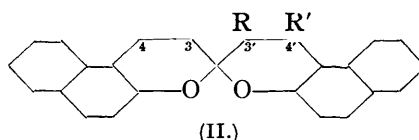
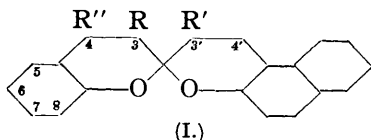


**299. Styrylpyrylium Salts. Part XVII. The Colour Phenomena Associated with 4-Phenylbenzo- $\beta$ -naphthaspiropyrans and 4-Phenyl- $\alpha\beta$ -dinaphthaspiropyrans.**

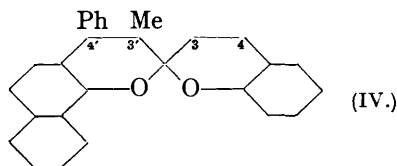
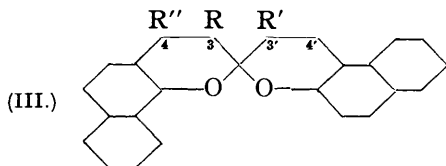
By I. M. HEILBRON, D. H. HEY, and A. LOWE.

In previous communications (J., 1927, 1699; 1928, 2077; 1929, 936; 1931, 1336) it was established that benzo- $\beta$ -naphthaspiropyrans (I) containing a substituent in the 3'-position, and di- $\beta$ -naphthaspiropyrans (II) containing substituents in both the 3- and the 3'-position, fail to give coloured solutions when heated in a high-boiling inert solvent, thus differing from *spiropyrans* unsubstituted at these positions. Subsequently (Heilbron, Heslop, and



Irving, J., 1933, 430), as a result of an examination of the effect of a phenyl group at position 4 in the benzo- $\beta$ -naphthaspiropyran molecule (I), it was stated that, contrary to previous experience, both 4-phenyl-3'-methylbenzo- $\beta$ -naphthaspiropyran (I; R=H, R'=Me, R''=Ph) and its 7-methoxy-derivative gave a coloration on heating in xylene solution. Further, it was not possible to synthesise similar phenyl derivatives of the di- $\beta$ -naphthaspiropyran series, but a new series of  $\alpha\beta$ -dinaphthaspiropyrans was prepared (III).

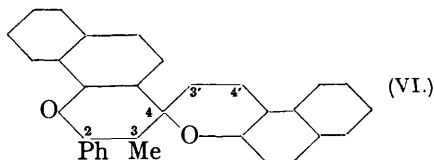
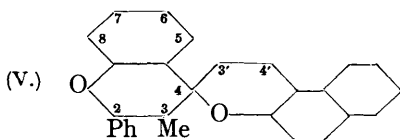
Of the latter series, 4-phenyl- (III; R=R'=H, R''=Ph), 4-phenyl-3-methyl- (III; R=Me, R'=H, R''=Ph), 4-phenyl-3'-methyl- (III; R=H, R'=Me, R''=Ph), and 4-phenyl-3 : 3'-dimethyl- $\alpha\beta$ -dinaphthaspiropyran (III; R=R'=Me, R''=Ph) were stated to give coloured solutions on heating in an inert solvent. The behaviour of this



series of compounds thus appeared to differ from that previously encountered in the di- $\beta$ -naphthaspiropyran series, since a coloration is developed even with both the 3- and the 3'-position substituted. One member of the benzo- $\alpha$ -naphthaspiropyran series was also prepared, *viz.*, 4'-phenyl-3'-methylbenzo- $\alpha$ -naphthaspiropyran (IV), and behaved normally in failing to give a coloured solution in high-boiling inert solvents.

