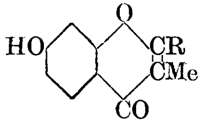
122. *Synthetical Experiments in the Chromone Group. Part VI. 2-Styrylchromones.*

By Ujagar Singh Cheema, Khushhal Chand Gulati, and Krishnasami Venkataraman.

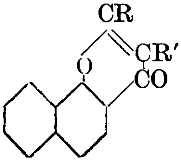
The occurrence of 2-styrylchromone derivatives in nature is doubtful, since fukugetin (Perkins and Phipps, J., 1904, **85**, 58), at one time suspected to be a compound of this class (Robinson and Shinoda, J., 1925, **127**, 1973), has now been shown to be differently constituted (Shinoda, *J. Pharm. Soc. Japan*, 1926, **535**, 736). Pratensol (Power and Salway, J., 1910, **97**, 231) may, however, be such a derivative.

Robinson and Shinoda (*loc. cit.*) synthesised 3-hydroxy-2-styrylchromones by the action of cinnamic anhydrides and the corresponding sodium salts on ω-methoxy-res- and -phlor-acetophenone. The synthesis of 2-styrylchromones unsubstituted in the 3-position has not been successful. The interaction of phloracetophenone, cinnamic anhydride and sodium cinnamate and alkaline hydrolysis of the product yielded a small amount of a substance which may be 5 : 7-*dicinnamoyloxy-2-styrylchromone.* Similarly, by using *p*-methoxycinnamic anhydride, a substance, probably 5 : 7-*di*-p-*methoxycinnamoyloxy-4′-methoxy-2-styrylchromone,* was obtained. From resacetophenone and 2-acetyl-1-naphthol no crystalline product was isolated. ω-Substituted ketones react normally (compare also Baker and Robinson, J., 1925, **127**, 1981). Thus the action of cinnamic anhydride or *p*-methoxycinnamic anhydride on respropiophenone, 2-propionyl-1-naphthol, 2-phenylacetyl-1-naphthol, and 2-β-phenylpropionyl-1-naphthol readily led to the corresponding 2-*styrylchromones* (I; R = $CH{:}CHPh$ or $CH{:}CH{\cdot}C_6H_4{\cdot}OMe$) and 2-*styryl*-1 : 4-α-*naphthapyrones* (II; R = $CH{:}CHPh$ or

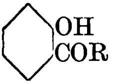
(I.)



(II.)



$CH{:}CH\cdot C_6H_4\cdot OMe$, $R' = Me$, Ph, or CH_2Ph). Other methods for the synthesis of styrylchromones unsubstituted in the 3-position were investigated. Ethyl cinnamate and sodium did not react with resacetophenone 4-methyl ether or with 2-acetyl-1-naphthol. The condensation of *o*-hydroxyacetophenone, gallacetophenone 3 : 4-dimethyl ether, and 2-acetyl-1-naphthol with cinnamaldehyde in presence of alkali led to the corresponding *cinnamylidene* ketones (III, IV, and V, respectively; $R = CH{:}CH\cdot CH{:}CHPh$), which could not be converted into the 2-styrylchromanones by treatment with boiling alcoholic sulphuric acid or prolonged contact with alkali.



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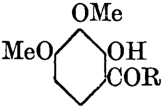

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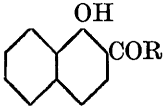
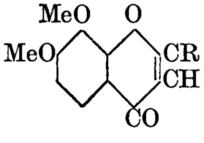
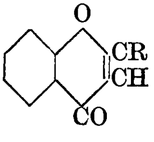


(V.)

