hydrogen chloride and only slowly absorbs bromine, hydrogen bromide being evolved (Found: C, 80.6; H, 6.3. $C_{17}H_{16}O_2$ requires C, 80.95; H, 6.35%).

After removal of dissolved ether by a current of warm air, the blood-red aqueous liquid, on saturation with either carbon dioxide or dilute hydrochloric acid, deposited a yellow solid which, on drying, became dull olive-green. By repeated precipitation from benzene or ethyl acetate by addition of light petroleum, it was obtained as an amorphous, yellow powder, melting above 250° and insoluble in aqueous alkali.

Derivatives of 3-Styryl-β-naphthapyrylium Chloride.—These salts were all prepared by the same general method—saturation of an alcoholic solution of 2-naphthol-1-aldehyde and the requisite styryl methyl ketone with hydrogen chloride. The styryl ketone was always used in slight excess, in order to avoid the formation of di-β-naphthapyrylium chloride (Betti and Mundici, *Atti R. Accad. Lincei*, 1904, v, 13, ii, 542; *Gazzetta*, 1905, 35, ii, 46). It was found advantageous to condense small amounts of material at a time, otherwise the product either failed to separate or was only obtained in small yield. As is the case with the corresponding benzopyrylium chlorides, formic acid was found to be the best crystallising medium,

ether being added to reduce the solubility. No melting points are recorded for these salts, as on heating they gradually decompose and pass into tars.

3-Styryl-β-naphthapyrylium chloride was prepared as above from styryl methyl ketone (Knoevenagel, *Annalen*, 1914, 402, 111) and 2-naphthol-1-aldehyde. The salt separated from formic acid, containing about 60% of anhydrous ether, in centimetre-long, thin plates which appeared blood-red in transmitted light and showed a pronounced beetle-green reflex. It is moderately easily soluble in water to an orange-yellow solution, readily so in alcohol or acetone to a deep orange liquid; in concentrated sulphuric acid the colour is orange-red. All the solutions have an intense greenish-yellow fluorescence (Found : C, 72.5; H, 4.9; Cl, 9.6. $C_{21}H_{15}OCl, HCO_2H$ requires C, 72.4; H, 4.7; Cl, 9.7%).*

3-p-Hydroxystyryl-β-naphthapyrylium chloride, prepared from *p*-hydroxystyryl methyl ketone (Buck and Heilbron, *J.*, 1922, 121, 1101), forms glistening, dark olive-green prisms, which are deep violet by transmitted light (under the microscope). The salt is slightly soluble in water to a cherry-red solution, which on dilution passes through violet to almost pure blue, the change being completed by addition of a drop of dilute sodium bicarbonate solution. The blue solutions slowly fade until they are almost colourless (10—15 minutes). With dilute aqueous sodium hydroxide, the blue colour persists for a few seconds only, after which a red colour, resembling that of the parent chloride, gradually develops. The salt dissolves in concentrated sulphuric acid to a reddish-orange liquid with an intense greenish-orange fluorescence (Found : C, 68.1; H, 4.6; Cl, 9.6. $C_{21}H_{15}O_2Cl, 2H_2O$ requires C, 68.0; H, 5.1; Cl, 9.6%).

3-3'-Methoxy-4'-hydroxystyryl-β-naphthapyrylium chloride, prepared from 3-methoxy-4-hydroxystyryl methyl ketone (McGookin and Sinclair, *J.*, 1926, 1578), forms aggregates of dull green needles, sparingly soluble in water to a pink solution. In alcohol the colour is bluish-purple, becoming purplish-red on addition of a little water. In its behaviour with water and alkalis it closely resembles the *p*-hydroxy-analogue. In concentrated sulphuric acid, it gives a red solution with a dark red fluorescence (Found : C, 65.8; H, 4.9; Cl, 8.9. $C_{22}H_{17}O_3Cl, 2H_2O$ requires C, 65.9; H, 5.2; Cl, 8.9%).

3-p-Methoxystyryl-β-naphthapyrylium chloride, prepared from *p*-methoxystyryl methyl ketone (Baeyer and Villiger, *Ber.*, 1902, 35, 1189), separates in prisms resembling the *p*-hydroxy-analogue but also showing a faint golden reflex. It is soluble in alcohol to a

* All halogen estimations were carried out by Stepanoff's method (*Ber.*, 1906, 39, 4056) as modified by van Duin (*Rec. trav. chim.*, 1926, 45, 343).

deep purplish-red solution with an intense red fluorescence, which disappears on addition of water. Its aqueous solution in high dilution is pink, which slowly fades to pale yellow, a slight opalescence being also present. In concentrated sulphuric acid, the solution is orange-red with a fluorescence similar to that of the *p*-hydroxy-compound (Found : C, 66.9; H, 5.2; Cl, 8.7. $C_{22}H_{17}O_2Cl, HCO_2H, H_2O$ requires C, 66.9; H, 5.1; Cl, 8.6%).

