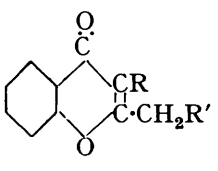
112. *Styrylpyrylium Salts. Part XIV. Further Study of the Colour Phenomenon associated with Benzonaphtha- and Dinaphtha-*spiro*pyrans.*

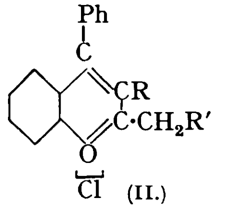
By I. M. Heilbron, R. N. Heslop, and F. Irving.

It has been previously ascertained (Dickinson and Heilbron, J., 1927, 1699) that benzo-β-naphtha*spiro*pyrans containing a substituent in the 3′-position fail to form coloured ions on heating, and that, further, the same phenomenon is shown by di-β-naphtha*spiro*pyrans substituted in both the 3- and the 3′-position.

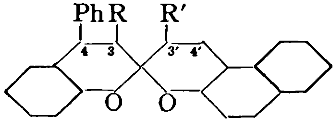
An examination has now been made of the effect of a phenyl group in position 4, with or without substituents in the 3- and 3′-positions. The general method employed for the preparation of these new *spiro*pyrans consists in converting the appropriate *o*-hydroxyphenyl ketone into the chromone (I, R and R′ = H or Me), from which the pyrylium salt (II) is obtained on treatment with phenylmagnesium bromide, followed by decomposition with hydrochloric acid. Condensation of (II) with 2-naphthol-1-aldehyde yields the naphthavinylpyrylium salt, from which the *spiro*pyran (III) results on hydrolysis.



(I.)



(II.)

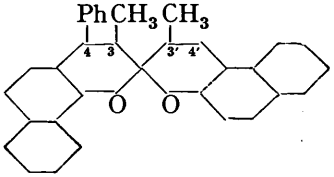


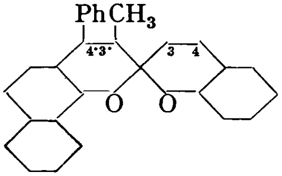
(III.)

As was anticipated, *7-methoxy-4-phenyl-3-methylbenzo-β-naphtha*spiro*pyran* readily gave the coloured ionic form on heating in xylene solution, but, contrary to all previous experience, the *3′-methyl* isomeride also produced a coloured solution with equal ease. That the colour production was not due to the influence of the 7-methoxy-group was shown by the fact that the unsubstituted *4-phenyl-3′-methylbenzo-β-naphtha*spiro*pyran* behaved in an analogous manner. Unfortunately, it was found impossible to examine 7-methoxy-4-phenyl-3 : 3′-dimethylbenzo-β-naphtha*spiro*pyran, for, although *7-methoxy-3-methyl-2-ethylchromone* was readily obtained and the Grignard reaction successfully carried out, the resulting pyrylium salt (II, R and R′ = Me) failed to condense with 2-naphthol-1-aldehyde.

In order to study further the effect of a phenyl group in position 4, attempts were made to apply the above reactions to β-naphthachromones, but probably owing to steric hindrance, these compounds failed to react satisfactorily with the Grignard reagent. On the other hand, α-naphthachromones readily give rise to the hitherto unknown αβ-dinaphtha*spiro*pyrans. Of these, *4-phenyl*, *4-phenyl-3-methyl-*, and *4-phenyl-3′-methyl-αβ-dinaphtha*spiro*pyrans* all ionise on heating, the degree of ionisation, as evidenced by the intensity of the colour developed, being greater than that observed in the corresponding di-β-naphtha-series. A further anomaly has here been met with, however, for *4-phenyl-3 : 3′-dimethyl-αβ-dinaphtha*spiro*pyran* (IV) also readily passes into its coloured ionic form. The benzo-α-naphtha*spiro*pyrans appear to react normally in that the *4′-phenyl-3′-methyl* derivative (V) fails to give coloured solutions in high-boiling inert solvents.

(IV.)