3-Phenyl-2-methyl-1 : 4-α-naphthapyrone and 3-benzyl-2-methyl-1 : 4-α -naphthapyrone (see preceding paper) condense with benzaldehyde, *o*-methoxybenzaldehyde, anisaldehyde, and veratraldehyde under the conditions described by Heilbron, Barnes, and Morton (J., 1923, **123**, 2565); eight 2-*styryl*-1 : 4-α -*naphthapyrones* [II; $R = CH{:}CHPh, CH{:}CH\cdot C_6H_4\cdot OMe$ (*o* or *p*), or $CH{:}CH\cdot C_6H_3(OMe)_2$, $R' = Ph$ or CH_2Ph] were thus prepared. Further styrylnaphthapyrones [II; $R{=}CH{:}CHPh, CH{:}CH\cdot C_6H_4\cdot OMe$, or $CH{:}CH\cdot C_6H_3(OMe)_2$, $R' = Me$] were obtained by the interaction of benzaldehyde, anisaldehyde, and veratraldehyde respectively with 2 : 3-*dimethyl*-1 : 4-α-*naphthapyrone* (II; $R = R' = Me$), itself

(VI.)





(VII.)

prepared by heating 2-propionyl-1-naphthol with acetic anhydride and sodium acetate; the first two styrylnaphthapyrones were identical with the products of the action of cinnamic anhydride and *p*-methoxycinnamic anhydride respectively on 2-propionyl-1-naphthol. These results are in agreement with the fact discovered by Chakravarti (*J. Indian Chem. Soc.*, 1931, **8**, 129; see also Canter, Curd, and Robertson, J., 1931, 1255) that 2-methylchromones substituted in the 7-position will condense with aromatic aldehydes (compare Heilbron, Barnes, and Morton, *loc. cit.*).

Although the 2-methylchromones mentioned above are substituted in the 3-position, we have found that this is not essential for the aldehyde condensation to take place. 2-Methyl-1 : 4-α-naphthapyrone condenses with benzaldehyde, *o*-methoxybenzaldehyde, anisaldehyde, and vertraldehyde, giving the *styrylnaphthapyrones* [II; R = $CH{:}CHPh,CH{:}CH{\cdot}C_6H_4{\cdot}OMe$ (*o* or *p*), or $CH{:}CH{\cdot}C_6H_3(OMe)_2$, R′ = H], and 7 : 8-dimethoxy-2-methylchromone with benzaldehyde and anisaldehyde, giving 7 : 8-*dimethoxy-2-styrylchromone* (VI; R = $CH{:}CHPh$) and 7 : 8 : 4′-*trimethoxy-2-styrylchromone* (VI; R = $CH{:}CH{\cdot}C_6H_4{\cdot}OMe$). Finally, 2-methylchromone was treated with benzaldehyde and yielded 2-*styrylchromone* (VII; R = $CH{:}CHPh$), the parent member of the series; with anisaldehyde and veratraldehyde, 4′-*methoxy*-2-*styrylchromone* and 3′ : 4′-*dimethoxy-2-styrylchromone* [VII; R = $CH{:}CH{\cdot}C_6H_4{\cdot}OMe$ and $CH{:}CH{\cdot}C_6H_3(OMe)_2$] were obtained.

EXPERIMENTAL.

5 : 7-*Dicinnamoyloxy-2-styrylchromone.*—Phloracetophenone (4 g.), cinnamic anhydride (45 g.), and sodium cinnamate (6 g.) were stirred at 180—185° for 8 hours. The powdered product was boiled with 50% alcohol (200 c.c.) for an hour, the solution poured into dilute aqueous sodium carbonate, and the undissolved portion (14 g.) crystallised from glacial acetic acid (200 c.c.). The crystals (1·2 g.) were twice crystallised from acetic acid and separated in yellow needles, m. p. 235° (Found: C, 77·5; H, 4·1. $C_{35}H_{24}O_6$ requires C, 77·8; H, 4·4%). The substance dissolves in sulphuric acid, giving a red solution with a very weak green fluorescence, and gives no crystalline material on hydrolysis.