As was later pointed out (Heilbron, Heslop, and Howard, J., 1933, 1263), in the synthesis of the 4-phenyl-3'-methylbenzo- $\beta$ -naphthaspiropyrans recourse was made to the Kostanecki reaction, the appropriate *o*-hydroxyacetophenone being used with propionic anhydride and fused sodium propionate. A detailed study of this reaction has since revealed that it cannot be employed as a general method for the synthesis of chromones, as was originally supposed, but that the product may consist of either a chromone, a coumarin, or a mixture

of both (Heilbron, Hey, and Lowe, J., 1934, 1311; Heilbron, Hey, and Lythgoe, *ibid.*, p. 1581; this vol., p. 295). The compounds employed by Heilbron, Heslop, and Irving (*loc. cit.*) and regarded as 2-ethyl- and 7-methoxy-2-ethyl-chromone and 2-ethyl- $\alpha$ -naphtha- $\gamma$ -pyrone\* are in reality 3:4-dimethyl- and 7-methoxy-3:4-dimethyl-coumarin and 3:4-dimethyl- $\alpha$ -naphtha- $\alpha$ -pyrone respectively. When treated with phenylmagnesium bromide, pyrylium salts are obtained which with 2-naphthol-1-aldehyde yield naphthavinylypyrylium salts from which *isospiro*pyrans result on hydrolysis, *viz.*, 2-phenyl-3-methylbenzo- $\beta$ -naphthaisospiropyran (V), its 7-methoxy-derivative, and 2-phenyl-3-methyl- $\alpha\beta$ -dinaphthaisospiropyran (VI) respectively (cf. Heilbron and Howard, J., 1934, 1571).



In each case, the 3'-position remains unsubstituted and thus the production of coloured solutions in high-boiling inert solvents is in agreement with the behaviour of the normal *spiro*pyrans. On the other hand, the identity of the 7-methoxy-3-methyl-2-ethylchromone and the 3-methyl-2-ethyl- $\alpha$ -naphtha- $\gamma$ -pyrone used by Heilbron, Heslop, and Irving (*loc. cit.*) has been confirmed (Heilbron, Hey, and Lowe, *loc. cit.*).

The preparation of 2-ethyl- and 7-methoxy-2-ethyl-chromone and 2-ethyl- $\alpha$ -naphtha- $\gamma$ -pyrone having been effected by an unambiguous method (Heilbron, Hey, and Lowe, *loc. cit.*), these chromones are now utilised in the preparation of the normal *spiro*pyrans substituted at the 3'-position. On treatment with phenylmagnesium bromide, followed by decomposition with hydrochloric acid, 4-phenylpyrylium salts are obtained, and condensation of these with 2-naphthol-1-aldehyde, followed by hydrolysis with aqueous ammonia, yields respectively 4-phenyl-3'-methylbenzo- $\beta$ -naphtha- (I; R = H, R' = Me, R'' = Ph), 7-methoxy-4-phenyl-3'-methylbenzo- $\beta$ -naphtha- and 4-phenyl-3'-methyl- $\alpha\beta$ -dinaphtha-*spiro*pyran (III; R = H, R' = Me, R'' = Ph). The first two compounds do not develop colour in boiling xylene, veratrole, or diphenyl ether solution. The alleged anomalies found by Heilbron, Heslop, and Irving (*loc. cit.*) in this series of *spiro*pyrans thus no longer exist. The third compound shows no coloration in boiling xylene, but a faint violet coloration is developed in boiling diphenyl ether solution; its behaviour therefore resembles that of 3:3'-trimethylenedi- $\beta$ -naphthaspiropyran (Dilthey and Wübken, *Ber.*, 1928, 61, 963).

