

**465.** *The Action of Sodium Ethoxide on Chroman-4-ones.*

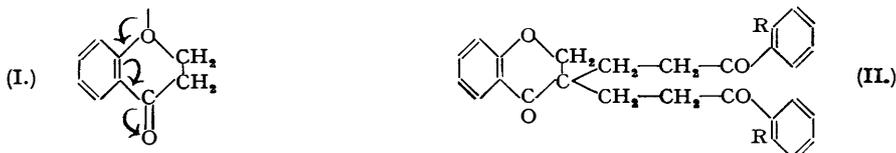
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Three crystalline substances have been isolated from the product formed when chroman-4-one is boiled with alcoholic sodium ethoxide. All are polymers of chromanone and there is evidence that one, m. p. 142°, is 3 : 3-di-(2-*o*-hydroxybenzoyl)ethylchroman-4-one, formed by interaction of two molecules of *o*-hydroxyphenyl vinyl ketone with one molecule of chromanone. 3 : 3-Di-(2-benzoyl)ethylchromanone has been obtained from phenyl vinyl ketone and chromanone, and also from 3 : 3-di-(2-chloroformyl)ethylchromanone and benzene. 7-Methoxychroman-4-one is not easily affected by sodium ethoxide, and it has been shown that 2-hydroxy-4-methoxyphenyl vinyl ketone is cyclised by alkali to give 7-methoxychromanone. Preparation of the latter from  $\beta$ -(3-*n*.ethoxyphenoxy)propionitrile is described.

VON BRAUN (and, in part, O. Bayer), having failed to effect the condensation of chroman-4-one with isatin under the alkaline conditions normally used to bring about the Pfitzinger reaction,

and finding that they could recover the isatin but not the chromanone, attempted to elucidate the action of alkali on chromanone (*Annalen*, 1927, 451, 54). They showed that on warming with aqueous alcoholic alkali a brown solution was rapidly formed, but they failed to isolate any pure substance from the material which acid precipitated from this solution. They showed that the crude product had a molecular weight between 500 and 600.

We found that the products of alkali-catalysed condensations of chromanone with aromatic aldehydes are often very difficult to purify, compared with the same substances prepared in alcoholic hydrogen chloride or acetic acid-hydrogen chloride solutions. It appeared that this was caused by self-condensations of chromanones in alkaline media. Self-condensations of ketones are, of course, well known. Chromanone might, however, be expected to be rather

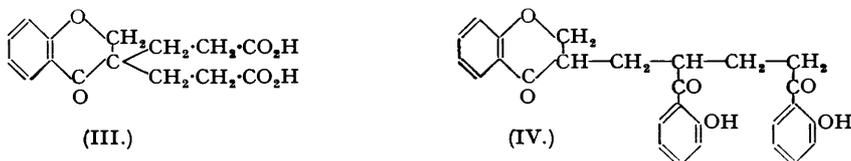


more unreactive in this respect than a ketone like indan-1-one because of the neutralising effect of the oxygen atom (I), and accordingly we found no evidence of the formation of compounds analogous to anhydroindanone and truxene: chromanone was recovered unchanged after many hours' boiling with aqueous sulphuric acid or with alcoholic hydrogen chloride.

We suspected, therefore, from analogy with the conversion of flavanones into *o*-hydroxy-chalkones by alkali and the condensation of chalkone with flavanones in the presence of alkali (Kaplash, Shah, and Wheeler, *J. Indian Chem. Soc.*, 1942, 19, 117), that the changes that chromanone undergoes in alkaline media might depend on a preliminary ring opening with the formation of *o*-hydroxyphenyl vinyl ketone rather than on an aldol-type reaction. It appears likely that this is so.

We, too, failed to obtain any crystalline material from the product obtained by warming chromanone with aqueous sodium hydroxide, but from the material formed when chromanone is boiled with alcoholic sodium ethoxide, three crystalline compounds have been isolated. All appear to be polymers of the parent substance. Two were obtained only in very small yield. Of these, (A), m. p. 107°, is a colourless neutral substance (C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub>, and (B), m. p. 172°, is a colourless alkali-soluble (phenolic) compound (C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>)<sub>n</sub>. (A) is converted into (B) by the action of sodium hydroxide. They have not, so far, been further investigated.