5 : 7-*Di*-p-*methoxycinnamoyloxy*-4′-*methoxy*-2-*styrylchromone* (?) was similarly prepared from phloracetophenone (5·5 g.), *p*-methoxycinnamic anhydride (60 g.), and sodium *p*-methoxycinnamate (8 g.). The product was dissolved in alcohol (200 c.c.) and boiled for 30 minutes after caustic potash (30 g.) in water (20 c.c.) had been added. Most of the alcohol was removed under diminished pressure, and the residue diluted with water. The precipitate crystallised from glacial acetic acid in small yellow needles, m. p. 240—241° (sintering at 230°) (Found: C, 71·1; H, 4·9. $C_{38}H_{30}O_9$ requires C, 71·2; H, 4·7%). The solution in sulphuric acid is red.

7-*Hydroxy-2-styryl-3-methylchromone* (I; R = $CH{:}CHPh$).—Resproplophenone (3·7 g.), cinnamic anhydride (19 g.), and potassium cinnamate (8·3 g.) were heated together at 185—190° for 6 hours, the powdered yellow mass refluxed with 10% alcoholic caustic potash (120 c.c.), the solution poured into water (2 litres), and the filtered liquid (which had a brilliant green fluorescence) saturated with carbon dioxide. The granular precipitate crystallised from glacial acetic acid in cream-coloured, stout, rectangular needles (2·1 g.), m. p. 307° (Found: C, 77·4; H, 5·1. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%).

The *acetyl* derivative formed very long, colourless needles, m. p. 159° (after shrinking at 152°), from alcohol (Found: C, 74·6; H, 5·1. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

7-Hydroxy-4′-methoxy-2-styryl-3-methylchromone (I; R = CH:CH·C_6H_4·OMe), similarly prepared from respropiophenone (2·5 g.), *p*-methoxycinnamic anhydride (15 g.), and sodium *p*-methoxycinnamate (5 g.), crystallised from alcohol–acetic acid in bright yellow needles (1·6 g.), m. p. 271—272° (Found: C, 74·0; H, 5·4. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%).

The *acetyl* derivative formed very pale yellow, silky needles, m. p. 181°, from alcohol (Found: C, 71·7; H, 5·3. $C_{21}H_{18}O_5$ requires C, 72·0; H, 5·1%).

The two preceding chromones are practically devoid of dyeing properties, give no coloration with alcoholic ferric chloride, and form yellow or orange-yellow solutions with a bright green fluorescence in sulphuric acid.

2-Styryl-3-methyl-1 : 4-α-naphthapyrone (II; R = CH:CHPh, R′ = Me), prepared from 2-propionyl-1-naphthol (3 g.), cinnamic anhydride (12 g.), and sodium cinnamate (5 g.), crystallised from alcohol in long, pale cream-coloured needles (1·9 g.), m. p. 166° (Found: C, 84·6; H, 5·0. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%). *4′-Methoxy-2-styryl-3-methyl-1 : 4-α-naphthapyrone* (II; R = CH:CH·C_6H_4·OMe, R = Me), prepared from 2-propionyl-1-naphthol (3 g.), *p*-methoxycinnamic anhydride (13·5 g.), and sodium *p*-methoxycinnamate (4·5 g.), crystallised from acetic acid–alcohol in pale greenish-yellow needles (2·3 g.), m. p. 169° (Found: C, 80·8; H, 5·3. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·2%). Their orange-yellow and bright orange solutions in sulphuric acid have a green fluorescence.

2-Cinnamylideneacetyl-1-naphthol (V; R = CH:CH·CH:CHPh.—A mixture of 2-acetyl-1-naphthol (3 g.), alcohol (10 c.c.), cinnamaldehyde (2·8 g.), and 10% caustic soda solution (12·5 c.c.) was left over-night and poured into water. The washed precipitate crystallised from alcohol in brownish-orange prisms (1·3 g.), m. p. 154° (Found: C, 84·1; H, 5·1. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

