342. *Styrylpyrylium Salts. Part XVI. The Conversion of Coumarins into* isospiro*Pyrans.*

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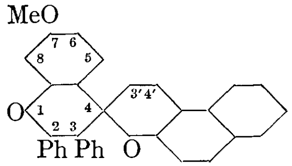
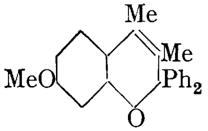
In a previous paper (cf. Heilbron, Heslop, and Howard, J., 1933, 1263; Heilbron, Heslop, and Irving, *ibid.*, p. 430) a brief description was given of the preparation of 2-phenyl-3-methylbenzo-β-naphtha*isospiro*pyran from 3 : 4-dimethylcoumarin.

(I.)





(II.)

The *isospiro*pyrans derived from the substituted 4-methylcoumarins exhibit in an enhanced degree the colour phenomena associated with the *spiro*pyran series having the 3′-position unsubstituted (Dickinson and Heilbron, J., 1927, 1699). This behaviour is exceptionally pronounced in the case of 7-*methoxy*-2 : 3-*diphenylbenzo*-β-*naphtha*isospiro*pyran* (I), a benzene solution of which exhibits a pale magenta colour even below 0°. Furthermore, the salt-forming capacity, as demonstrated by the ease of colour development on the addition of glacial acetic acid to an ethereal solution of the *isospiro*pyran, is considerably greater in this series than with the corresponding members of the *spiro*pyran group.

In every case the 3 : 4-disubstituted coumarins, on treatment with the Grignard reagent, either hot or cold, gave the corresponding 2-phenylbenzopyrylium chlorides in high yield (60—80%), and thus resemble the 3-substituted coumarins (cf. Heilbron, Hill, and Walls, J., 1931, 1701). On the other hand, 7-methoxy-4-methylcoumarin behaves similarly to 4-methyl- and 4-phenyl-coumarin, giving mainly the corresponding Δ^3-chromene.

Experimental.

7-*Methoxy*-2-*phenyl*-4-*methylbenzopyrylium Chloride.*—A solution of phenylmagnesium bromide (prepared from bromobenzene, 12·5 g., in dry ether, 200 c.c.) was slowly added (1 hour) at room temperature to a solution of 7-methoxy-4-methylcoumarin (5 g.), and after 12 hours the reaction mixture was decomposed with concentrated hydrochloric acid (30 c.c.) and the acid and solvent layers were separated. The pyrylium chloride was obtained by neutralising the acid layer with dilute aqueous ammonia in the presence of ether, followed by reprecipitation from the washed and dried ethereal solution with dry hydrogen chloride (yield, 0·7 g.). 7-*Methoxy*-2 : 2-*diphenyl*-4-*methyl*-Δ^3-*chromene* was obtained on evaporation of the ether–benzene layer as a thick oil, which crystallised from ether–methyl alcohol in hard colourless prisms, m. p. 90—91° (yield, 80%) (Found : C, 84·1; H, 6·2. $C_{23}H_{20}O_2$ requires C, 84·1; H, 6·1%).

7-*Methoxy*-2-*phenyl*-3-*methylbenzo*-β-*naphtha*isospiro*pyran.*—A solution of 7-methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (3·4 g.) (Heilbron and Zaki, J., 1926, 1902) and 2-naphthol-1-aldehyde (2·2 g.) in absolute alcohol (32 c.c.) was saturated with hydrogen chloride and left over-night at 0°. The resultant naphthavinylpyrylium salt, which separated in purplish-red needles, was recrystallised from alcohol and hydrolysed by shaking with aqueous ammoniacal ether. The isospiro*pyran*, obtained by evaporation of the dried ethereal extract, separated from acetone in prisms, m. p. 166—167° (to a purple liquid). Its solutions in benzene and xylene are colourless in the cold but become magenta on warming; it dissolves in warm ethereal acetic acid to yield a blue solution (Found : C, 83·0; H, 5·3. $C_{29}H_{22}O_3$ requires C, 83·2; H, 5·3%).

7-*Methoxy*-2 : 2-*diphenyl*-3 : 4-*dimethyl*-Δ^3-*chromene* (II), obtained by treating 7-methoxy-3 : 4-dimethylcoumarin in the hot with a large excess of the Grignard reagent (4 mols.), crystallised from ethyl alcohol in needles, m. p. 162—163° (Found : C, 84·1; H, 6·4. $C_{24}H_{22}O_2$ requires C, 84·2; H, 6·4%).