The third product of the reaction, m. p. 142°, is most probably 3:3-di-(2-*o*-hydroxybenzoyl)ethylchroman-4-one (II; R = OH), formed by interaction of chromanone and two molecules of *o*-hydroxyphenyl vinyl ketone. This constitution has not been proved, but there appears sufficient evidence to justify the formula (II; R = OH) for the compound, m. p. 142°. The substance is insoluble in aqueous sodium carbonate, but it dissolves slowly in dilute sodium hydroxide, forming a pale yellow solution from which it is reprecipitated by acid. Addition of benzenediazonium chloride to the alkaline solution gives an orange-coloured precipitate, and when an alcoholic solution of (II; R = OH) is treated with aqueous ferric chloride a brownish-violet coloration is produced. Acetylation gives a diacetyl derivative (II; R = OAc) which can be hydrolysed to give (II; R = OH) again. Methylation with methyl iodide and potassium carbonate affords a dimethoxy-compound (II; R = OMe) which is no longer soluble in alkali, suggesting that phenolic hydroxyl groups have been methylated. The molecular weight of 3:3-di-(2-*o*-hydroxybenzoyl)ethylchroman-4-one, determined by Rast's method, was discordant, but the molecular weight of the diacetyl derivative (II; R = OAc), determined cryoscopically in benzene, was correct. The compound (II; R = OH) forms a dioxime and a bisphenyl-hydrazone as would be expected, because it is unlikely that the carbonyl group in the ring would

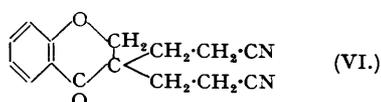
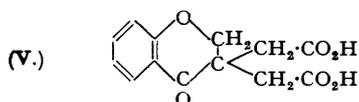


react easily with ketonic reagents. [It has been shown that 3:3-di-(2-carboxyethyl)chroman-4-one (III) does not react with hydroxylamine even on long boiling: the crude recovered substance does not contain nitrogen.] The compound (II; R = OH) took up about two molecules of

bromine in acetic acid solution, and on hydrogenation in the presence of Adams's catalyst, about four molecules of hydrogen were slowly absorbed to give a product that was essentially non-phenolic. Neither of these reactions, however, afforded crystalline material.

These facts do not exclude the formula (IV) for the substance, m. p. 142°, though this might perhaps be expected to yield a trioxime; the structure (II; R = OH) is, however, preferred for another reason given later.

An attempt was made to oxidise the dimethoxy-compound (II; R = OMe) with selenium dioxide in the hope that if formula (II; R = OH) is correct a tetraketone would be formed and could be degraded to give (V) (compare Morrell, Pickering, and Smith, *J. Inst. Petroleum*, 1948, **34**, 687). The dimethoxy-compound, however, failed to react at all with selenium dioxide: it appears that the carbonyl groups in this substance are comparatively unreactive as it also fails to form an oxime. Oxidation of the diacetyl compound (II; R = OAc) with selenium dioxide took place, but the yellow product of the reaction failed to give (V) on further oxidation with



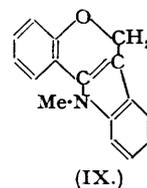
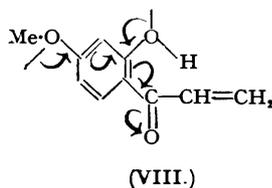
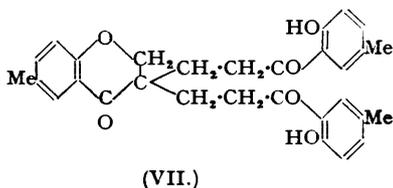
hydrogen peroxide and sodium hydroxide. The only crystalline product isolated from the alkaline solution so obtained was salicylic acid, although a small quantity of a phenolic substance, m. p. 119—120°, and not identified, was obtained from the solid residue. The results of the experiment were therefore inconclusive.

It has been shown that phenyl vinyl ketone reacts with chromanone in the presence of sodium ethoxide to give a small yield of 3:3-di-(2-benzoyl ethyl)chroman-4-one (II; R = H); this substance was also obtained when phenyl vinyl ketone was prepared from 2-chloropropiophenone in the presence of chromanone (compare Allen and Bridgess, *J. Amer. Chem. Soc.*, 1929, **51**, 2151). In both reactions most of the phenyl vinyl ketone polymerised to a gum. (II; R = H) has also been synthesised. Acrylonitrile condensed smoothly with chromanone in dioxan solution to give 3:3-di-(2-cyanoethyl)chroman-4-one (VI). The acid chloride corresponding to (VI) reacted with benzene in the presence of aluminium chloride to give 3:3-di-(2-benzoyl ethyl)chroman-4-one, identical with the substance prepared as described above.