2-Hydroxycinnamylideneacetophenone (III; R=CH:CH·CH:CHPh), was similarly prepared from *o*-hydroxyacetophenone (5·1 g.), alcohol (30 c.c.), cinnamaldehyde (5 g.), and 10% caustic soda solution (20 c.c.). Crystallised from acetic acid, and then from light petroleum containing a little ethyl acetate, it formed small turmeric-yellow prisms (1·2 g.), m. p. 156—157° (Found: C, 81·8; H, 5·7. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

2-Hydroxy-3 : 4-dimethoxycinnamylideneacetophenone (IV; R = CH:CH·CH:CHPh), obtained from gallacetophenone dimethyl ether (3·7 g.), alcohol (10 c.c.), cinnamaldehyde (2·5 g.), and 10% caustic soda solution (10 c.c.), and crystallised twice from acetic acid and from alcohol, formed deep yellow, silky needles (1·3 g.), m. p. 141—142° (Found: C, 73·4; H, 5·8. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%).

These three ketones give red, bright orange, and orange solutions in sulphuric acid and brownish-orange, dark brown, and brownish-red colorations with alcoholic ferric chloride and dye mordanted wool in various shades of yellow or brown.

3-Phenyl-2-styryl-1 : 4-α-naphthapyrone (II; R = CH:CHPh, R′ = Ph).—3-Phenyl-2-methyl-1 : 4-α-naphthapyrone (preceding paper) (1 g.), absolute alcohol (75 c.c.), alcoholic sodium ethoxide (from 0·1 g. of sodium), and benzaldehyde (0·4 g.) were shaken together and left for 12 hours, refluxed for 30 minutes, and again left over-night. The solid product, having been washed with cold alcohol, crystallised from alcohol in very pale cream-coloured, silky needles (0·5 g.), m. p. 262—263° (Found: C, 86·5; H, 4·9. $C_{27}H_{18}O_2$ requires C, 86·6; H, 4·8%). The bright yellow solution in sulphuric acid has a green fluorescence. The substance readily decolorises alkaline permanganate. The colourless solution in boiling glacial acetic acid turns bright yellow on addition of a drop of sulphuric acid and develops a green fluorescence. An alcoholic solution is unaffected by magnesium and hydrochloric acid and by sodium amalgam. The substance (0·5 g. in 50 c.c. of carbon disulphide) and bromine (0·2 g. in 5 c.c.) gave, on evaporation of some of the carbon disulphide after a few hours, the *dibromide*, which crystallised from alcohol–benzene in colourless rhombohedral prisms (0·5 g.), m. p. 198° (Found: Br, 29·7. $C_{27}H_{18}O_2Br_2$ requires Br, 30·0%).

*3-Phenyl-2-*o*-methoxystyryl-1 : 4-α-naphthapyrone* (II; R = CH:CH·C_6H_4·OMe, R′ = Ph), prepared by the above reaction from 3-phenyl-2-methylnaphthapyrone (1·5 g.), sodium (0·2 g.), and *o*-methoxybenzaldehyde (0·8 g.), crystallised in bright yellow needles (0·7 g.), m. p. 231° (Found: C, 83·5; H, 4·9. $C_{28}H_{20}O_3$ requires C, 83·2; H, 4·9%).

*3-Phenyl-2-*p*-methoxystyryl-1 : 4-α-naphthapyrone*, obtained when anisaldehyde was substituted for *o*-methoxybenzaldehyde in the reaction, crystallised in stout, deep yellow needles (0·8 g.), m. p. 224—225° (Found: C, 82·8; H, 4·9%).

3-Phenyl-2-(3′ : 4′-dimethoxystyryl)-1 : 4-α-naphthapyrone, obtained from 3-phenyl-2-methylnaphthapyrone (1·5 g.), sodium (0·2 g.), and veratraldehyde (1 g.), crystallised in deep yellow, stout, rectangular needles (1 g.), m. p. 215—216° (Found : C, 79·8; H, 5·1. $C_{29}H_{22}O_4$ requires C, 80·2; H, 5·0%).