The preparation of 4-phenyl-3:3'-dimethyl- $\alpha\beta$ -dinaphthaspiropyran (III; R = R' = Me, R'' = Ph) has also been re-examined. It was obtained from 3-methyl-2-ethyl- $\alpha$ -naphtha- $\gamma$ -pyrone by Heilbron, Heslop, and Irving (*loc. cit.*), who recorded that it passed into a coloured ionic form on heating. Our compound is identical with that previously described, but, although it gives a faint violet-blue coloration in boiling diphenyl ether solution, no colour is developed in boiling benzene or xylene. It thus resembles the above-mentioned 4-phenyl-3'-methyl- $\alpha\beta$ -dinaphthaspiropyran. The single member of the benzo- $\alpha$ -naphthaspiropyran series prepared by Heilbron, Heslop, and Irving, *viz.*, 4'-phenyl-3'-methylbenzo- $\alpha$ -naphthaspiropyran (IV), gave no colour when heated in an inert solvent, but it is not yet known if members of this series, generally, behave similarly to those of the corresponding benzo- $\beta$ -naphthaspiropyran series, since attempts to prepare 4'-phenylbenzo- $\alpha$ -naphthaspiropyran, which might be expected to give rise to colour formation, have not been successful.

#### EXPERIMENTAL.

4-Phenyl-3'-methylbenzo- $\beta$ -naphthaspiropyran (I; R = H, R' = Me, R'' = Ph).—A concentrated ethereal solution of phenylmagnesium bromide, prepared from bromobenzene (22 g.), magnesium (3.5 g.), and dry ether (75 c.c.), was added carefully to a boiling solution of 2-ethyl-

\* The terms naphtha- $\alpha$ -pyrone and naphtha- $\gamma$ -pyrone are now used in place of the more usual but incorrect naphthacoumarin and naphthachromone (cf. Robinson and Rose, J., 1933, 1469, footnote).

chromone (11 g.) in sodium-dried benzene (120 c.c.). After 3 hours' heating under reflux, the cold red solution was treated with concentrated hydrochloric acid (60 c.c.) and saturated with hydrogen chloride. After standing over-night at 0°, the benzene layer was decanted and washed with concentrated hydrochloric acid. The total aqueous acid extract was diluted and neutralised with aqueous ammonia. The carbinol base thus liberated was extracted with ether and dried. Evaporation of the ether left a yellow oil, which was redissolved in dry ether and saturated with hydrogen chloride. The 4-phenyl-2-ethylbenzopyrylium chloride separated as a deep-red viscous oil. A portion, dissolved in glacial acetic acid and treated with 20% perchloric acid solution, yielded the perchlorate, which crystallised from glacial acetic acid in yellow needles, m. p. 121—123° (decomp.). A solution of 2-naphthol-1-aldehyde (4 g.) in ethyl acetate (25 c.c.) was added to a solution of the pyrylium chloride (5 g.) in ethyl acetate (50 c.c.), and the whole was saturated with dry hydrogen chloride at 0°. After standing over-night, deep red crystals of the naphthavinylyl salt separated, which were collected and washed with ether. A portion treated with perchloric acid, in the manner previously described, yielded the perchlorate, which separated from glacial acetic acid in small red needles, m. p. 236—238° (decomp.). Hydrolysis of the naphthavinylylpyrylium chloride with warm aqueous ammonia gave the *spiropyran* as a bluish-white solid, which crystallised from benzene in fine white needles, m. p. 219—220° (to a colourless liquid) (Found: C, 86.8; H, 5.1.  $C_{28}H_{20}O_3$  requires C, 86.6; H, 5.2%). Solutions of the *spiropyran* in boiling benzene, xylene, veratrole, and diphenyl ether remained colourless. In glacial acetic acid solution a pink coloration developed on heating, and in trichloroacetic acid solution a deep crimson colour was produced.