The formation of (II; R = H) from chromanone and phenyl vinyl ketone supports the formula (II; R = OH) for the compound, m. p. 142°, because by analogy with the reactions of acrylonitrile with other ketones, there can be no doubt that the dicyanide formed here is 3:3-di-(2-cyanoethyl)chroman-4-one (VI).

An unsuccessful attempt to synthesise (II; R = OH) was made by heating the diphenyl ester of (III) with aluminium chloride under conditions favourable to bringing about an ortho-Fries rearrangement. The product, m. p. 185—200°, although it could not be obtained in a chemically pure condition, seemed to be essentially  $C_{27}H_{24}O_6$ , but it appears probable, in view of the higher m. p., that at any rate part of the change has involved a *para*-rearrangement. The failure of this reaction to produce the substance considered to be (II; R = OH) in no way disproves the proposed formula. Attempts have also been made to prepare (II; R = OMe) by decomposing various Mannich bases from *o*-methoxyacetophenone in the presence of chromanone, but so far this method has not led to success. The hydrochloride of *o*-hydroxyphenyl 2-dimethylaminoethyl ketone has been prepared, but when it was decomposed by boiling with water in the presence of chromanone an uncrystallisable gum and not (II; R = OH) was obtained. A similar gummy product, and not chromanone, resulted when it was refluxed with water.

Direct synthesis of (II; R = OH) by a Friedel-Crafts reaction similar to that used to prepare (II; R = H) is impossible because this would require *o*-substitution into the phenol or anisole nucleus, and so far attempts to synthesise (VII), which might be expected to be formed from 6-methylchromanone, have not been pursued very far because the product actually obtained from 6-methylchromanone is very difficult to purify.



It is clear that substituents in the chromanone nucleus modify the ease of polymerisation very greatly. For instance, 7-methoxychromanone has been recovered almost quantitatively after 2 hours' boiling with alcoholic sodium ethoxide, although much longer boiling gradually converts it into a phenolic substance which is being investigated. The methoxyl group clearly makes the chromanone ring harder to open and, indeed, 2-hydroxy-4-methoxyphenyl vinyl ketone (VIII), which it should give if ring opening occurred, has been prepared and found to be a stable yellow substance that shows no tendency to polymerise and is actually cyclised to give 7-methoxychromanone with aqueous sodium hydroxide. Bergel, Haworth, Morrison, and Rinderknecht (*J.*, 1944, 163) claim to have prepared the dinitrophenylhydrazone from 2-hydroxy-4-methoxyphenyl vinyl ketone obtained by decomposing an appropriate Mannich base. The substance that they describe is almost certainly the isomeric 2 : 4-dinitrophenylhydrazone of 7-methoxychromanone. This substance has now been made and shown to melt at 245°, as does the compound described by these authors. The vinyl compound (VIII) yields, with dinitrophenylhydrazine, a product that has not been obtained in a crystalline condition, and (VIII) can be reconverted into 2-hydroxy-4-methoxyphenyl 2-chloroethyl ketone from which it was prepared, by treatment with hydrochloric acid.

Like Harradence, Hughes, and Lions (*J. Proc. Roy. Soc. N. S. Wales*, 1938, 72, 273), we were unable to prepare an indole from chromanone phenylhydrazone and we also found that the *p*-nitrophenylhydrazone was unaffected by acid reagents. Chromanone phenylmethylhydrazone, however, yielded 1'-methylindolo(3' : 2'-3 : 4)chrom-3-en (IX) on treatment with dilute sulphuric acid.

#### EXPERIMENTAL.

*Chroman-4-one.*—Chromanone was prepared by Powell's method (*J. Amer. Chem. Soc.*, 1923, 55, 2711) which we found preferable to Arndt and Kallner's (*Ber.*, 1924, 57, 204). The use of *dry* benzene did not increase the yield (52%) and we found purification by steam distillation best.

$\beta$ -(3-Methoxyphenoxy)propionitrile (prepared from resorcinol monomethyl ether and acrylonitrile by the method since described by Bachmann and Levine, *J. Amer. Chem. Soc.*, 1948, 70, 599, but with use of a little sodium as condensing agent) decomposes very readily on distillation (b.p. 191—195°/15 mm.) unless it is quite free from all traces of the alkali used to remove the unchanged phenol.