3-*Benzyl*-2-*styryl*-1 : 4-α-*naphthapyrone* (II; R = CH:CHPh, R′ = CH_2Ph), obtained from 3-benzyl-2-methyl-1 : 4-α-naphthapyrone (preceding paper) (0·6 g.), sodium (0·05 g.), and benzaldehyde (0·3 g.), crystallised in colourless needles (0·3 g.), m. p. 223° (Found : C, 86·4; H, 5·1. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·1%). The *dibromide* crystallised from alcohol–benzene in colourless leaflets, m. p. 167° (Found : Br, 29·3. $C_{28}H_{20}O_2Br_2$ requires Br, 29·2%).

3-*Benzyl*-2-o-*methoxystyryl*-1 : 4-α-*naphthapyrone*, obtained when *o*-methoxybenzaldehyde was substituted for benzaldehyde in the preceding reaction, crystallised in felted masses of long yellow needles (0·4 g.), m. p. 200° (Found : C, 83·1; H, 5·1. $C_{29}H_{22}O_3$ requires C, 83·3; H, 5·3%).

3-*Benzyl*-2-p-*methoxystyryl*-1 : 4-α-*naphthapyrone*, obtained from 3-benzyl-2-methylnaphthapyrone (1·4 g.), sodium (0·1 g.), and anisaldehyde (0·7 g.), crystallised in long, bright yellow needles (0·8 g.), m. p. 216—217° (Found : C, 83·1; H, 5·1%).

3-*Benzyl*-2-(3′ : 4′-*dimethoxystyryl*-1 : 4-α-*naphthapyrone*, obtained from 3-benzyl-2-methylnaphthapyrone (0·6 g.), sodium (0·05 g.), and veratraldehyde (0·4 g.), crystallised in long, yellow, rectangular needles (0·2 g.), m. p. 215° (Found : C, 80·0; H, 5·3. $C_{30}H_{24}O_4$ requires C, 80·4; H, 5·4%).

The preceding seven naphthapyrones, and the last three of the following four, were crystallised from alcohol–acetic acid. The crystals were coloured orange or red by sulphuric acid and the yellow or orange solutions in this acid had a more or less intense green fluorescence.

2 : 3-*Dimethyl*-1 : 4-α-*naphthapyrone* (II).—A mixture of 2-propionyl-1-naphthol (13 g.), fused sodium acetate (29 g.), and acetic anhydride (120 g.) was refluxed at 155—160° for 8 hours. The excess of anhydride was removed by distillation, the residue treated with boiling 10% alcoholic potash (400 c.c.) during 1 hour, the solution poured into water, and the long colourless needles which separated recrystallised from ligroin; yield 8 g., m. p. 142° (Found : C, 80·2; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·4; H, 5·4%). The pale yellow solution in sulphuric acid has a brilliant deep blue fluorescence.

2-*Styryl*-3-*methyl*-1 : 4-α-*naphthapyrone* (II; R = CH:CHPh, R′ = Me).—2 : 3-Dimethylnaphthapyrone (1·5 g.) was condensed in the usual manner with benzaldehyde (0·8 g.) and sodium (0·2 g.) in absolute alcohol. The pale yellow product, after being washed with cold alcohol, crystallised in long, pale cream-coloured needles (0·7 g.), m. p. 166° (Found : C, 84·3; H, 5·2. Calc. for $C_{22}H_{16}O_2$: C, 84·6; H, 5·1%).

2-*p*-Methoxystyryl-3-methyl-1 : 4-α-naphthapyrone, obtained from dimethylnaphthapyrone (1·5 g.), sodium (0·2 g.), and anisaldehyde (1 g.), crystallised in pale greenish-yellow, long, woolly needles (0·6 g.), m. p. 169° (Found : C, 80·4; H, 5·4. Calc. for $C_{23}H_{18}O_3$: C, 80·7; H, 5·2%).

