296. *Styrylpyrylium Salts. Part XV. A Correction and Note on the Production of α-Benzopyrones by the Kostanecki Reaction.*

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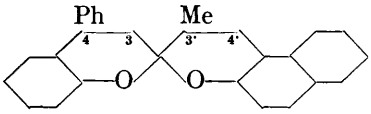
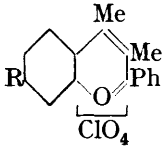
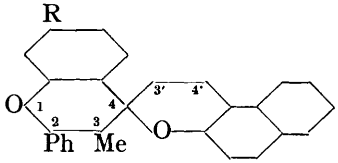
It was stated in Part XIV that both 4-phenyl-3′-methylbenzo-β-naphtha*spiro*pyran (I) and its 7-methoxy-derivative, each containing a methyl radical in the 3′-position, ionise in hot high-boiling inert solvents to give coloured solutions. This phenomenon, which is wholly at variance with all previous experience, has led us to re-investigate the various stages involved in their syntheses. As starting products for the preparation of the *spiro*pyrans, 2-ethylchromone and 7-methoxy-2-ethylchromone were required, and here recourse was made to the Kostanecki reaction using the appropriate *o*-hydroxyacetophenone together with propionic anhydride and fused sodium propionate, which by analogy with the work of previous investigators (Kostanecki and Różycki, *Ber.*, 1901, **34**, 102; Kostanecki and Lloyd, *ibid.*, p. 2942; Venkataraman, J., 1929, 2219; Canter, Curd, and Robertson, J., 1931, 1245) was confidently expected to give rise to 1 : 4-benzopyrone formation.



(I.)



(II.)



(III.)

Actually, however, we have now found that the substitution of propionic anhydride and sodium propionate for acetic anhydride and sodium acetate leads to the formation of coumarins, and the compounds described as 2-ethylchromone and 7-methoxy-2-ethylchromone are in reality 3 : 4-dimethylcoumarin and its 7-methoxy-analogue. These findings have been verified experimentally by mixed m. p. determination with authentic specimens of the coumarins and by hydrolysis to the appropriate αβ-dimethylcinnamic acids (compare Simonis and Peters, *Ber.*, 1908, **41**, 837; Canter, Curd, and Robertson, J., 1931, 1255; Canter and Robertson, *ibid.*, p. 1875).

Arising from this, what was previously described as 4-phenyl-2-ethylbenzopyrylium perchlorate is in reality 2-phenyl-3 : 4-dimethylbenzopyrylium perchlorate (II, R = H); similarly with the 7-methoxy-derivative (II, R = OMe) (compare Canter, Curd, and Robertson, *loc. cit.*; Heilbron and Zaki, J., 1926, 1902) and hence the *spiro*pyrans obtained by the condensation of (II; R = H or OMe) with 2-naphthol-1-aldehyde must have the structures (III; R = H or OMe).

For this new type we propose the name *isospiro*pyran, the compounds in question being *2-phenyl-3-methylbenzo-β-naphtha*isospiro*pyran* and its 7-methoxy-derivative. In both these *isospiro*pyrans the colour-inhibiting substituent in the 3′-position is absent and they are thus apparently comparable with the normal *spiro*pyrans as regards ionising capacity.

The facts now brought to light are of particular interest in showing that the Kostanecki reaction cannot be relied upon as a general method of chromone synthesis, but that its course is governed by many factors (compare Bargellini, *Atti R. Accad. Lincei*, 1925, **2**, 178, 261; Baker, J., 1929, 2897; Wittig, *Ber.*, 1924, **57**, 88). The structures of other alleged chromones described by Heilbron, Heslop, and Irving (this vol., p. 430), especially 7-methoxy-3-methyl-2-ethylchromone, 2-ethyl-α-naphthachromone, and 3-methyl-2-ethyl-α-naphthachromone, are now open to doubt, and it is our intention to re-investigate their constitutions in detail. We are also commencing a comprehensive investigation of the effect of various acid anhydrides on *o*-hydroxy-ketones of both the benzene and the naphthalene series in order to determine the conditions leading to 1 : 2- or 1 : 4-benzopyrone formation.

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