$\beta$ -(3-Methoxyphenoxy)propionic Acid.—The above nitrile (5 g.) on refluxing for 8 hours with concentrated hydrochloric acid (50 c.c.) affords  $\beta$ -(3-methoxyphenoxy)propionic acid, m. p. 82°, best purified by extraction in a Soxhlet apparatus with petroleum (b.p. 40—60°) (yield 4 g.). If decomposition products of the nitrile are present in the material subjected to hydrolysis, the acid obtained is very difficult to purify.

$\beta$ -(4-Methylphenoxy)propionitrile, prepared as above from *p*-cresol and acrylonitrile, separates from methyl alcohol as colourless needles, m. p. 48° (Found : N, 8.3. C<sub>10</sub>H<sub>11</sub>ON requires N, 8.7%).

7-Methoxychroman-4-one.— $\beta$ -(3-Methoxyphenoxy)propionitrile (5 g.) and powdered anhydrous zinc chloride (5 g.) in dry ether (20 c.c.) were treated with dry hydrogen chloride at 0° for 4 hours, and the mixture was kept at room temperature until next day. The crystalline solid formed was separated, washed with ether, and refluxed with water for one hour, a yellow oil being obtained. This was extracted with ether and dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent removed. Distillation *in vacuo* (b. p. 197°/30 mm.) gave 7-methoxychromanone, identical (mixed m. p.) with that substance, m. p. 76—78°, prepared as described by Perkin, Ray, and Robinson (*J.*, 1926, 945) (yield, 3.5 g.). Bachmann and Levine (*loc. cit.*) found cyclisation of this nitrile with sulphuric acid or phosphoric oxide unsatisfactory. When 7-methoxychromanone (0.6 g.) and 2 : 4-dinitrophenylhydrazine (0.5 g.) were melted together on a steam-bath the product solidified and, after extraction with hot alcohol, a red solid, m. p. 244—245°, remained. Recrystallisation from glacial acetic acid afforded 7-methoxychromanone 2 : 4-dinitrophenylhydrazone as red needles, m. p. 245° (Found : C, 53.8; H, 3.9. C<sub>16</sub>H<sub>14</sub>O<sub>8</sub>N<sub>4</sub> requires C, 53.6; H, 3.9%).

*Polymerisation of Chroman-4-one.*—Chromanone (20 g.) was refluxed for 1½ hours with an alcoholic solution of sodium ethoxide [sodium (3.2 g.) in alcohol (170 c.c.)]; the mixture was then stirred into dilute hydrochloric acid, and the semi-solid mass which was precipitated crystallised when treated with ether. Recrystallisation from alcohol gave 3 : 3-di-(2-o-hydroxybenzoyl)ethylchroman-4-one (II; R = OH) as colourless needles, m. p. 142° (5.6 g.) (Found : C, 72.9; H, 5.4. C<sub>27</sub>H<sub>24</sub>O<sub>6</sub> requires C, 72.9; H, 5.4%). The aqueous acid from the above was extracted with ether which was then combined with that from which (II; R = OH) first separated, and the ethereal solution so obtained was washed with sodium hydroxide (10%). After drying (Na<sub>2</sub>SO<sub>4</sub>) and distillation of the ether, a crystalline solid (A) remained. Recrystallisation from methyl alcohol afforded colourless plates, m. p. 107° [Found : C, 72.8; H, 5.0%; M (Rast), 276. (C<sub>27</sub>H<sub>24</sub>O<sub>6</sub>)<sub>2</sub> requires C, 72.9; H, 5.4%; M, 296]. Acidification of the above aqueous sodium hydroxide and extraction with ether gave a little more of the compound, m. p. 142°, and a small quantity of a substance (B), ultimately obtained as colourless needles, m. p. 172°, from alcohol [Found : C, 72.4; H, 5.3. (C<sub>27</sub>H<sub>24</sub>O<sub>6</sub>)<sub>2</sub> requires C, 72.9; H, 5.4%]. When (A), which is insoluble in cold alkali, was boiled for 5 minutes with sodium hydroxide (10%) a clear yellow solution was obtained and acidification afforded (B), m. p. 172°, after recrystallisation from alcohol.