2-(3′ : 4′-*Dimethoxystyryl*)-3-*methyl*-1 : 4-α-*naphthapyrone*, obtained in the preceding reaction when veratraldehyde (1·2 g.) was substituted for anisaldehyde, crystallised in large, greenish-yellow, rectangular plates (0·5 g.), m. p. 204° (Found : C, 77·0; H, 5·5. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%).

2-Methyl-1 : 4-α-naphthapyrone was prepared as described by Wittig, Baugert, and Richter (*Annalen*, 1925, **446**, 155), but for the ring closure of 2-acetylaceto-1-naphthol it was found preferable to use 10% alcoholic sulphuric acid.

2-*Styryl*-1 : 4-α-*naphthapyrone* (II; R = CH:CHPh, R′ = H).—2-Methylnaphthapyrone (1·7 g.) was dissolved in the minimum quantity of absolute alcohol, and benzaldehyde (1 g.) added, followed by sodium (0·2 g.) in absolute alcohol. The mixture was left overnight, and the crystalline product then twice recrystallised from alcohol, giving long, pale golden-yellow needles (0·7 g.), m. p. 177° (Found : C, 84·4; H, 4·7. $C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%). The bright yellow solution in sulphuric acid has a green fluorescence. The colourless solution in boiling glacial acetic acid assumes a bright yellow colour and a green fluorescence on addition of a drop of sulphuric acid. The colourless alcoholic solution is unaffected by sodium amalgam, but turns pale orange on treatment with magnesium and hydrochloric acid.

2-o-*Methoxystyryl*-1 : 4-α-*naphthapyrone*, prepared from 2-methylnaphthapyrone (1·4 g.), *o*-methoxybenzaldehyde (0·9 g.), and sodium (0·15 g.), crystallised from alcohol–acetic acid in long, silky, yellow needles (0·3 g.), m. p. 169° (Found : C, 80·3; H, 5·0. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). The crystals are coloured orange-red by sulphuric acid and the orange-yellow solution has a weak green fluorescence.

2-p-*Methoxystyryl*-1 : 4-α-*naphthapyrone* was obtained from 2-methylnaphthapyrone (1 g.), anisaldehyde (0·7 g.), and sodium (0·1 g.). The pale green solution was poured into water; the precipitate produced crystallised from alcohol, containing a few drops of acetic acid, in long, brilliant golden-yellow needles (0·3 g.), m. p. 207° (Found : C, 80·1; H, 4·8%). The substance is coloured deep orange-red in contact with sulphuric acid; on addition of more acid the crystals dissolve, giving a bright orange-yellow solution with a green fluorescence.

2-(3′ : 4′-*Dimethoxystyryl*)-1 : 4-α-*naphthapyrone* was prepared from 2-methylnaphthapyrone (1·4 g.), veratraldehyde (1·1 g.), and sodium (0·2 g.). The crude product was dark green, but after two crystallisations from alcohol–acetic acid (charcoal) dark yellow, irregular plates (0·2 g.), m. p. 211—212°, were obtained (Found : C, 77·2; H, 5·1. $C_{23}H_{18}O_4$ requires C, 77·1; H, 5·0%). The substance is coloured blood-red by sulphuric acid and the pale brown solution exhibits a dark green fluorescence.

7 : 8-*Dimethoxy-2-methylchromone* (compare Blumberg and Kostanecki, *Ber.*, 1903, **36**, 2192).—To a solution of gallacetophenone dimethyl ether (8·5 g.) in warm ethyl acetate (15 g.), finely divided sodium (4 g.) was added. When the reaction had moderated, the mixture was heated on the water-bath for 4 hours, left over-night, and poured into ice-cold dilute acetic acid. The precipitate was collected, treated with boiling 20% alcoholic sulphuric acid (50 c.c.) during 2 hours, and poured into water. After concentration to small bulk and cooling, the chromone crystallised. Recrystallised from hot water, it formed colourless needles, m. p. 85—86°, and 102° after drying at 115° (yield, 2·2 g.) (Blumberg and Kostanecki give m. p. 102°).

