Reactions of 4-Thionchromones with Amino-compounds, and with Methyl Iodide.

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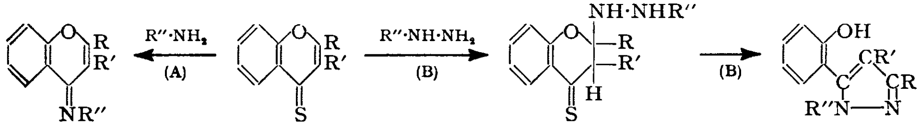
The study of the behaviour of 4-thionchromones with primary aliphatic amines, certain carbonyl reagents, and methyl iodide has been extended. Reagents containing primary amino-groups usually give derivatives of either chromone imine (II) or *o*-hydroxyphenylpyrazole (IV).

The reaction of 4-thionchromones (*e.g.*, I) with primary amino-compounds has been but little studied (see Campaigne, *Chem. Reviews*, 1946, **39**, 64), and we now record an extension of our previous investigation (see Baker, Harborne, and Ollis, *J.*, 1952, **1303**, where references to earlier work are included).

The following 4-thion-chromones and -flavones have been prepared from the corresponding chromones and flavones by reaction with phosphorus pentasulphide: 2-ethoxycarbonyl, 2-2′-furyl-, 2-methyl-3-phenyl-, and 2 : 3-diphenyl-4-thionchromones, 4-thion*iso*flavone, and 3-hydroxy-, 7-methoxy-, 4′-methoxy-, 5 : 7-dimethoxy-, and 3-methyl-4-thionflavone. The behaviour of these compounds with benzylamine, hydrazine, phenylhydrazine, and methyl iodide has been investigated. With the reagents containing primary amino-groups, two types of reaction are encountered.

Reaction (A) is simple condensation with elimination of hydrogen sulphide; it occurs with nearly all 4-thionflavones (I; R = Ph, R′ = H) to give derivatives of 4-iminoflavone, *e.g.*, flavone benzylimine, hydrazone, and phenylhydrazone (II; R = Ph, R′ = H, R″ = Ph·CH_2, NH_2, and Ph·NH). The same reactivity of the thione group is observed if the phenyl group in position 2 is replaced by an α-furyl group (I; R = 2-furyl, R′ = H). A 4-thionflavone having a methyl, phenyl, or hydroxyl group in position 3 (I; R = Ph, R′ = Me, Ph, or OH) is either inert or undergoes the second type of reaction.

Reaction (B) is exemplified by 4-thionchromone (I; R = R′ = H), 2-methyl-4-thionchromone (I; R = Me, R′ = H), or 5 : 7-dimethoxy-4-thionflavone, which undergo opening of the pyrone ring with hydrazine or with phenylhydrazine to give colourless, phenolic pyrazoles (IV). The reaction is probably initiated by attack on the cationoid carbon atom 2 by the anionoid NH_2-group of the hydrazine. The resulting addition product (III) must then rearrange to the phenolic open-chain hydrazone, and subsequently cyclise with loss of hydrogen sulphide to give the pyrazole (IV) (see Baker, Harborne, and Ollis, *loc. cit.*; Baker and Butt, *J.*, 1949, 2144). 7-Methoxy-4-thionflavone reacts with hydrazine to give 7-methoxyflavone hydrazone (reaction A), and a trace of the related pyrazole (reaction B).

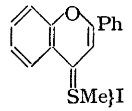


(II) (I) (III) (IV)

2-Methyl-4-thionchromone does not react with benzylamine in boiling alcoholic solution. The most sensitive reagent for distinguishing between the two types of 4-thionchromone is hydrazine under mild conditions which gives either a bright yellow chromone hydrazone (II; R″ = NH_2) (reaction A), or a colourless pyrazole (IV; R″ = H) (reaction B). Under vigorous conditions the product is in all cases the *o*-hydroxyphenylpyrazole, since the chromone hydrazones are converted into the isomeric phenolic pyrazoles when boiled with ethanolic hydrazine.