*Derivatives and Reactions of 3 : 3-Di-(2-o-hydroxybenzoyl)ethylchroman-4-one* (II; R = OH).—This compound (2 g.), methyl iodide (10 c.c.), dry potassium carbonate (20 g.), and acetone (60 c.c.) were refluxed together for 6 hours. The solvent was distilled, water was added, and extraction of the residue

with ether gave, after drying ( $\text{Na}_2\text{SO}_4$ ) and evaporation, a colourless gum which crystallised when treated with methyl alcohol. 3 : 3-Di-(2-*o*-methoxybenzoyl)ethylchroman-4-one was obtained as colourless prisms, m. p. 176°, from methyl alcohol (Found: C, 73.5; H, 6.0.  $\text{C}_{29}\text{H}_{28}\text{O}_6$  requires C, 73.7; H, 5.9%). Methylation with methyl sulphate and sodium hydroxide was not successful. The compound (II; R = OH) (1.5 g.) in dry pyridine was treated with excess of acetic anhydride. After 12 hours, dilute hydrochloric acid was added and a gum separated. This crystallised with alcohol and was recrystallised from alcohol, 3 : 3-di-(2-*o*-acetoxybenzoyl)ethylchroman-4-one separating as colourless needles, m. p. 135—139° (1.05 g.) [Found: C, 70.2; H, 5.4%; M (cryoscopic in benzene), 535.  $\text{C}_{23}\text{H}_{20}\text{O}_6$  requires C, 70.4; H, 5.3%; M, 528]. Careful purification did not change the m. p. The same compound can be obtained if (II; R = OH) is boiled with acetic anhydride and a little fused sodium acetate for exactly 4 minutes: longer boiling produces an uncrystallisable gum. Hydrolysis was effected when the diacetyl compound (0.3 g.) was suspended in a little alcohol with sodium hydroxide (0.2 g.) and the mixture was kept overnight. Acidification of the yellow solution formed gave a solid which, after recrystallisation, melted at 142° alone or mixed with (II; R = OH). The compound (II; R = OH) (1 g.), hydroxylamine hydrochloride (2 g.), and crystalline sodium acetate (4 g.) were refluxed in alcohol for 4 hours. Dilution with water precipitated a white solid which was recrystallised from alcohol and then acetic acid. A *dioxime* was obtained as colourless needles, m. p. 213—221° (decomp.) (Found: C, 68.8; H, 5.6; N, 5.5.  $\text{C}_{27}\text{H}_{26}\text{O}_6\text{N}_2$  requires C, 68.3; H, 5.5; N, 5.9%). The compound (II; R = OH) (0.5 g.) was warmed on a steam-bath with excess of phenylhydrazine for 5 minutes, and rubbing with acetic acid precipitated a solid which crystallised from alcohol. Recrystallisation from acetic acid yielded a *bisphenylhydrazone* as yellow plates, m. p. 230—233° (decomp.) (Found: C, 74.8; H, 6.2; N, 8.1.  $\text{C}_{35}\text{H}_{34}\text{O}_4\text{N}_4$  requires C, 75.0; H, 5.8; N, 8.9%).

*Oxidation of 3 : 3-Di-(2-*o*-acetoxybenzoyl)ethylchroman-4-one.*—A mixture of the diacetyl compound (3 g.), dioxan (25 c.c.), and selenium dioxide (1.4 g.) was refluxed for 3 hours; a further quantity of selenium dioxide (1.4 g.) was then added, and boiling continued for 6 hours more. The solution was decanted from the selenium into water, and the precipitate formed was dissolved in ether and dried ( $\text{MgSO}_4$ ), the solvent removed, and the residue suspended in hydrogen peroxide (50 c.c.; 30%) and carefully treated with sodium hydroxide (7.5 g. in water, 40 c.c.) with constant mixing. After 2 hours the alkaline solution was separated from some solid, washed with ether, acidified, and extracted many times with ether. From this extract salicylic acid was the only crystalline material isolated. From the solid above, a very small quantity of an unidentified phenolic substance, colourless plates, m. p. 119—120°, from alcohol, was obtained (Found: C, 69.2; H, 5.0%).

3 : 3-Di-(2-cyanoethyl)chroman-4-one.—Chromanone (20 g.) in pure dioxan (60 c.c.) and methylalcoholic potassium hydroxide (2 c.c.; 30%) was treated with acrylonitrile (14.3 g.), dropped in with vigorous stirring during one hour. Stirring was continued at room temperature for 8 hours. After dilution with water and acidification with hydrochloric acid, the dioxan and other unchanged materials were steam-distilled. The resulting brown oil crystallised from alcohol and was recrystallised first from alcohol and then from acetic acid, 3 : 3-di-(2-cyanoethyl)chroman-4-one separating as colourless prisms, m. p. 87° (Found: C, 71.3; H, 5.4.  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$  requires C, 70.9; H, 5.5%).