7 : 8-*Dimethoxy-2-styrylchromone* (VI; R = CH:CHPh).—A mixture of 7 : 8-dimethoxy-2-methylchromone (1 g.) in the minimum quantity of absolute alcohol, benzaldehyde (0·5 g.), and alcoholic sodium ethoxide (0·16 g. of sodium) was left over-night; the crystalline precipitate, recrystallised from alcohol–acetic acid, gave pale yellow, woolly needles (0·4 g.), m. p. 171° (Found : C, 74·1; H, 5·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%).

7 : 8 : 4′-*Trimethoxy-2-styrylchromone*, obtained by using anisaldehyde (0·6 g.) instead of benzaldehyde, crystallised from alcohol, containing a few drops of acetic acid, in silky clusters of long, greenish-yellow needles (0·4 g.), m. p. 178° (Found : C, 71·2; H, 5·4. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3%). Sulphuric acid imparts an orange colour to the crystals of these two chromones and gives bright yellow and orange-yellow solutions with a green fluorescence.

2-*Methylchromone* (compare Wittig and others, *loc. cit.*).—This was prepared from *o*-hydroxyacetophenone (20 g.), ethyl acetate (52 g.), and sodium (14 g.) (compare the 7 : 8-dimethoxy-derivative) and isolated, after the ring closure, by extraction with benzene and precipitation from the extract, after concentration, by ligroin at 0°; yield 4·6 g., m. p. 68—69° (Wittig and others, 70—71°).

2-*Styrylchromone* (VII; R = CH:CHPh).—The condensation was carried out with 2-methylchromone (1·5 g.), benzaldehyde (1 g.), and sodium (0·22 g.). After 12 hours the dark green alcoholic solution was poured into water, the precipitate collected and dissolved in aqueous alcohol–acetic acid (charcoal), and after a few hours the liquid filtered; on slow evaporation, long yellow needles (0·4 g.), m. p. 131°, separated (Found: C, 82·3; H, 4·6. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·8%). The substance is coloured intensely red by sulphuric acid and the pale brownish-yellow solution exhibits a distinct green fluorescence. The almost colourless solution in boiling glacial acetic acid becomes bright orange-yellow on addition of a drop of mineral acid. The almost colourless solution in alcohol turns pale orange on addition of magnesium and hydrochloric acid: with sodium amalgam, the colour first becomes pale orange and then rapidly bright orange-red. When dry hydrogen chloride is passed into a solution of the substance in chloroform, a bright orange-red coloration is obtained and deep orange-coloured crystals of the hydrochloride are soon deposited; on exposure to air, the colour is rapidly bleached. The substance is insoluble in water, moderately easily soluble in cold ethyl and methyl alcohol, and very readily in the boiling solvents; it is readily soluble in ethyl acetate, chloroform, benzene, and glacial acetic acid, and moderately readily in light petroleum.

4′-*Methoxy*-2-*styrylchromone*, obtained from 2-methylchromone (1·4 g.), anisaldehyde (1·3 g.), and sodium (0·2 g.) and purified as in the previous case, formed bright yellow, long, silky needles (0·5 g.), m. p. 140° (Found: C, 77·6; H, 5·0. $C_{18}H_{14}O_3$ requires C, 77·7; H, 5·0%). The crystals are coloured bright orange-red by sulphuric acid and the yellow solution has a vivid green fluorescence.

3′ : 4′-*Dimethoxy*-2-*styrylchromone* was obtained from 2-methylchromone (1·5 g.), veratraldehyde (1·6 g.), and sodium (0·25 g.). The yellow crystalline solid which separated over-night was recrystallised from alcohol, giving pale green, long, woolly needles (0·3 g.), m. p. 165° (Found: C, 74·2; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). The substance is coloured bright orange by sulphuric acid and the yellow solution has a scarcely perceptible green fluorescence.

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