Methyl iodide reacts rapidly with 4-thionflavones to give methiodides (as V) which are hydrolysed by boiling water to flavones. 2-2′-Furyl-4-thionchromone reacts similarly, but 3-phenyl- and 3-hydroxy-4-thionflavone do not react. 2-Methyl-, 2 : 3-dimethyl-, 2-methyl-3-phenyl-, and 3-phenyl-4-thionchromone give unstable methiodides which are hydrolysed rapidly on exposure to air with loss of methanethiol.

A somewhat different reaction is shown by 4-thionchromone, 3-methyl-4-thionflavone, and 2-ethoxycarbonyl-4-thionchromone, which with excess of methyl iodide at room temperature give methotri-iodides (*e.g.*, VI) in *ca.* 20% yield. The extra iodine doubtless arises by the photo-decomposition of methyl iodide; if free iodine is added to the mixture the yield of methotri-iodide is quantitative. Although periodides are well known (see "The Chemical Elements and their Compounds," Sidgwick, Oxford Univ. Press, 1950, p. 1194), their formation under these conditions does not appear to have been observed previously.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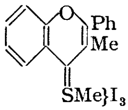
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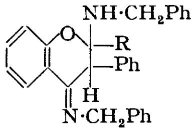
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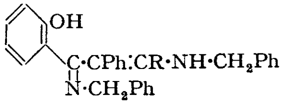
(VIII)

4-Thion*iso*flavone and 2 : 3-diphenyl-4-thionchromone each react with two molecules of benzylamine to yield products, formulated as (VII; R = H and Ph respectively), which are non-phenolic and non-fluorescent. The only alternative structures (VIII; R = H or Ph) represent compounds which would be phenolic and strongly fluorescent (cf. compounds such as 2-β-benzylaminocinnamoylphenol; Baker, Harborne, and Ollis, *J.*, 1952, 1294). Compounds (VII) doubtless arise by initial addition of benzylamine to the 2 : 3-double bond of the chromone nucleus, followed by condensation of the second molecule of benzylamine with the thione group.

Attempts have been made to rationalise the foregoing experimental facts, but satisfactory explanations cannot be advanced in the present state of our knowledge.

Note on Flavone Benzylimine Methiodide.—A compound, m. p. 266°, was prepared by heating flavone benzylimine with methanolic methyl iodide, and was described as flavone benzylimine methiodide (Baker, Harborne, and Ollis, *J.*, 1952, 1294). Attention was, however, drawn to the fact that hydrolysis gave flavone and benzylamine in place of the expected *N*-methylbenzylamine. Re-investigation of this substance has shown that it is flavone benzylimine hydriodide, and that it can be prepared quantitatively from flavone benzylimine and hydriodic acid. The true flavone benzylimine methiodide, m. p. 210—212°, has been prepared from flavone benzylimine and methyl iodide at room temperature. We have noticed (unpublished observations) that the benzylimines of xanthone and of coumarin also form hydriodides and not methiodides when heated with methanolic methyl iodide, and two other cases have been reported amongst the alkaloids (see Barger, Madinaveitia, and Streuli, *J.*, 1939, 510; Moore, *J.*, 1911, **99**, 1231).

EXPERIMENTAL

Preparation of 4-*Thionchromones.*—These compounds were prepared by heating the chromones with pure phosphorus pentasulphide in benzene, toluene, or xylene for 2—4 hr. (Baker, Harborne, and Ollis, *J.*, 1952, 1303), and crystallised from ethanol or light petroleum. The yields are given in parentheses.

2-2′-Furylchromone (Ollis and Weight, *J.*, 1952, 3826) gave 2-2′-*furyl*-4-*thionchromone*, thick, purple needles, m. p. 108° (40%) (Found: C, 67·8; H, 3·7; S, 14·3. $C_{13}H_8O_2S$ requires C, 68·4; H, 3·5; S, 14·0%).

2-Ethoxycarbonylchromone (Schmutz *et al.*, *Helv. Chim. Acta*, 1951, **34**, 767) gave 2-ethoxycarbonyl-4-thionchromone, deep green prisms, which appeared purple in bulk, m. p. 101—103° (70%) (Found: C, 61·5; H, 4·3; S, 13·6. Calc. for $C_{12}H_{10}O_3S$: C, 61·5; H, 4·3; S, 13·7%). Schmutz *et al.* record m. p. 100—101°.

