CXLV.—*Styrylpyrylium Salts. Part XII.* spiro*Pyrans derived from 9-Methyl- and 9-Ethyl-xanthylium Salts.*

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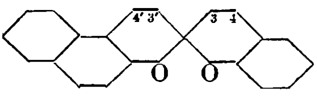
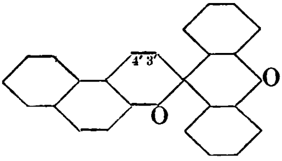
It has been shown by Atkinson and Heilbron (J., 1926, 676) that the 9-styrylxanthylium salts are strictly analogous in their colour reactions to the 2-styrylbenzopyrylium derivatives (Buck and Heilbron, J., 1922, **121**, 1198). A study has now been made of the condensation of 9-methyl- and 9-ethyl-xanthylium chloride with *o*-hydroxy-aldehydes and of the *spiro*pyrans produced on hydrolysis, in order to compare the latter compounds with the benzonaphtha*spiro*pyrans. Dickinson and Heilbron (J., 1927, 1699) have shown that only *spiro*pyrans having at least one of the pyran rings attached to a naphthalene nucleus have the power of forming coloured ions on the application of heat and, further, that this only occurs when this pyran ring is unsubstituted in the 3′-position (I). *Xantha-β-naphtha*spiro*pyran* (II) fulfils the above conditions and, as was anticipated, develops a strawberry colour when heated in hot diphenyl ether and also when melted; in both cases the colour disappears on cooling. On the other hand, *3′-methylxantha-β-naphtha*spiro*pyran*, which is analogous to 3′-methylbenzo-β-naphtha*spiro*pyran, fails to give a colour on heating; *benzoxantha*spiro*pyran* also remains colourless.

(I.)





(II.)

The xanthylium salts from which these *spiro*pyrans are derived are less stable than the corresponding pyrylium compounds; for instance, in the condensation of 2-naphthol-1-aldehyde with 9-methylxanthenol in ethereal solution by means of dry hydrogen chloride a mixture of the xanthylium salt and the *spiro*pyran was obtained, but with 9-ethylxanthenol, 3′-methylxantha-β-naphtha*spiro*pyran alone separated (compare Dickinson, Heilbron, and O'Brien, J., 1928, 2077). The *spiro*pyrans themselves are reconverted into the xanthylium salts only with difficulty; they give xanthylium salt colorations, not with glacial acetic acid, but only when trichloroacetic acid is used.

EXPERIMENTAL.

*Xantha-β-naphtha*spiro*pyran* (II).—To a dry solution of 9-methylxanthenol prepared from xanthone (10 g.) by Atkinson and Heilbron's method (*loc. cit.*), the theoretical quantity of 2-naphthol-1-aldehyde (8·5 g.) was added, and a slow stream of hydrogen chloride introduced. The yellow solution gradually darkened and an oil separated and then redissolved, an intense green solution being finally obtained. On standing in the cold for 48 hours a mixture of small bronze crystals and larger, faintly coloured prisms crystallised. These were separated by means of acetone, in which the latter product (the spiro*pyran*) was almost insoluble. The acetone and ether mother-liquors gave a further quantity of the *spiro*pyran on treatment with dilute ammonia until the colour was discharged. This substance on recrystallisation from benzene gave small colourless crystals which melted at 201° to a deep red liquid, the colourless *spiro*pyran again being formed on solidification. The solution of the compound in boiling xylene was colourless, but in boiling veratrole a faint strawberry tinge developed, and by using boiling diphenyl ether as solvent a deep strawberry colour, which disappeared on cooling, was obtained. In cold glacial acetic acid no colour was observed, but on boiling, a very faint pink colour, which faded on cooling, was produced; the addition of trichloroacetic acid to the solution in glacial acetic acid gave rise to an intense green xanthylium salt coloration (Found: C, 86·5; H, 4·7. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%).

*Benzoxantha*spiro*pyran*.—The theoretical quantity of salicylaldehyde (6·5 g.) was added to a dry solution of 9-methylxanthenol prepared from xanthone (10 g.), and a slow stream of hydrogen chloride introduced. A red oil rapidly separated and then redissolved as the solution became saturated, a deep purple solution resulting. As no chloride separated after long standing at 0°, perchloric acid (9 c.c. of 70%) was added and in a short time large purple needles with a bronze reflex began to appear. After 2 days the salt was removed and hydrolysed by means of dilute aqueous ammonia in presence of ether. The crude spiro*pyran* obtained on evaporation of the ethereal layer was recrystallised several times from acetone (charcoal), giving colourless prisms (faintly yellow when viewed in bulk), m. p. 154°, sparingly soluble in acetone, alcohol, or cold glacial acetic acid (Found: C, 84·6; H, 4·7. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%). Its solutions in boiling diphenyl ether and in boiling dodecahydrosqualene (over 300°) were colourless. In hot glacial acetic acid also it gave a colourless solution, but on the addition of trichloroacetic acid a purple xanthylium salt coloration was produced.

3′-*Methylxantha*-β-*naphtha*spiro*pyran*.—A solution of xanthone (10 g.) in boiling benzene (85 c.c.) was slowly treated with an ethereal solution of magnesium ethyl iodide prepared from ethyl iodide (28 g.). An orange colour developed immediately and a yellow solid was deposited, this dissolving again as more Grignard reagent was added. After refluxing for 1½ hours, the solvent was distilled off and the thick residue decomposed by the addition of ice-water. The product (9-ethylxanthenol) was removed by ether extraction. After the ethereal solution, which was assumed to contain the theoretical amount of product, had been dried, 2-naphthol-1-aldehyde (8·5 g.) was added, and the whole saturated with dry hydrogen chloride; an oil then separated, redissolving later to a solution which was purple when viewed in thin layers and deep red in bulk. On standing over-night at 0°, a considerable amount of colourless crystalline substance separated which after recrystallisation from benzene had m. p. 271°. Solutions of this *compound* in boiling diphenyl ether or glacial acetic acid were colourless, but the addition of trichloroacetic acid to the latter solution gave an intense green coloration (Found: C, 86·1; H, 4·8. $C_{26}H_{18}O_2$ requires C, 86·2; H, 5·0%).

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