*7-Methoxy-4-phenyl-3'-methylbenzo-β-naphthaspiropyran*.—The benzopyrylium chloride was prepared by the method described above, the same quantity of phenylmagnesium bromide being used and a solution of 7-methoxy-2-ethylchromone (14 g.) in sodium-dried benzene (120 c.c.). The crude 7-methoxy-4-phenyl-2-ethylbenzopyrylium chloride, which partly separated in small needles, was neutralised together with the acid washings, the resulting carbinol base being obtained as a yellow oil. The pyrylium chloride was obtained in greenish needles, and the perchlorate separated from glacial acetic acid in dark green plates, m. p. 163—165° (decomp.). The naphthavinylylpyrylium chloride, prepared in the manner described above from 2-naphthol-1-aldehyde (3.5 g.) and the pyrylium chloride (5 g.) in a mixture of absolute alcohol (25 c.c.) and dry ethyl acetate (40 c.c.), was obtained in dark blue crystals with a bronze reflex. The perchlorate separated from glacial acetic acid in deep purple needles, m. p. 287—289° (decomp.). The *spiropyran* obtained on hydrolysis of the chloride with dilute aqueous ammonia was repeatedly crystallised from benzene, separating in fine white needles, m. p. 256—258° (to a colourless liquid) (Found: C, 83.5; H, 5.3.  $C_{29}H_{22}O_3$  requires C, 83.3; H, 5.3%). No colour was developed in solution in boiling xylene, veratrole, or diphenyl ether. In glacial acetic acid solution a pink coloration was developed on warming; and a red solution was obtained in trichloroacetic acid.

*4-Phenyl-3'-methyl-α-β-dinaphthaspiropyran* (III; R = H, R' = Me, R'' = Ph).—The 4-phenyl-2-ethyl-α-naphthapyrylium chloride was obtained in yellow needles in the usual manner from the interaction of phenylmagnesium bromide, prepared from bromobenzene (18 g.), magnesium (2.7 g.), and dry ether (75 c.c.), and 2-ethyl-α-naphtha-γ-pyrone (8 g.) in dry benzene (75 c.c.). To the pyrylium chloride, dissolved in a mixture of dry ethyl acetate (75 c.c.) and absolute alcohol (25 c.c.), was added a solution of 2-naphthol-1-aldehyde (6 g.) in ethyl acetate, and the mixture, saturated with hydrogen chloride at 0°, was kept at that temperature for two days. The deep violet-red solution was partially evaporated at room temperature under reduced pressure, poured into water, and made alkaline with aqueous ammonia. The crude *spiropyran* (12 g.) which separated was purified by crystallisation from acetone–absolute alcohol. It crystallised in very pale yellow leaflets, m. p. 207—208° (Found: C, 87.6; H, 5.2.  $C_{32}H_{22}O_2$  requires C, 87.7; H, 5.0%). No coloration was developed in boiling xylene, but a pale violet coloration was produced in boiling diphenyl ether solution. In trichloroacetic acid solution a deep purple colour was produced.

*4-Phenyl-3 : 3'-dimethyl-α-β-dinaphthaspiropyran* (III; R = R' = Me, R'' = Ph).—The preparation of this *spiropyran* was carried out in the usual manner from 4-phenyl-3-methyl-2-ethyl-α-naphthapyrylium chloride (8 g.), but in the condensation with 2-naphthol-1-aldehyde (5 g.) a mixture of absolute alcohol (50 c.c.) and dry ethyl acetate (100 c.c.) was used as solvent and the condensation was effected at 0° (cf. Heilbron, Heslop, and Irving, *loc. cit.*, p. 434). The naphthavinylylpyrylium chloride separated in blue needles with a bronze reflex. The pure *spiropyran* crystallised from acetone–ethyl alcohol in fine colourless needles, m. p. 181—182° (to a blue liquid) (Found: C, 87.8; H, 5.1. Calc. for  $C_{33}H_{24}O_2$ : C, 87.6; H, 5.3%). No

coloration was developed on boiling in benzene or xylene solution, but in boiling diphenyl ether a pale violet-blue colour was produced. An intense blue-green coloration was developed in trichloroacetic acid solution.

Attempts to obtain 4'-phenylbenzo- $\alpha$ -naphthaspiropyran from 4-phenyl-2-methyl- $\alpha$ -naphthapyrylium chloride and salicylaldehyde were unsuccessful under a variety of experimental conditions of temperature and solvent (cf. Heilbron, Heslop, and Irving, *loc. cit.*).

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