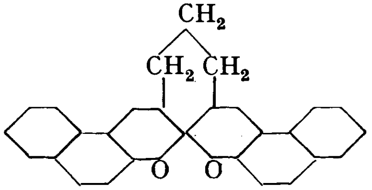


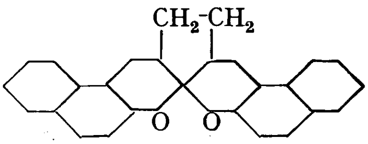
(V.)

The results given above show that the "chelate" hypothesis advanced by Dickinson and Heilbron (*loc. cit.*) to account for the colour effects is no longer tenable. As regards the function of the 4-phenyl group in assisting ionisation, it would appear as though its influence were exerted in such a way as to induce a weakening of the valency bonds of the opposite naphthapyran ring.

*Dinaphtha*spiro*pyrans prepared from Cyclic Ketones.*—Whereas 3 : 3′-dimethyldi-β-naphtha*spiro*pyran (Dickinson and Heilbron, *loc. cit.*) fails to give a coloured solution in any high-boiling solvent, Dilthey and Wübken (*Ber.*, 1928, **61**, 963) have shown that 3 : 3′-trimethylenedi-β-naphtha*spiro*pyran (VI) develops a quite perceptible violet colour in boiling diphenyl ether, from which these authors deduce that the inhibitive effect of 3 : 3′-disubstitution is not absolute.

(VI.)





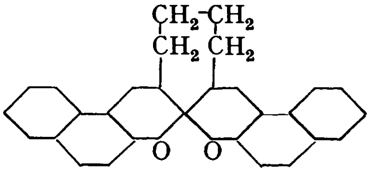
(VII.)

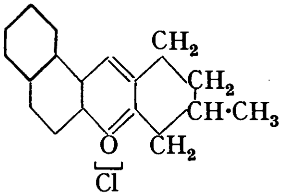
In order to study this effect in greater detail we have now prepared 3 : 3′*-dimethylene-* (VII) and 3 : 3′*-tetramethylene-di-β-naphtha*spiro*pyran* (VIII) by condensing respectively *cyclo*pentanone and *cyclo*heptanone with 2-naphthol-1-aldehyde in presence of hydrogen chloride, followed by hydrolysis of the resultant pyrylium salt. Whereas (VII) readily develops colour in boiling xylene solution, (VIII) fails entirely to show any colour even in boiling diphenyl ether.

3 : 3′-(*β-Methyltrimethylene*)*di-β-naphtha*spiro*pyran*, prepared from 2-naphthol-1-aldehyde and 4-methyl*cyclo*hexanone, like the 3 : 3′-trimethylene derivative (VI), gives no colour in boiling xylene but is faintly coloured in boiling diphenyl ether. An attempt was also made to prepare the *spiro*pyran from 2-naphthol-1-aldehyde and 3-methyl*cyclo*hexanone

but without success. It would appear from the red colour developed that the condensation in this case stops when the simple pyrylium salt (IX) is formed, further condensation being seemingly inhibited by the proximity of the methyl group to the normally reactive methylene.

(VIII.)





(IX.)

In the preparation of the above *spiro*pyrans from cyclic ketones, particular care must be taken to purify the naphthavinylpyrylium salts prior to hydrolysis. Crystallisation at this stage removes traces of impurities, the presence of which renders the *spiro*pyrans yellow in colour and fluorescent in solution.

Dilthey and Wübken (*loc. cit.*) have emphasised the relation between ease of salt formation and ionisation, failure to develop colour being associated, according to these authors, with the presence of certain substituents which effect a decrease in the basicity of the molecule. In this connexion the following table is of interest, but it is difficult to understand why there should be any marked variation in the basicity of such structurally similar compounds.