3-3' : 4'-*Dimethoxystyryl-β-naphthapyrylium chloride*, prepared from 3 : 4-dimethoxystyryl methyl ketone (Kaufmann and Radosević, *Ber.*, 1916, 49, 675), crystallises in dark green prisms with a bronze reflex. In its properties it closely resembles the *p*-methoxy-analogue, except that its alcoholic solution does not fluoresce and in concentrated sulphuric acid the fluorescence is very weak (Found : C, 65.1; H, 5.3; Cl, 7.8. $C_{23}H_{19}O_3Cl, HCO_2H, H_2O$ requires C, 65.1; H, 5.2; Cl, 8.0%).

3-3' : 4'-*Methylenedioxytyryl-β-naphthapyrylium chloride* was obtained as a felted mass of minute, dark green needles (Found : C, 64.6; H, 4.5; Cl, 8.4. $C_{22}H_{15}O_3Cl, HCO_2H, H_2O$ requires C, 64.7; H, 4.5; Cl, 8.3%).

3-*p*-*Dimethylaminostyryl-β-naphthapyrylium Perchlorate*.—A solution of *p*-dimethylaminostyryl methyl ketone (2.1 g.) and 2-naphthol-1-aldehyde (2 g.) in glacial acetic acid (20 c.c.) was saturated with dry hydrogen chloride, acetic acid (10 c.c.) and 60% perchloric acid (5 c.c.) were added, and the whole was kept over-night. The separated solid, after being washed with acetic acid and with ether, consisted of small, chocolate-brown needles with a steely blue reflex. On treatment with acetone, a minute amount dissolved, giving a bright green solution; the residue was converted into a mass of emerald-green needles. Both crystalline forms are very sparingly soluble in alcohol to greenish-blue solutions, which with water change to pure azure blue. The brown crystals probably contain some addendum, for on keeping over solid potassium hydroxide in an exsiccator they slowly become dark green. Neither form has been analysed, owing to the explosive character of the compound.

3-(β-2'-*Hydroxy-1'-naphthylvinyl*)-β-*naphthapyrylium Chloride* (IV).—A solution of 2-naphthol-1-aldehyde (5 g.) in alcohol (75 c.c.) and acetone (10 c.c.) was saturated with hydrogen chloride. The liquid, at first deep indigo-blue, finally exhibited pleochroism, being brownish-red in thick and olive-green in thin layers. After 12 hours, the crystalline deposit was collected and recrystallised in the usual way, being obtained as a felted mass of small, dark green needles. It is insoluble in water, and moderately easily soluble in alcohol to an indigo-blue solution. Hot water rapidly hydrolyses the compound to the *spiropyran*. On keeping over solid potassium hydr-

oxide, a continuous slow loss of hydrogen chloride takes place; the substance loses its crystalline form and is converted into a dirty, purplish-coloured, amorphous mass, which contains a small amount of chlorine even after 3 months' keeping in a vacuum. Analysis of the salt was carried out immediately the compound had lost all odour of formic acid (Found: C, 69.2; H, 5.1; Cl, 8.0. $C_{25}H_{17}O_2Cl, HCO_2H, H_2O$ requires C, 69.6; H, 4.7; Cl, 7.9%).

Di-β-naphthaspiropyran (VII) was prepared from the foregoing pyrylium salt by two methods. (i) The salt was dissolved in alcohol, and water added to the warm solution. (ii) The chloride was heated with water and treated with sodium acetate to ensure complete hydrolysis. The resultant pale blue solid was twice recrystallised from xylene, separating in colourless, irregular, thin plates, with a pearly lustre, which darkened at 240° and became tarry at about 260°. The *spiropyran* is insoluble in water, and only sparingly soluble in the usual low-boiling solvents. It is soluble in warm, high-boiling liquids such as xylene, phenetole, nitrobenzene, and naphthalene. When it is heated with such a solvent, a purple colour develops at about 100°, becoming progressively darker as the temperature rises. In phenol or glacial acetic acid, the solution is intensely coloured in the cold. Suspended in alcohol and treated with hydrogen chloride, the *spiropyran* reverts to the original pyrylium salt. When it is boiled with aqueous-alcoholic sodium hydroxide, a pink colour develops, which changes to blood-red after several hours' refluxing. The carmine solution in concentrated sulphuric acid shows a dark red fluorescence (Found: C, 85.8; H, 4.7; *M*, ebullioscopic in nitrobenzene, 344, 352, 334. $C_{25}H_{16}O_2$ requires C, 86.2; H, 4.6%; *M*, 348).

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