4′-Methoxyflavone gave 4′-*methoxy*-4-*thionflavone*, red needles, m. p. 137° (74%) (Found: C, 71·4; H, 4·4; S, 11·8. $C_{16}H_{12}O_2S$ requires C, 71·6; H, 4·5; S, 12·0%).

7-Methoxyflavone was prepared (66%) by the method of Virkar and Shah (*Chem. Abs.*, 1943, **37**, 2375), except that in the Baker–Venkataraman rearrangement of 2-benzoyloxy-4-methoxyacetophenone, powdered potassium hydroxide in pyridine was used in preference to sodium in benzene. 7-*Methoxy*-4-*thionflavone* formed large red or small orange needles, m. p. 134—136° (53%) (Found: C, 71·9; H, 4·0; S, 11·85. $C_{16}H_{12}O_2S$ requires C, 71·6; H, 4·5; S, 11·95%).

In the preparation of 5 : 7-dimethoxyflavone (Baker, Harborne, and Ollis, *J.*, 1952, 1294) the yield in the Baker–Venkataraman rearrangement was increased to 88% by allowing the solution of ester in pyridine and potassium hydroxide to stand for 3 days at room temperature. 5 : 7-*Dimethoxy-4-thionflavone* formed dark green prisms, m. p. 184° (Found: C, 68·8; H, 4·8; S, 10·7. $C_{17}H_{14}O_3S$ requires C, 68·4; H, 4·7; S, 10·7%).

2-Methyl*iso*flavone (Chadha, Mahal, and Venkataraman, *J.*, 1933, 1461) gave 2-*methyl-4-thion*iso*flavone*, bright red needles, m. p. 134° (54%) (Found: C, 76·3; H, 4·5; S, 13·1. $C_{16}H_{12}OS$ requires C, 76·2; H, 4·8; S, 12·7%).

3-Methylflavone is best prepared by the Allan–Robinson fusion method (Dunne *et al.*, *J.*, 1950, 1258), but, contrary to the experience of these authors, *o*-benzoyloxypropiophenone underwent the Baker–Venkataraman rearrangement, to give, after draining of the crude product on a tile, a 4% yield of 1-*benzoyl*-1-o-*hydroxybenzoylethane*, colourless plates, m. p. 112° (Found: C, 75·1; H, 5·1. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%), which gave a deep red colour with ferric chloride. 3-*Methyl-4-thionflavone* formed purple plates, m. p. 128—129° (55%) (Found: C, 76·4; H, 5·2; S, 11·6. $C_{16}H_{12}OS$ requires C, 76·2; H, 4·8; S, 12·7%).

*iso*Flavone (Joshi and Venkataraman, *J.*, 1934, 513) gave 4-*thion*iso*flavone*, thin, slate-coloured plates or thick, purple plates, m. p. 94° (63%) (Found: C, 75·9; H, 4·1. $C_{15}H_{10}OS$ requires C, 75·6; H, 4·2%). Solutions of 4-thion*iso*flavone are sky-blue in light petroleum and violet in ethanol.

2 : 3-Diphenylchromone (Chadha, Mahal, and Venkataraman, *loc. cit.*) gave 2 : 3-*diphenyl-4-thionchromone*, deep purple plates, m. p. 175° (69%) (Found: C, 79·5; H, 4·3; S, 10·0. $C_{21}H_{14}OS$ requires C, 80·2; H, 4·5; S, 10·2%).

Flavonol (Algar and Flynn, *Proc. Roy. Irish Acad.*, 1934, **42**, *B*, 1) gave 4-*thionflavonol*, red needles, m. p. 80—82° (55%) (Found: C, 70·9; H, 3·9. $C_{15}H_{10}O_2S$ requires C, 70·8; H, 3·9%). It gave an intense green colour with ferric chloride solution.