*spiro*Pyran (3 : 3′-substitution).	Colour in cold glacial acetic acid.	Colour in trichloroacetic acid.	Colour in boiling inert solvents.
1. Dimethylenedi-β-naphtha-	Deep purplish-blue (rapid)	Deep blue	Strong blue colour in xylene
2. Trimethylenedi-β-naphtha-	Pink colour (slow)	Deep reddish-purple	Faint colour in diphenyl ether
2*a*. (β-Methyltrimethylene)di-β-naphtha-	Pink colour similar to (2)	Deep reddish-purple	Faint colour in diphenyl ether
3. Tetramethylenedi-β-naphtha-	Faint pink (slow)	Deep red	No colour

At the present time no satisfactory explanation can be advanced to accommodate the whole of the observed facts, and we are now engaged in further studies of the dinaphtha-*spiro*pyrans, especially members of the hitherto unknown αα-series and the isomeric series derived from 2-hydroxy-3-naphthaldehyde.

The value of the *spiro*pyran colour reaction as applied by Heilbron and Irving (J., 1929, 936) to the determination of the reactive group in ketones of the type $Me{\cdot}CO{\cdot}CH_2R$ is in no way impaired by the anomalies now brought to light.

EXPERIMENTAL.

7-*Methoxy*-2-*ethylchromone*.—A mixture of 2-hydroxy-4-methoxyacetophenone (23 g.) with propionic anhydride (70 g.) and fused sodium propionate (70 g.) was heated under reflux at 200—210° during 5 hr. The reaction mixture was poured into H_2O, and any unchanged reactants removed by steam distillation. The crude *chromone* was isolated by stirring the residual tarry solid with Et_2O and was crystallised from EtOH, forming colourless needles (9 g.), m. p. 141—142° (Found: C, 70·4; H, 5·8. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%).

7-*Methoxy*-4-*phenyl*-2-*ethylbenzopyrylium Chloride*.—A conc. ethereal solution of PhMgBr (2 mols.) prepared from PhBr (11 g.) was carefully added to a boiling solution of 7-methoxy-2-ethylchromone (7 g.) in dry C_6H_6 (70 c.c.), the Et_2O being allowed to escape. After heating under reflux for 3 hr., the now orange-red solution was cooled with ice and decomposed by the careful addition of conc. HCl (35 c.c.). The crude pyrylium salt which separated after standing for 12 hr. at 0° was crystallised from CH_2O_2, separating in bright yellow needles. The *ferrichloride* crystallised from AcOH in golden-yellow needles, m. p. 110—111° (Found: Fe, 11·9. $C_{18}H_{17}O_2Cl_4Fe$ requires Fe, 12·1%).

7-*Methoxy*-4-*phenyl*-3′-*methylbenzo*-β-*naphtha*spiro*pyran*.—A suspension of 7-methoxy-4-phenyl-2-ethylbenzopyrylium perchlorate (prepared from the chloride above and crystallised from AcOH) (2 g.) in Et_2O was hydrolysed to the carbinol base by the addition of dil. NH_3 aq.; to the dried ethereal solution, evaporated to 30 c.c., 2-naphthol-1-aldehyde (1 g.) was added, and the whole saturated with HCl. After standing over-night at 0°, the resulting naphthavinylpyrylium salt, which separated in red crystals with a green reflex, was hydrolysed in Et_2O suspension by means of dil. NH_3 aq., and the crude spiro*pyran* isolated by evaporating the dried ethereal extract. The pure compound, obtained after repeated crystn. from acetone, formed colourless prisms, m. p. 165—166° to a purple liquid (Found: C, 83·3; H, 5·4. $C_{29}H_{22}O_3$ requires C, 83·3; H, 5·3%).

Solutions of this *spiro*pyran in xylene or veratrole readily became purple on heating to the boiling point, reversion to the colourless form taking place on cooling.

Unless other details are given, the other substances described below have been prepared by methods similar to those described above for the corresponding compounds.

2-*Ethylchromone*, prepared from *o*-hydroxyacetophenone (Freudenberg and Orthner, *Ber.*, 1922, **55**, 1749: the semicarbazone, not previously described, has m. p. 207°), crystallises from EtOH in long colourless needles, m. p. 116° (Found: C, 75·6; H, 5·8. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%).