3 : 3-Di-(2-carboxyethyl)chroman-4-one.—The above cyanide was hydrolysed by boiling it with concentrated hydrochloric acid. The product was purified by dissolving it in sodium carbonate, washing with ether, reprecipitating with acid, and recrystallising from aqueous acetic acid (50%), from which 3 : 3-di-(2-carboxyethyl)chroman-4-one separated as colourless prisms, m. p. 169°, sintering at 155° (17 g.) [Found: C, 61.2; H, 5.6%; equiv., 144.8.  $\text{C}_{13}\text{H}_{14}\text{O}_4(\text{CO}_2\text{H})_2$  requires C, 61.6; H, 5.5%; equiv., 146.5]. Crude 3 : 3-di-(2-chloroformylethyl)chroman-4-one was prepared by boiling this acid with excess of thionyl chloride for 2 hours. After removal of thionyl chloride, the acid chloride remained as a syrup. It could be hydrolysed to the acid with water.

3 : 3-Di-(2-benzoyl)ethylchroman-4-one.—(a) The above acid chloride (1.4 g.) was dissolved in pure benzene (20 c.c.) and treated with aluminium chloride (1.0 g.). After 1½ hours the mixture was refluxed for 20 minutes, acidified with hydrochloric acid, and the benzene removed in steam. The product was separated and crystallised in contact with ether. Recrystallisation from acetic acid afforded a small quantity of 3 : 3-di-(2-benzoyl)ethylchroman-4-one as colourless needles, m. p. 185—187°, identical (mixed m. p.) with the substance described below.

(b) Chromanone (4.5 g.), 2-chloropropiophenone (10.4 g.), and potassium acetate (10 g.) were mixed in methyl alcohol (60 c.c.), and during 1½ hours a solution of sodium (1.4 g.) in methyl alcohol (48 c.c.) was added as the solution boiled under reflux. Dilute acid was then added, methyl alcohol and chromanone were steam-distilled, and the residual solid crystallised from glacial acetic acid as colourless needles, m. p. 185—187° (Found: C, 78.3; H, 6.0.  $\text{C}_{27}\text{H}_{24}\text{O}_4$  requires C, 78.6; H, 5.8%) (yield 0.3 g.).

(c) Freshly prepared phenyl vinyl ketone (7 g.) and chromanone (3.9 g.) were added to a solution of sodium (0.6 g.) in alcohol (25 c.c.), and after the mixture had boiled for one hour the solution was decanted from the resin formed, into dilute acid which was then extracted with ether. The ether was washed with sodium hydroxide, dried ( $\text{Na}_2\text{SO}_4$ ), and distilled. A small quantity of 3 : 3-di-(2-benzoyl)ethylchromanone, m. p. 185—187° (from alcohol), was obtained.

3 : 3-Di-(2-dicarboxyethyl)chroman-4-one.—Crude 3 : 3-di-(2-chloroformylethyl)chroman-4-one (17 g.) and phenol (10.2 g.) were heated together on a steam-bath for 2 hours. The product was dissolved in ether, and the solution washed with sodium hydroxide; much of the product crystallised from the ether and was filtered off. The ether was dried ( $\text{MgSO}_4$ ) and evaporated. The total solid was recrystallised from alcohol, and 3 : 3-di-(2-carboxyethyl)chroman-4-one separated as colourless prisms, m. p. 102° (Found: C, 72.7; H, 5.3.  $\text{C}_{27}\text{H}_{24}\text{O}_6$  requires C, 72.9; H, 5.4%) (10.5 g.). When this ester (6.5 g.) and aluminium chloride (13 g.) were heated together in an oil-bath at 160° for 1½ hours and the product was treated with dilute hydrochloric acid, a brown gum was obtained. This was dissolved in glacial acetic acid, filtered, and precipitated with water, and the solid so obtained was dissolved in ether and

dried ( $\text{Na}_2\text{SO}_4$ ). On concentration, crystalline material separated, but repeated recrystallisation from acetic acid failed to produce completely homogeneous material; the m. p. was 185–200° (Found: C, 72.0; H, 5.3. Calc. for  $\text{C}_{27}\text{H}_{24}\text{O}_8$ : C, 72.9; H, 5.4%).