Reaction of 4-Thionchromones with Benzylamine.—The 4-thionchromones were heated with excess of benzylamine (*ca.* 2 equivs.) in ethanol for 1—2 hr. and, if reaction occurred, hydrogen sulphide was evolved and the deep colour of the solution faded. The product was then isolated by pouring the solution into water, and crystallised from ethanol. Except for 2-ethoxycarbonyl-4-thionchromone and 4-thionchromone, which were decomposed by this treatment, only the four thiones mentioned below and 4-thionflavone reacted with benzylamine.

2-2′-Furyl-4-thionchromone gave 2-2′-furylchromone benzylimine in 72% yield, colourless needles, m. p. 120—122°, alone and when mixed with an authentic specimen (Baker, Harborne, and Ollis, *J.*, 1952, 1301). 4′-Methoxy-4-thionflavone gave 4′-methoxyflavone benzylimine in 71% yield, colourless needles, m. p. and mixed m. p. 134·5—135° (*idem, ibid.*, p. 1300). 4-Thion*iso*flavone gave the benzylimine (VII; R = H) in 80% yield, thick yellow plates, m. p. 109—110·5° (Found: C, 82·8; H, 6·1; N, 6·6. $C_{29}H_{26}ON_2$ requires C, 83·2; H, 6·3; N, 6·7%). 2 : 3-Diphenyl-4-thionchromone, when heated with benzylamine in ethanol for 12 hr., gave the *benzylimine* (VII; R = Ph) in 52% yield, as irregular, yellow prisms, m. p. 154—155° (Found: C, 85·0; H, 5·7; N, 6·0. $C_{35}H_{30}ON_2$ requires C, 85·0; H, 6·1; N, 5·7%).

Reaction of 4-Thionchromones with Hydrazine.—Hydrazine hydrate was added dropwise to a solution of the thionchromone in warm ethanol, until the deep colour of the solution faded to pale yellow or the solution became colourless, and hydrogen sulphide was liberated. After ½ hr., the product, either a chromone hydrazone or an *o*-hydroxyphenylpyrazole, was isolated by addition of water, and purified by crystallisation from a suitable solvent. Yields are given in parentheses.

The chromone hydrazones are bright yellow, insoluble in 2N-sodium hydroxide, and give no colour with aqueous-alcoholic ferric chloride. Their ultra-violet absorption curves (cf. flavone hydrazone) are very different from those of the *o*-hydroxyphenylpyrazoles.

Flavone hydrazone [light absorption in ethanol, $\lambda_{\max.}$ (mμ) (log ε): 239 (4·32); 282 (4·22); 338 (4·13)] has been prepared before (Baker, Harborne, and Ollis, *loc. cit.*, p. 1306), but the following three compounds are new. 2-2′-*Furylchromone hydrazone*, bright yellow needles, m. p. 139—140°, from aqueous methanol (87%) (Found: C, 69·15; H, 4·5; N, 12·6. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·4; N, 12·4%). 4′-*Methoxyflavone hydrazone*, bright yellow needles, m. p. 169°, from benzene (69%) (Found: C, 71·6; H, 5·2; N, 10·5. $C_{16}H_{14}O_2N_2$ requires C, 72·15; H, 5·3; N, 10·5%). 7-*Methoxyflavone hydrazone* crystallises from aqueous methanol as yellow solvated needles, m. p. 84—94° (variable) [Found, after drying in *vacuo* at 56° over $Mg(ClO_4)_2$: C, 71·6; H, 5·3; N, 10·6. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3; N, 10·5%]. Material, which had been purified by chromatography in benzene solution on alumina in order to remove traces of the isomeric *o*-hydroxyphenylpyrazole, retained benzene of crystallisation even after subsequent crystallisation from cold aqueous methanol. The *benzene* complex formed deep yellow needles, m. p. 118—120° (Found: C, 74·4, 74·4; H, 5·9, 5·8; N, 9·3, 8·9. $C_{16}H_{14}O_2N_2,\frac{1}{2}C_6H_6$ requires C, 74·7; H, 5·6; N, 9·2%). The N-*acetyl* derivative separated from dioxan as pale-green needles, m. p. 271—273° (Found: C, 69·8; H, 5·2; N, 8·9. $C_{18}H_{16}O_3N_2$ requires C, 70·1; H, 5·2; N, 9·1%).