6-*Methoxy*-3 : 4-*dimethylcoumarin.*—6-Hydroxy-3 : 4-dimethylcoumarin (Robertson, Sandrock, and Hendry, J., 1931, 2430) was methylated in acetone solution by heating under reflux with methyl iodide and anhydrous potassium carbonate. 6-*Methoxy*-3 : 4-*dimethylcoumarin* separated from methyl alcohol in needles, m. p. 177—178° (Found : C, 70·0; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·5; H, 5·9%). This compound was also obtained in poor yield by directly condensing quinol monomethyl ether with α-methylacetoacetic ester.

6-Methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (light brown, non-hygroscopic crystals) was prepared in a yield of 80% when the foregoing coumarin (1 mol.) was treated at the ordinary temperature with phenylmagnesium bromide (2 mols.). The *ferrichloride*, prepared in the usual manner, crystallised from glacial acetic acid in brown plates, m. p. 80° (decomp.) (Found : C, 46·6; H, 3·7. $C_{18}H_{17}O_2Cl_4Fe$ requires C, 46·7; H, 3·6%).

6-*Methoxy*-2-*phenyl*-3-*methylbenzo*-β-*naphtha*isospiro*pyran* was prepared by condensing 6-methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (3 g.) with 2-naphthol-1-aldehyde (2 g.). It crystallised from benzene–ligroin in needles, m. p. 168—169° (Found : C, 83·2; H, 5·5. $C_{29}H_{28}O_3$ requires C, 83·2; H, 5·3%).

7-*Methoxy*-2 : 3-*diphenylbenzo*-β-*naphtha*isospiro*pyran*.—7-Methoxy-3-phenyl-4-methylcoumarin was prepared by methylating the corresponding hydroxycoumarin either with methyl iodide and potassium carbonate or with methyl sulphate and alkali. It melts at 106—107°, and not at 87° as recorded by Jacobson and Ghosh (J., 1915, **107**, 1051). Bargellini (*Atti R. Accad. Lincei*, 1925, **2**, 180), who prepared this compound from resacetophenone and phenylacetic anhydride, gives m. p. 102° (Found : C, 76·6; H, 5·3. Calc. for $C_{17}H_{14}O_3$: C, 76·7; H, 5·1%). For further characterisation the ether has also been prepared from resorcinol monomethyl ether and α-phenylpropionitrile, and has m. p. 105° alone or admixed.

7-Methoxy-2 : 3-diphenyl-4-methylbenzopyrylium chloride, prepared in the usual manner (yield, 70%), condensed readily with 2-naphthol-1-aldehyde to yield 7-methoxy-2 : 3-diphenyl-4-(β-2′-hydroxy-1′-naphthavinyl)benzopyrylium chloride, which formed deep purple, permanganate-like crystals. The *ferrichloride* crystallised from glacial acetic acid in red plates with a pronounced green reflex (Found : C, 60·2; H, 3·6. $C_{34}H_{25}O_3Cl_4Fe$ requires C, 60·1; H, 3·7%).

The naphthavinylpyrylium chloride yielded on hydrolysis a *hydrate* of the *isospiro*pyran, which crystallised from acetone–methyl alcohol in colourless needles, m. p. 126—127° (Found : C, 83·2; H, 5·5. $C_{34}H_{24}O_3,H_2O$ requires C, 83·8; H, 5·2%); the water-free compound was obtained on crystallisation of the hydrated compound from benzene–ligroin, from which it separated in needles, m. p. 173° (to a purple liquid) (Found : C, 84·8; H, 5·3. $C_{34}H_{24}O_3$ requires C, 85·0; H, 5·0%). An ethereal solution of this *isospiro*pyran gives an instantaneous deep blue colour on addition of a drop of glacial acetic acid.

7-*Methoxy*-3 : 4-*diphenylcoumarin*, prepared by methylating the corresponding hydroxycoumarin (Ghosh, J., 1916, **109**, 105) with methyl sulphate and alkali, crystallised from dilute alcohol (charcoal) in flat needles, m. p. 168° (Found : C, 80·0; H, 4·9. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). On treatment with phenylmagnesium bromide it yielded 7-methoxy-2 : 3 : 4-triphenylbenzopyrylium chloride (60% yield), the *ferrichloride* of which formed golden-brown plates, m. p. 140—142° (decomp.) (Found : C, 57·2; H, 3·7. $C_{28}H_{21}O_2Cl_4Fe$ requires C, 57·2; H, 3·6%).

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