*o*-Hydroxyphenyl 2-Dimethylaminoethyl Ketone Hydrochloride.—A mixture of *o*-hydroxyacetophenone (7.5 g.), methylamine hydrochloride (6 g.), paraformaldehyde (2.25 g.), and alcohol (15 c.c., containing four drops of hydrochloric acid) was refluxed for one hour. On cooling, the salt crystallised and recrystallisation from alcohol gave *o*-hydroxyphenyl 2-dimethylaminoethyl ketone hydrochloride as colourless prisms, m. p. 176° (Found: N, 6.0.  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{NCl}$  requires N, 6.1%). This salt decomposed to give a yellow gum when boiled with water, or with chromanone and water.

2-Hydroxy-4-methoxyphenyl 2-Chloroethyl Ketone.— $\beta$ -Chloropropionic acid (10 g.) and phosphorus trichloride (9 g.) were heated together on a steam-bath until the reaction was over, and then benzene (100 c.c.) was added. The mixture was decanted from the phosphorous acid, mixed with resorcinol dimethyl ether (14 g.), and slowly added to aluminium chloride (15 g.) cooled in ice, and after an hour at room temperature it was heated on a steam-bath for one hour. On pouring into ice–dilute hydrochloric acid some solid separated. This was filtered off and the benzene layer was dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated, giving a further quantity of solid. The two were combined and recrystallised from alcohol. 2-hydroxy-4-methoxyphenyl 2-chloroethyl ketone separating as colourless prisms, m. p. 93–94° (7.5 g.) (Found: C, 55.9; H, 5.2.  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Cl}$  requires C, 55.6; H, 5.1%).

2-Hydroxy-4-methoxyphenyl Vinyl Ketone.—The above chloro-compound (4 g.) and anhydrous potassium acetate (2 g.) were refluxed in alcoholic solution for  $\frac{1}{2}$  hour and poured into water. A yellow solid separated and was dried. Recrystallisation from petroleum (b. p. 40–60°) gave 2-hydroxy-4-methoxyphenyl vinyl ketone as yellow prisms, m. p. 53°, in almost quantitative yield (Found: C, 67.5; H, 5.4.  $\text{C}_{10}\text{H}_{10}\text{O}_3$  requires C, 67.4; H, 5.6%). Treatment with warm concentrated hydrochloric acid reconverted it into 2-hydroxy-4-methoxyphenyl 2-chloroethyl ketone, and with dinitrophenylhydrazine, either in alcohol or without a solvent, it reacted to form a resinous mass which did not crystallise. It dissolved freely in aqueous sodium hydroxide (10%) to give a yellow solution, the colour of which faded during a few minutes as an oil separated and finally crystallised. It was 7-methoxychromanone, m. p. 78°, identical (mixed m. p.) with the substance described by Perkin, Ray, and Robinson (*loc. cit.*). This chromanone condensed with veratraldehyde, in the presence of alcoholic hydrogen chloride, to give 7-methoxyveratrylidene-chromanone, m. p. 141°, identical (mixed m. p.) with that substance obtained by the above authors (*loc. cit.*).

1'-Methylindolo(3':2'-3:4)chrom-3-en.—Chromanone (5 g.) and phenylmethylhydrazine (4.1 g.) were heated for  $\frac{1}{2}$  hour on a steam-bath, and on being dissolved in a little alcohol and set aside, the product slowly crystallised. Recrystallisation from alcohol gave chromanone phenylmethylhydrazine as yellow prisms, m. p. 70° (1.9 g.) (Found: C, 76.5; H, 6.5.  $\text{C}_{18}\text{H}_{16}\text{ON}_2$  requires C, 76.2; H, 6.3%). This was suspended in dilute sulphuric acid (30 c.c. of 20% by vol.). It dissolved slowly, and the indole began to separate. After being warmed on a steam-bath for a few minutes, the mixture was set aside for 24 hours, during which the product solidified. Recrystallisation from aqueous alcohol afforded 1'-methylindolo-(2':3'-3:4)chrom-3-en in two different forms, colourless needles, m. p. 115°, and colourless plates, m. p. 117° (mixed m. p. 116°) (Found: C, 81.6; H, 5.7.  $\text{C}_{16}\text{H}_{13}\text{ON}$  requires C, 81.7; H, 5.5%) (yield 0.9 g.).

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