When boiled with ethanolic hydrazine for 2—3 hr., these chromone hydrazones are isomerised to the corresponding *o*-hydroxyphenylpyrazoles. Alternatively, if the reaction of the thionchromone with hydrazine is carried out under more vigorous conditions, the chief product is the pyrazole. For example, 4′-methoxy-4-thionflavone was heated under reflux for 1 hr. with ethanolic hydrazine hydrate, and the cold solution was poured into N-sodium hydroxide. Ether-extraction gave an 8% yield of 4′-methoxyflavone hydrazone, m. p. and mixed m. p. 168—169°. Acidification of the aqueous layer gave 3(5)-o-*hydroxyphenyl*-5(3)-p-*methoxyphenylpyrazole*, colourless plates, m. p. 139—140°, from methanol (Found: C, 72·3; H, 5·3; N, 10·3. $C_{16}H_{14}O_2N_2$ requires C, 72·15; H, 5·3; N, 10·5%). This pyrazole gave an intense purple-green colour with alcoholic ferric chloride. The *o*-hydroxyphenylpyrazoles are colourless, soluble in 2N-sodium hydroxide, and give intense colours in alcoholic solution with aqueous ferric chloride, and characteristic absorption maxima in ultra-violet light (see *idem*, *loc. cit.*, for a table of ultra-violet spectral data, and compare with the values given below).

The pyrazoles formed from thionchromone and its 2-methyl and 2 : 3-dimethyl derivatives have been described in the earlier paper. The following five are new, and all gave an intense green colour with ferric chloride, except for 3(5)-*o*-hydroxyphenyl-4-phenylpyrazole, which gave a blue colour.

5 : 7-Dimethoxy-4-thionflavone gave 3(5)-(2-*hydroxy*-4 : 6-*dimethoxyphenyl*)-5(3)-*phenylpyrazole*, prisms, m. p. 116—117° (from methanol) (81%) (Found: C, 67·8; H, 5·2; N, 9·3. $C_{17}H_{16}O_3N_2$ requires C, 68·9; H, 5·4; N, 9·5%).

2-Methyl-3-phenyl-4-thionchromone gave 3(5)-o-*hydroxyphenyl*-5(3)-*methyl*-4-*phenylpyrazole*, needles, m. p. 180° (from dilute methanol) (83%) (Found: C, 76·6; H, 5·6; N, 11·0. $C_{16}H_{14}ON_2$ requires C, 76·8; H, 5·6; N, 11·2%).

3-Methyl-2-phenyl-4-thionchromone gave 3(5)-o-*hydroxyphenyl*-4-*methyl*-5(3)-*phenylpyrazole*, needles, m. p. 138—140° (from carbon tetrachloride) (70%) (Found: C, 76·3; H, 5·7; N, 11·1. $C_{16}H_{14}ON_2$ requires C, 76·8; H, 5·6; N, 11·2%). Light absorption in ethanol, $\lambda_{max.}$ (mμ) (log ε) : 214 (4·66); 249 (4·60); 288 (4·12).

4-Thion*iso*flavone gave 3(5)-o-*hydroxyphenyl*-4-*phenylpyrazole*, solvated needles, m. p. after drying 114—116° [from chloroform–light petroleum (b. p. 40—60°)] (90%) (Found, in material dried at 78° in *vacuo*: C, 76·2; H, 5·0; N, 11·9. $C_{15}H_{12}ON_2$ requires C, 76·2; H, 5·1; N, 11·9%). Light absorption in ethanol: intense absorption, max. at *ca.* 205; $\lambda_{max.}$ (mμ) (log ε) : 254 (4·04); 293 (3·74).

2 : 3-Diphenyl-4-thionchromone gave 3(5)-o-*hydroxyphenyl*-4 : 5(3 : 4)-*diphenylpyrazole*, needles, m. p. 230—231° (decomp.) [from light petroleum (b. p. 100—120°)] (85%) (Found: C, 80·9; H, 5·1; N, 9·0. $C_{21}H_{16}ON_2$ requires C, 80·7; H, 5·2; N, 9·0%).