4-*Phenyl*-3′-*methylbenzo*-β-*naphtha*spiro*pyran*, prepared from 4-phenyl-2-ethylbenzopyrylium perchlorate [fine yellow needles from AcOH, m. p. 207—209° (decomp.)], crystallises from acetone in colourless needles, m. p. 153—154° (to a purple liquid). Its solutions in ether, xylene or veratrole developed an intense purple colour on heating (Found: C, 86·3; H, 5·2. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·2%).

2-*Hydroxy*-4-*methoxyphenyl Ethyl Ketone*.—This compound, which was required for the preparation of 7-methoxy-3-methyl-2-ethylchromone, was first described by Nagai (*Ber.*, 1891, **25**, 1288) and is conveniently prepared by the following method. A solution of 2 : 4-dihydroxyphenyl ethyl ketone (30 g.), prepared according to Sonn's method (*Ber.*, 1921, **54**, 773), in MeOH (100 c.c.) was treated with Me_2SO_4 (38 g.) and then during 30 min. with conc. NaOH aq. (12 g.), the solution being cooled and thoroughly agitated. After 2 hr. H_2O was added, the MeOH distilled off, and the solution acidified and steam distilled. The distillate was rendered alkaline and extracted with Et_2O to remove the small amount of dimethyl ether formed in the reaction, the required product being obtained on acidifying the alkaline solution, m. p. 58—59° (yield, 22 g.).

7-*Methoxy*-3-*methyl*-2-*ethylchromone* crystallises from EtOH aq. in colourless needles, m. p. 85—86° (Found: C, 71·3; H, 6·3. $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5%). On treatment with PhMgBr it yields 7-*methoxy*-4-*phenyl*-3-*methyl*-2-*ethylbenzopyrylium perchlorate*, which separates from AcOH in golden-yellow leaflets, m. p. 203—205° (decomp.) (Found: C, 60·6; H, 5·5. $C_{19}H_{19}O_6Cl$ requires C, 60·2; H, 5·1%).

7-*Methoxy*-4-*phenyl*-3-*methylbenzo*-β-*naphtha*spiro*pyran* was prepared in the usual manner starting from 7-methoxy-2 : 3-dimethylchromone (Canter, Curd, and Robertson, J., 1931, 1245). The pure compound is obtained after repeated crystn. from acetone–MeOH in colourless crystals, m. p. 198—199° (to a purple liquid) (Found: C, 83·2; H, 5·5. $C_{29}H_{22}O_3$ requires C, 83·3; H, 5·3%). Solutions of this spiro*pyran* in xylene become purple on heating to the boiling point.

2-*Methyl*-α-*naphthachromone*.—This compound has been obtained by Wittig (*Annalen*, 1926, **446**, 155) by converting 2-aceto-1-naphthol into 2-acetylaceto-1-naphthol by the action of Na and EtOAc and then ring-closing the purified intermediate with H_2SO_4. In repeating this prepn. it was found that the diketone was difficult to purify owing to contamination with the chromone itself and it was therefore treated directly with conc. H_2SO_4; the resulting chromone was then purified without trouble.

4-*Phenyl*-αβ-*dinaphtha*spiro*pyran* was obtained from 2-methyl-α-naphthachromone *via* 4-phenyl-2-methyl-α-naphthapyrylium perchlorate, which separates from AcOH in dark green crystals, m. p. 197—199° (decomp.). The purified spiro*pyran* crystallises from acetone–MeOH in glistening plates, m. p. 193—194° (to a deep purple liquid) (Found: C, 87·7; H, 4·9. $C_{31}H_{20}O_2$ requires C, 87·7; H, 4·7%).

2-*Ethyl*-α-*naphthachromone*, prepared from 2-aceto-1-naphthol, propionic anhydride, and fused PrONa in the usual manner, forms pale yellow needles from EtOH, m. p. 199—200° (Found: C, 80·6; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·4; H, 5·4%). With PhMgBr this chromone yields 4-phenyl-2-ethyl-α-naphthapyrylium perchlorate, which separates from AcOH in dark brown crystals, m. p. 221° (decomp.).