Reaction of 4-Thionchromones with Phenylhydrazine.—The reaction of thionchromones with phenylhydrazine (1·5—2 equivs.) in ethanol is much slower than with hydrazine, and is carried out at 100° for 2—3 hr. or longer. In the absence of alkali, only 4-thionflavone, 2-2′-furyl-4-thionchromone, and 4-thionchromone react; with a trace of dilute alkali present, 2-methyl-, 2 : 3-dimethyl-, and 2-methyl-3-phenyl-4-thionchromones react. The other thionchromones tested were heated for 2—6 hr. with ethanolic phenylhydrazine, and recovered unchanged. The new products only are described below; the others are described in the earlier paper (*loc. cit.*).

2-2′-*Furylchromone phenylhydrazone* was obtained as deep yellow needles, m. p. 156—158°, in 23% yield, by heating the corresponding thione with ethanolic phenylhydrazine overnight (Found: C, 75·5; H, 4·4; N, 9·2. $C_{19}H_{14}O_2N_2$ requires C, 75·5; H, 4·7; N, 9·3%).

5-o-*Hydroxyphenyl*-1-*phenylpyrazole* was produced in 89% yield by warming 4-thionchromone with phenylhydrazine in ethanol for 1 hr. It separated from aqueous ethanol as colourless needles, m. p. 105—106° (Found: C, 76·7; H, 5·1; N, 11·9. $C_{15}H_{12}ON_2$ requires C, 76·2; H, 5·1; N, 11·9%). Light absorption in ethanol: intense absorption, max. at *ca.* 205; $\lambda_{max.}$ (mμ) (log ε) : 286 (4·28); 303 (4·21).

3(5)-o-*Hydroxyphenyl*-5(3)-*methyl*-1 : 4-*diphenylpyrazole* was obtained by heating 2-methyl-3-phenyl-4-thionchromone (500 mg.), phenylhydrazine (2 c.c.), 5N-sodium hydroxide (3 drops), and *n*-propanol (20 c.c.) at 100° for 3 hr. and then acidifying the mixture. The pyrazole (505 mg., 78%) separated from aqueous methanol (charcoal) as colourless prisms, m. p. 219—220° (Found: C, 80·2; H, 5·4; N, 8·4. $C_{22}H_{18}ON_2$ requires C, 80·95; H, 5·6; N, 8·6%).

Reaction of 4-Thionchromones with Methyl Iodide.—Except for 4-thionflavonol and 2 : 3-diphenyl-4-thionchromone, all the thiones examined readily react with methyl iodide at room temperature, to give methiodides of varying stability. To avoid the possibility of decomposition during crystallisation, most of the products were analysed directly without further purification.

(*a*) *Formation of stable methiodides.* It was found that four of the thionchromones formed stable methiodides when dissolved in methyl iodide. The products crystallised from the solution, in some cases within a few minutes, and were collected after 24 hr., washed with ether and dried.

2-2'-Furyl-4-thionchromone methiodide, maroon needles, m. p. 195° (92%) (Found : C, 45·0; H, 2·9; S, 9·3. $C_{14}H_{11}O_2SI$ requires C, 45·4; H, 3·0; S, 8·7%). *4'-Methoxy-4-thionflavone methiodide,* red needles, m. p. 206—207° (decomp.) (83%) (Found : C, 49·5; H, 3·8; S, 5·8; I, 29·6. $C_{17}H_{15}O_2SI$ requires C, 49·8; H, 3·7; S, 7·8; I, 30·9%). *7-Methoxy-4-thionflavone methiodide,* orange needles, m. p. 210—212° (decomp.) (100%) (Found : C, 50·4; H, 3·6; S, 6·9. $C_{17}H_{15}O_2SI$ requires C, 49·8; H, 3·7; S, 7·8%). *5 : 7-Dimethoxy-4-thionflavone methiodide* maroon cubes, m. p. 214° (decomp.) (Found : C, 49·35; H, 4·2; S, 6·8. $C_{18}H_{17}O_3SI$ requires C, 49·1; H, 3·9; S, 7·3%). These four methiodides were hydrolysed by boiling water in 10—20 min. to the corresponding chromones in high yield (cf. conversion of 4-thionflavone methiodide into flavone; *idem, ibid.*).

(*b*) *Formation of methotri-iodides.* The following 4-thionchromones form stable methotri-iodides in low yield, when set aside in methyl iodide.

When kept overnight, a solution of 2-ethoxycarbonyl-4-thionchromone (131 mg.) in methyl iodide (2 c.c.) deposited carmine needles, m. p. 166° of the methotri-iodide (35 mg., 17%) (Found: C, 25·1, 25·05; H, 2·5, 2·1; S, 4·5, 5·45. $C_{13}H_{13}O_3SI_3$ requires C, 24·8; H, 2·1; S, 5·1%).

Ether was added to a solution of 3-methyl-4-thionflavone in methyl iodide which had been kept for 24 hr., giving the *methotri-iodide* as brown needles, m. p. 99—100° (20%) (Found : C, 32·7; H, 2·6; S, 4·8. $C_{17}H_{15}OSI_3$ requires C, 31·5; H, 2·3; S, 4·9%).

A solution of 4-thionchromone (200 mg.) in methyl iodide (3·4 c.c.) deposited crystals of the *methotri-iodide* (155 mg., 23%) during 4 hr. It formed large, purple-red or small, brown needles, m. p. 148—150° (Found : C, 21·7; H, 1·8; S, 6·7; I, 66·4. $C_{10}H_9OSI_3$ requires C, 21·5; H, 1·6; S, 5·75; I, 68·2%). In a second experiment, 4-thionchromone (210 mg.), methyl iodide (10 c.c.), and iodine (310 mg.) were kept for 12 hr., and the crystals washed with ether and chloroform; the product had m. p. 148—150° (695 mg., 95%).

(*c*) *Formation of unstable methiodides.* The following four thionchromones gave unstable methiodides.

2 : 3-Dimethyl-4-thionchromone (500 mg.), chloroform (5 c.c.), and methyl iodide (5 c.c.) were kept overnight. On addition of ether, deep purple needles, m. p. 75°, separated (172 mg., 20%)]. This methiodide could not be analysed as it quickly decomposed with loss of methanethiol. 2-Methyl-4-thionchromone methiodide had similar properties.

The violet solution of 4-thion*iso*flavone (100 mg.) in methyl iodide (2 c.c.) became red during 24 hr. No solid separated on the addition of ether, but the odour of methanethiol was evident. The solution was then evaporated at 15°, and the residue crystallised from ethanol (charcoal), giving *iso*flavone, m. p. and mixed m. p. 130—131° (45 mg., 48%). Similarly 2-methyl-4-thion-*iso*flavone was converted into 2-methyl*iso*flavone.

Flavone Benzylimine Hydriodide.—The substance, m. p. 266°, previously prepared (Baker, Harborne, and Ollis, *loc. cit.*) was reanalysed (previous figures in parentheses) [Found : C, 59·6 (60·3); H, 3·7 (4·2); (N, 3·3); I, 29·2 (28·8). $C_{22}H_{17}ON,HI$ requires C, 60·1; H, 4·1; N, 3·2; I, 28·9%]. It was prepared in quantitative yield by addition of hydriodic acid (*d* 1·5) to a solution of flavone benzylimine in acetic acid.

Flavone Benzylimine Methiodide.—Flavone benzylimine (2·1 g.) in methyl iodide (20 c.c.) was left at room temperature for 4 days, and the crystalline product was collected, washed with ether, and dried. The *methiodide* (2·69 g., 88%) crystallised from acetone–ether as bright yellow needles, m. p. 210—212° (decomp.) (Found : C, 61·0; H, 4·9; N, 3·1. $C_{22}H_{17}ON,CH_3I$ requires C, 60·9; H, 4·5; N, 3·1; I, 28·0%).

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