4-*Phenyl*-3′-*methyl*-αβ-*dinaphtha*spiro*pyran*, obtained from the previously mentioned pyrylium salt, crystallises from acetone–EtOH in colourless glistening needles, m. p. 188—190° (to a blue liquid) (Found: C, 87·9; H, 4·9. $C_{32}H_{22}O_2$ requires C, 87·7; H, 5·0%).

4-*Phenyl*-3-*methyl*-αβ-*dinaphtha*spiro*pyran*.—4-Phenyl-2 : 3-dimethyl-α-naphthapyrylium perchlorate [golden-brown laminæ from AcOH, m. p. 223—224° (decomp.)] was first prepared from 2 : 3-dimethyl-α-naphthachromone (Cheema, Gulati, and Venkataraman, J., **1932**, 926) and then converted into the spiro*pyran*, which separated from acetone in colourless needles, m. p. 181—182° (to a blue liquid) (Found : C, 87·7; H, 5·2. $C_{32}H_{22}O_2$ requires C, 87·7; H, 5·0%).

4′ *Phenyl*-3′-*methylbenzo*-α-*naphtha*spiro*pyran*.—4-Phenyl-2 : 3-dimethyl-α-naphthapyrylium perchlorate was condensed with salicylaldehyde, and the product hydrolysed to the spiro*pyran* in the usual manner. The pure compound obtained by crystn. from acetone–EtOH formed pale yellow crystals, m. p. 115—116° (Found : C, 86·5; H, 5·0. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·1%).

3-*Methyl*-2-*ethyl*-α-*naphthachromone*, prepared from 2-propionyl-1-naphthol, crystallises from EtOH in colourless needles, m. p. 102—103° (Found : C, 80·5; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%). On treatment with PhMgBr in the usual manner this chromone yields 4-phenyl-3-methyl-2-ethyl-α-naphthapyrylium perchlorate, which crystallises from AcOH in golden-yellow plates, m. p. 228—230° (decomp.).

4-*Phenyl*-3 : 3′-*dimethyl*-αβ-*dinaphtha*spiro*pyran*.—In condensing the previously mentioned pyrylium salt with 2-naphthol-1-aldehyde the temp. must be kept at 40—45°. The remainder of the prepn. follows the normal course and the pure spiro*pyran* crystallises from acetone–EtOH in colourless needles, m. p. 181—182° (to a blue liquid) (Found : C, 87·7; H, 5·1. $C_{33}H_{24}O_2$ requires C, 87·6; H, 5·3%).

3 : 3′-*Dimethylenedi*-β-*naphtha*spiro*pyran* (VII).—A solution of 2-naphthol-1-aldehyde (3·5 g.) and *cyclo*pentanone (1·0 g.) (Aschan, *Ber.*, 1912, **45**, 1603) in EtOH (15 c.c.), saturated with HCl in the cold, rapidly assumed a blue colour due to the formation of the naphthavinylpyrylium salt, which began to separate after ½ hr. This product after washing with Et_2O was crystallised from formic acid and then hydrolysed to the spiro*pyran* in the usual manner. The pure compound separated from C_6H_6 in small colourless needles, m. p. 229—230° (to a purple liquid) (Found : C, 86·7; H, 4·9. $C_{27}H_{18}O_2$ requires C, 86·6; H, 4·8%).

3 : 3′-*Tetramethylenedi*-β-*naphtha*spiro*pyran* (VIII) was prepared from 2-naphthol-1-aldehyde and *cyclo*heptanone (Mossettig and Burger, *J. Amer. Chem. Soc.*, 1930, **52**, 3456). It crystallised from acetone–EtOH in colourless rhombs, m. p. 245—246° (Found : C, 86·6; H, 5·5. $C_{29}H_{22}O_2$ requires C, 86·6; H, 5·5%).

3 : 3′-(β-*Methyltrimethylene*)*di*-β-*naphtha*spiro*pyran* separated from C_6H_6 in colourless rhombs, m. p. 253—254° (Found : C, 86·6; H, 5·5. $C_{29}H_{22}O_2$ requires C, 86·6; H, 5·5%).

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